COMBINING RESEARCH IN PHYSICAL CHEMISTRY AND CHEMICAL EDUCATION

Part A:
The Femtosecond Molecular Dynamics Of Small Gas-Phase Anion Clusters
Part B:
Surveying Student Beliefs About Chemistry And The Development Of Physical Chemistry Learning Tutorials

by

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Combining research in physical chemistry and chemical education.
Part A: The Femtosecond Molecular Dynamics Of Small Gas-Phase Anion Clusters
Part B: Surveying Student Beliefs About Chemistry And The Development Of Physical Chemistry Learning Tutorials

Thesis directed by Professors W. Carl Lineberger and Carl E. Wieman

This dissertation combines work in the areas of experimental physical chemistry and chemical education. In the area of physical chemistry, femtosecond pump-probe spectroscopy is used to interrogate the time-dependence for energy redistribution, solvent reorientation, and dissociation dynamics in small gas-phase anion clusters. The chemical education research addressed in this manuscript include the development and validation of a survey to measure students' beliefs about chemistry and the learning of chemistry and the development and testing of learning tutorials for use in undergraduate physical chemistry courses in thermodynamics and kinetics.

In the first part of this dissertation, the Cu(CD_3OD) dynamics are investigated using a combination of femtosecond pump-probe experiments and *ab initio* calculations. Dissociation of this complex into Cu and CD_3OD occurs on two distinct time scales: 3 and 30 ps, which arise, respectively, from the coupling of intermolecular solvent rotations and excited methyl rotor rotation into the Cu–O dissociation component upon electron photodetachment of the precursor anion.

In the second part of this dissertation, the time-resolved recombination of photodissociated $IBr^-(CO_2)_n$ ($n = 5 - 10$) cluster anions is investigated. Upon excitation to the A′ $^2\Pi_{1/2}$ state of the chromophore, the bare anion results in I^- and Br products, upon solvation with CO_2, the IBr^- chromophore regains near-IR absorption after recombination and vibrational relaxation on the ground electronic state. The recombination times vary with the number of solvent molecules from 12 ps for n = 5 to 900 ps for n = 10. Extensive electronic structure and non-adiabatic molecular dynamic simulations provide a framework to understand this behavior.

In the third part of this dissertation, the modification and validation of the Colorado Learning Attitudes about Science Survey (CLASS) for use in chemistry is presented in detail. The CLASS survey is designed to measure student beliefs about chemistry and the learning of chemistry. This instrument is a modification of the original CLASS-Phys survey designed for use in physics. Statements on the chemistry version (CLASS-Chem) are validated using chemistry students with a broad range of experience levels to ensure clarity in wording and meaning. The chemistry version addresses additional belief areas important in learning chemistry but not physics, specifically, beliefs about reactions and molecular structure. Statements are grouped into statistically robust categories using reduced basis factor analysis.

The final part of this dissertation addresses the development and testing of learning tutorials for use in undergraduate physical chemistry. The tutorials are designed to promote the active mental engagement of students in the process of learning. Questions within the pencil-paper format guide students through the reasoning needed to apply concepts to real-world situations. Each tutorial is connected to a physical model or computer simulation providing students with additional hands-on investigations to strengthen their connection with the concepts addressed in the tutorial. Currently tutorials connected with the First and Second Laws of Thermodynamics as well as Kinetics have been developed and tested.

This thesis is dedicated to my grandmother, for all her love and support.

Mary C. Amarante

(1921 – 2002)

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I decided on Purdue instead? Mischel is my best friend and I value her as my partner in life. Without her support throughout my graduate tenure I would certainly have never made it to this point. She was always willing to talk about my frustrations as well as my successes and consistently provided a gauge of the important things in life. For all but the first five months of our relationship I have been in school, I look forward to the additional time I will get to spend with my best friend now that I an finally done with school. I promise to learn Italian now so we can take another trip to Milan and stay for more than 12 hours!

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Contents

List of Tables and Figures

Chapter I

Solute Dynamics in Size Selected Solvents

1.1 Motivation

Solvated ions are ubiquitous in chemical and biological systems. Understanding the interactions between solvent and solute is important in determining the outcome of chemical reactions. Detailed analyses of these interactions are hindered by several factors. First, solvent-solute systems traditionally contain many molecules which make it impossible to consider individual molecular interactions. The molecular dynamics that take place within and between these molecules occurs on extremely fast time scales. Finally, each solvent and solute molecule is different due to its local environment. An alternative approach to gain insight on the nature of these interactions is to look at a simplified problem with a known number of solvent molecules. Gas-phase ionic complexes can be combined with mass and optical spectroscopies to probe the nature of solvation in charged solvent-solute systems.[1-11]

The work presented here uses the combination of gas-phase anionic clusters and femtosecond pump-probe spectroscopy to gain insight to the nature of molecular dynamics in small clusters. Gas-phase clusters provide a controllable, well-defined solvent environment which allows for the study of detailed interactions between solvent and solute.[12-19] These details are lost in condensed phase studies due to the statistical averaging needed in describing these systems. An additional benefit of investigations using gas-phase clusters comes with the use of easily generated charged species. The use of ionic species allows these studies to be performed within an ion mass spectrometer[20] providing easy control of molecular speeds and product separation.

Coupling these ionic species with femtosecond laser techniques allows step-wise monitoring of dynamics occurring within these systems. Femtosecond time-resolved methods for the study of gas-phase molecular dynamics have a long history and have provided breakthroughs in understanding fundamental chemical processes.[13,21-23] These studies involve a pump-probe scheme where first an ultrafast pump pulse initiates a reaction, creates a nonstationary state or wave packet, and the evolution of this reaction is monitored as a function of time using a probe pulse.

1.2 The femtosecond dynamics of $Cu(CD_3OD)$

In this study, time-resolved pump-probe laser spectroscopy is used to examine the dissociation dynamics initiated upon electron photodetachment of $Cu^-(CD_3OD)$. This group has previously used similar pump-probe techniques to examine the dynamics of $Cu^-(H_2O)_n$,[24,25] and such anion-water complexes have been the subject of numerous theoretical and experimental investigations.[10,11,26-35]

Our studies employ photodetachment-photoionization (PDPI) spectroscopy in probing the neutral dynamics of the clusters of interest. In this method, the neutral dynamics are initiated when an ultrafast laser pulse photodetaches electrons from a mass selected anion cluster, as shown in figure 1.1. The nascent neutral is interrogated by resonance enhanced multiphoton ionization (REMPI)[36,37] at various times (Δt) following electron photodetachment; this probe results in a time dependent cation signal which, following a detailed analysis, provides insight to the state of the neutral complex.

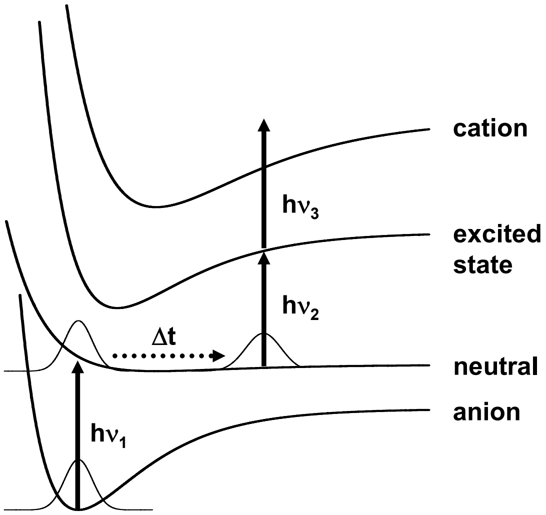

Figure 1.1 Femtosecond photodetachment-photoionization scheme used to interrogate dynamics on neutral potential energy surface.

The PDPI method combines many techniques which aid in the investigation of neutral molecular dynamics. First, complexes prepared as negative ions can be carefully mass selected providing careful studies on known cluster sizes. Because photodetachment occurs rapidly compared to the time of nuclear motion, photodetachment of these anionic complexes provides a neutral molecule with a well defined initial nuclear configuration. The dynamics of this neutral complex are initiated upon photodetachment to the electronic ground state (Fig. 1.1). The time-delayed REMPI probe not only allows a sensitive determination of the instantaneous geometry of the neutral but also allows mass separation of the various cationic photoproducts. Our method of PDPI spectroscopy is a modified version of that introduced by Wöste and co-workers in 1995.[38] The employment of a pulsed supersonic expansion in our instrument allows for the production of colder negative ions. The simultaneous detection of both neutral and charged photoproducts allows us to account for any signal drifts due to ion production or laser intensity.

In previous studies of $Cu^-(H_2O)$,[24,39] electron photodetachment was shown to lead to large-amplitude H_2O reorientation within and dissociation from $Cu(H_2O)$, due to the difference in topology between the anion and neutral potential energy surfaces. The $Cu^-(H_2O)$ complex has a hydrogen-bonded, Cu—HOH, minimum energy configuration, while neutral $Cu(H_2O)$ has a Cu–O interaction, favoring $Cu–OH_2$, that determines its minimum energy configuration. Electron photodetachment from $Cu^-(H_2O)$ produces an ensemble of vibrationally excited $Cu(H_2O)$ complexes with an average internal energy near the dissociation threshold of the complex. For the $Cu(H_2O)$ study, following electron photodetachment from Cu^-—HOH, dissociation of $Cu(H_2O)$ occurred on three different timescales, each separated by an order of magnitude. Some 30% of the nascent $Cu(H_2O)$ complexes directly dissociated. The remaining bound complexes dissociated on a 10 ps timescale via coupling of H_2O internal rotation to the $Cu–H_2O$ dissociation coordinate and on a 100 ps timescale by coupling of the H_2O intramolecular bend vibrations with the $Cu–H_2O$ dissociation coordinate.[24,39,40]

Hydrogen and methyl substituents, and functional groups in general, play pivotal roles in a wide array of chemical reactions. Substitutions of CH_3 for H, and vice versa, can influence reactivity, especially due to steric interactions. Methyl groups have been shown to affect the structure and binding energy in $I^-(ROH)$ complexes, ($R = H, CH_3$),[41] and have recently been part of an investigation of infrared spectral features in $Cl^-(ROH)$ complexes, ($R = H, CH_3, CH_3CH_2$).[42] In this thesis, the effects of a methyl group addition on the dissociation dynamics of a metal-ligand complex are investigated. We are interested in determining how the methyl group affects the solvent reorientation and dissociation dynamics in a $Cu^-(ROH)$ ($R = H, CH_3$), complex. For experimental reasons, the spectroscopic studies are carried out using fully deuterated methanol. Reports from previous investigations[24,25] on $Cu^-(H_2O)_n$ show no significant difference in the time-evolution of the dissociating neutral complexes upon deuteration.

1.3 The time-resolved solvent induced recombination of $IBr^{-}(CO_2)_n$

In this study, femtosecond pump-probe spectroscopy is used to examine the recombination and relaxation of an excited IBr^{-} chromophore. This process is highly influenced by the interaction of the chromophore with its surrounding solvent molecules. The stepwise investigation of this influence provides insight not available in condensed phase studies. The utilization of anions as a tool to probe chemical dynamics of this nature has recently been discussed by Neumark[13].

Although it may seem surprising that a small cluster can serve as an adequate prototype of a much larger condensed phase system, it has been demonstrated that certain solvent-induced phenomena require very few solvent molecules to occur. Examples of such phenomena are the "cage" effect,[43-65] and the solvent-induced recombination, which in some cases can be observed with as few as only one solvent molecule present.[66,67]

The investigation in this chapter continues an extensive experimental study of dihalide ion clusters $XY^{-}L_n$ (X,Y = I, Br, Cl; L = CO_2, OCS, Ar) that display the profound effects of the solvent on the dissociation dynamics of the XY^{-} core.[2,7,67-76] In the present work we investigate dependence of the rate of solvent-induced recombination in size-selected $IBr^{-}(CO_2)_n$, n = 5-10 clusters excited to the $A'\ ^2\Pi_{1/2}$ state of the IBr^{-} chromophore, as a function of number of solvent molecules. The investigation encompasses a range of solvation where the recombination has been shown to be nearly complete,[77] and where past experience[7,75,78,79] indicates the likelihood both of very rapid recombination rates and of rates that increase with increasing solvation.

Potential energy curves of the unsolvated IBr^{-} anion are shown in Fig. 1.2.[77] Excitation of this unsolvated anion with 790 nm radiation produces only I^{-} and Br fragments, indicating that the $A'\ ^2\Pi$ state is the only state excited at this wavelength. Our earlier investigation of IBr^{-} showed[77] that the addition of a single CO_2 solvent results in the appearance of the Br^- ion, indicating a solvent-induced non-adiabatic process. The first "caged" product, IBr^-, appears from excitation of $IBr^-(CO_2)_2$. The cage fraction rises to 90 % for $IBr^-(CO_2)_5$, and, for clusters with $n \geq 8$, only recombined ionic products are detected. This behavior is very similar to that observed for $I_2^-(CO_2)_n$,[79] and, consequently, trends in the timescales of the recombination processes for $IBr^-(CO_2)_n$ and $I_2^-(CO_2)_n$ were expected to be comparable. However, a preliminary measurement of the recombination time for $IBr^-(CO_2)_8$ found a nanosecond recombination time, some two orders of magnitude

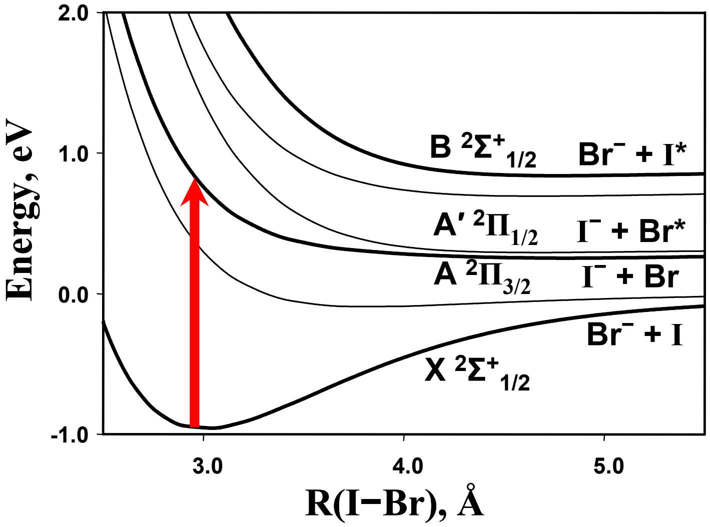

Figure 1.2 Calculated potential energy curves for the lowest six electronic states of IBr^-. The arrow indicates the pump/probe transition from the ground state (X) to the first excited state (A′).

slower than that of $I_2^-(CO_2)_n$ clusters.[77] Such a drastic discrepancy must reflect a fundamental difference between $IBr^-(CO_2)_n$ and $I_2^-(CO_2)_n$. In order to help understand this difference, we have carried out a more thorough experimental measurement of recombination times for a number of $IBr^-(CO_2)_n$ clusters. When complemented by extensive calculations,[80] these experiments provide the likely explanation for the anomalous recombination of

$IBr^{-}(CO_2)_n$ as arising from a solvent–induced trap on the IBr^{-} $A' \, {}^2\Pi_{1/2}$ surface, a trap that arises from the solvent asymmetry, and is deepest for 5-10 CO_2 solvent molecules.

1.4 Dissertation overview Part A: Experimental Physical Chemistry

The work presented in this section of the dissertation is divided into three chapters. Chapter II presents the experimental setup and laser system configurations for both studies. Chapter III presents the femtosecond photodetachment-photoionization investigation of $Cu(CD_3OD)$. Chapter IV presents the time resolved recombination studies on CO_2 solvated IBr^{-}. Due to the diverse nature of the work presented in this dissertation, each individual chapter will present conclusions and outline future directions depending on the investigation.

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Chapter II

Experimental Apparatus

2.1 Overview

Both sets of experiments described in this portion of the dissertation involve the combination of femtosecond pump-probe laser pulses with mass selected anions in a tandem time-of-flight (TOF) mass spectrometer. Following this interaction, either anionic or cationic photoproducts are detected. This experimental apparatus section first describes the two types of cluster ion sources used in each experiment; second, the mass spectrometer is described in detail; next, the laser system and optical components for each experiment are presented; and finally, the data acquisition procedures are outlined.

2.2 Cluster ion and discharge sources

Cluster anions are created in one of two different sources (Fig. 2.1) depending on the nature of the starting materials. The $Cu^-(CD_3OD)$ anion experiment requires the generation of gas-phase copper metal, this is achieved via a high pressure pulsed sputtering discharge ion source. Solid IBr crystals have a high enough vapor pressure to produce $IBr^-(CO_2)_n$ cluster ions by crossing a neutral supersonic expansion perpendicularly with a high energy beam of electrons.

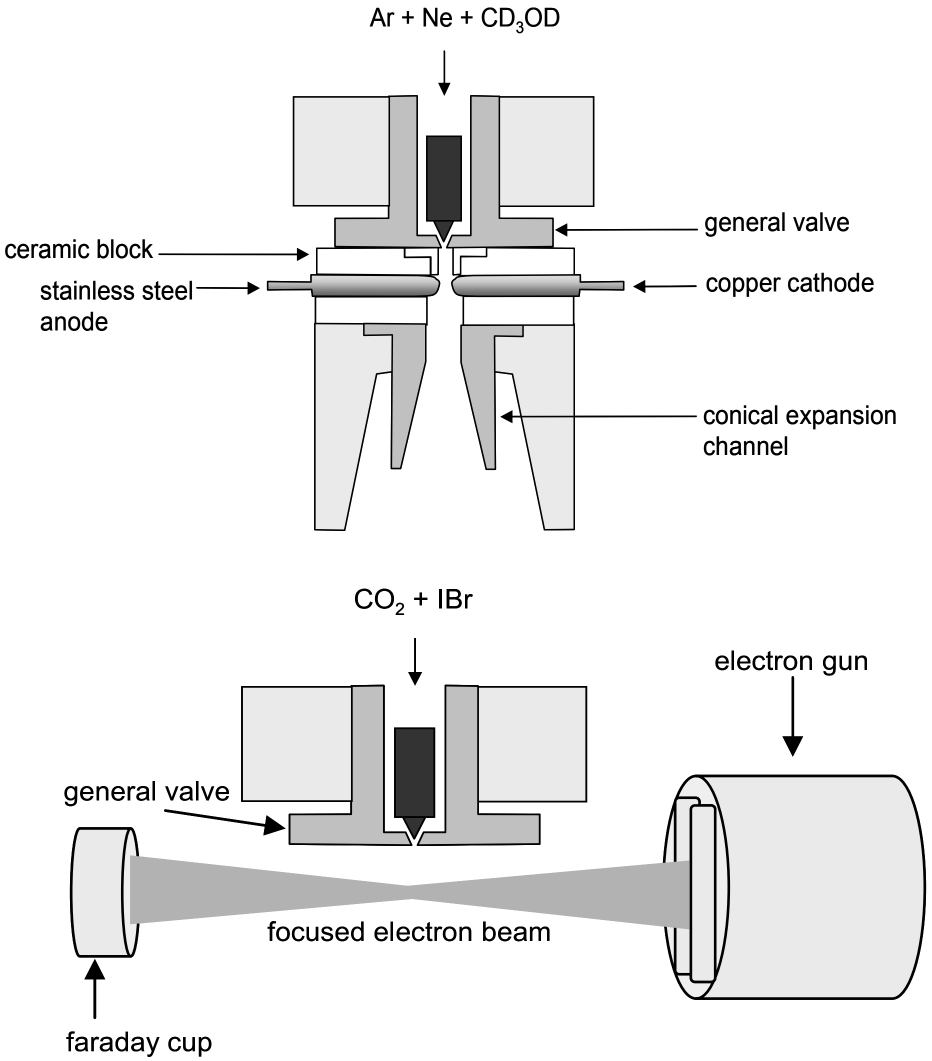

Figure 2.1 Schematic diagram of the sputtering discharge ion source for generation of $Cu^{-}(CD_3OD)$ and electron gun source for generation of $IBr^{-}(CO_2)_n$ clusters.

To generate copper-methanol anions a mixture of 80% Ne and 20% Ar at stagnation pressures between 6–8 atm, flows through a small stainless steel vial containing liquid methanol-d_4 (CD_3OD, Aldrich, CAS# 811-98-3) at room temperature and is expanded into vacuum through a pulsed (200 Hz) General Valve (0.8 mm orifice). Copper anions are produced when the carrier gas flows past a 1 mm gap between a copper rod cathode maintained at negative 2–3 kV and a stainless steel anode maintained at ground, as seen in

Fig. 2.1. Immediately following the discharge, cluster anions form in the expanding gas. The gas enters a 40° cone used to cool and stabilize clusters upon introduction into the ~ 5 x 10^{-5} Torr pressure of the source chamber. Along with $Cu^-(CD_3OD)_n$ ions, the source generates Cu^-_n, $Cu^-(D_2O)_n$, Cu^-D_n, Cu^-OD, $Cu^-(CD_3O)$, and $CD_3O^-(CD_3OD)_n$ anions. In order to avoid mass contamination of $^{63}Cu^-(CD_3OD)$ with $^{65}Cu^-(CD_3O)$, the less abundant, but isotopically pure, *m/*z 101 ion packet is studied, $^{65}Cu^-(CD_3OD)$. Photodetachment-photoionization experiments on $^{65}Cu^-(CH_3OH)$ were not performed due to the congestion of the mass spectrum in that region.

While evaporative cooling[1,2] allows estimates of anion cluster temperatures, rotational and vibrational temperatures of the anions produced in our sputtering discharge source have not been well characterized. Previous anion cluster studies estimate the temperature of $(H_2O)^-_{18}$ and $I_2^-(CO_2)_{16}$ cluster ions[3,4] and indicate these cluster temperatures to be ~ 150 K and ~ 50 K, respectively. These studies are used to estimate the temperature for our smaller $Cu^-(CD_3OD)$ clusters ($m/z = 101$) to be greater than 150 K. For the purpose of calculations in this study, a vibrational temperature of 200 K is used. The qualitative conclusions, however, do not depend on the exact temperature.

The $IBr^-(CO_2)_n$ cluster ions are formed[5] in the supersonic expansion of a gas mixture obtained by passing 2-3 atm of CO_2 through a glass reservoir containing crystals of IBr (Aldrich, 98% purity, CAS# 7789-33-5) at room temperature. The time required to passivate the supply gas line was reduced from a week[6] to less than a day by replacing stainless steel lines with Teflon tubing.[7] The mixture enters a source chamber through the 0.8 mm diameter nozzle of a General Valve operating at 100 Hz repetition rate and is immediately intersected by a 300 μA, 1 keV electron beam. Attachment of slow secondary electrons produces IBr^-, from which $IBr^-(CO_2)_n$ clusters grow via ion-neutral collisions. Based on prior modeling of the expansion conditions,[8,9] we estimate the resultant cluster ion internal energy to correspond to a temperature of 40-70 K.

2.3 Mass spectrometer

The time-of-flight (TOF) mass spectrometer has been described in detail previously,[5,10,11] only relevant details will be given here. After ions are produced in either source, negative ions are extracted into a differentially-pumped Wiley-McLaren[12] TOF mass spectrometer (Fig 2.2) by a pulsed transverse electric field located 10 cm below the expansion nozzle. This extraction field provides the first acceleration stage in the mass spectrometer with a pulse risetime of 10 ns and a 1 ms duration, the voltage varies between -500 and -1000 V depending on the ion focusing conditions. In the second acceleration region, the ions are further accelerated to a total energy of ~3.5 keV, and brought to a spatial and temporal focus at the laser interaction region, 1.5 m downstream. Immediately after the acceleration region, horizontal and vertical deflectors are used to steer the ions. An einzel lens, operating in decelerating mode, is used to focus the ion packet.

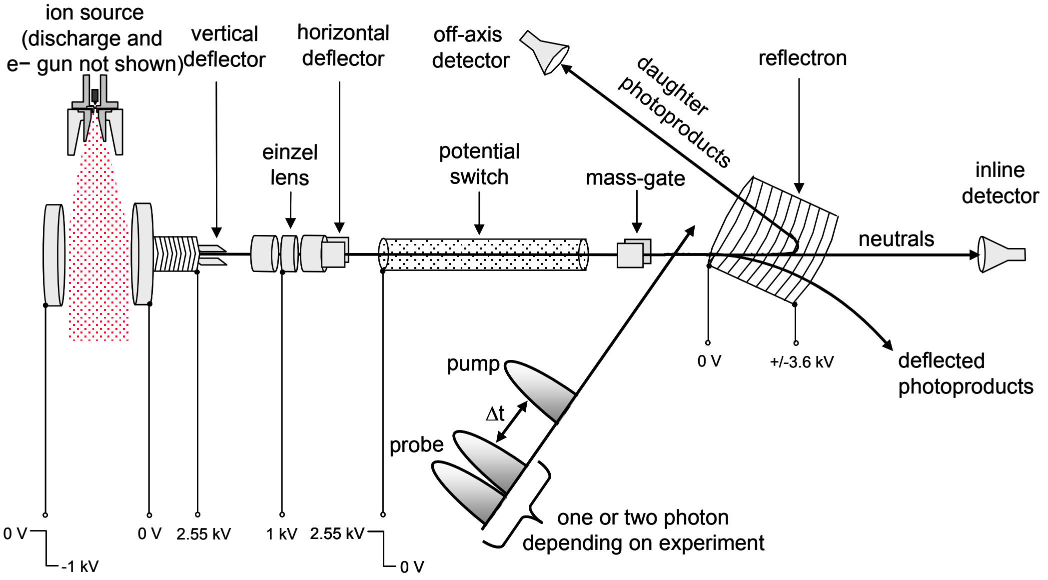

Figure 2.2 Schematic diagram of the Wiley-McLaren time-of-flight mass spectrometer.

After the einzel lens, the ions are deflected around a 1.5° bend in the flight path which separates neutral particles from the ion beam. Ions in the mass spectrometer enter a field-free 'potential switch' region,[13] which switches the reference potential of the ions from +2.55 kV to ground. This relieves the need to float the detector region of the instrument at +2.55 kV. The potential switch is a 40 cm long cylindrical mesh with 2.5 cm diameter apertures at both ends. This mesh is electrically isolated from the rest of the flight tube. The ions enter the cylinder, which is initially biased at the same +2.55 kV potential as the final element of the second acceleration region. Once inside the field-free cylinder, a pulse generator (Directed Energy, model PVX-4140) switches its potential to ground ($\Delta t \leq 25$ ns), and the ions present in the switch exit into the detector region referenced to ground. In the m/e = 100 amu range, this potential switch provides an effective transmission window of Δ m/e $\approx$ 80 amu.

The field free region of the mass spectrometer is 1.5 m in length, after traveling this distance; ions are separated by mass into discrete packets. For example, the two isotopes of copper (m/e = 63 and 65) are separated by $\Delta t \approx 200$ ns. This separation is sufficient enough to allow a pulsed mass gate to transmit the ion packet of interest while deflecting all other ions. This serves in reducing noise arising from scattered ions. The mass gate is operated at a deflecting potential of -1 kV, with a field-free transmission window of width $\Delta t \approx 200$–500 ns. Deflected anions are collected by a tube mounted on the front aperture of the reflectron in order to reduce scatter into the detector mounted above. To further reduce noise, a horizontal plate is extended from the off-axis detector housing to the front face of the reflectron, this prevents anion scatter from the front faces of the mass gate or the reflectron, from striking the off-axis detector. The addition of this horizontal plate reduced background counts from ~ 30 counts in 800 laser shots to less than 5 counts. Approximately 5 cm after the ion packet of choice exits the mass gate, the packet is intersected by the laser beams. At this point, the ion packet has a ~3 mm waist and ~3 mm length and is estimated to contain $10^3 – 10^4$ ions. The pump-probe process which takes place at this intersection varies depending on the experiment but ultimately produces daughter ion fragments.

In the copper-methanol experiment a pump pulse produces neutral clusters which are then resonantly ionized via a two-photon probe pulse. The packet of anions, neutrals and cations enter a single field reflectron mass spectrometer.[14] In this experiment, the reflectron serves two purposes. First, it separates the anions from the neutral and cation photoproducts: reflecting and spatially focusing either anions or cations onto an off-axis detector while transmitting the undeflected neutrals to an in-line detector. Second, it provides secondary mass analysis of the parent and photofragment ions. The reflecting potential varies from ground, at the entrance, to typically ±3.6 kV at the exit of the reflectron. The reflecting potential is set either negative or positive to decelerate, reflect and focus the trajectories of anions or cations, respectively, while deflecting the ions of opposite charge. The small mass difference between the parent cation, $Cu^+(CD_3OD)$, and the cation photofragment, Cu^+, does not necessitate variation of the reflectron potential to separately optimize their spatial foci at, and positions on the off-axis detector.

For the $IBr^-(CO_2)_n$ studies, both pump and probe photons have enough energy to promote the chromophore to a low-lying dissociative excited state. Recombination and relaxation from this excited state produces various daughter fragments based on the size of the parent. The ion packet containing both parent and daughter cluster ions enters the reflectron where they are mass separated. The mass of the parent and daughter clusters varies by more than 200 amu on average. This large mass difference requires variation of the reflectron voltage in order to allow transmission of either the parent anionic cluster or the dissociation products. Typical reflectron voltages range from -1 kV for the smaller clusters to -3.5 kV for the parent clusters.

Ions which exit the reflectron impinge upon a detector displaced 10° above the primary axis of the ion beam. The off-axis detector is a dual microchannel (MCP) plate pair

(Burle Electro-Optics 31558, diameter = 25 mm), located ~20 cm from the reflectron exit. The entrance housing of the off-axis detector contains a mesh grid biased at -200 V, this potential eliminates low energy electrons from the ion beam reducing detector noise. In order to enhance the detector efficiency, the ions receive an additional 3 keV of energy before striking the first MCP plate. The off-axis detector is operated in one of two modes. When detecting parent negative ions the detector is operated at low gain, in analog mode. The front of the first MCP is maintained at the flight potential of +3.00 kV, the front of the second MCP at +4.35 kV, and the MCP anode at +4.55 kV. When employed to detect daughter ions, the detector is operated at a higher voltage in a gain saturated (particle counting) mode. For example in the IBr anion cluster experiments, the front of the first MCP is maintained at the flight potential of +3.00 kV, the front of the second MCP at +4.90 kV, and the MCP anode at +5.10 kV.

Neutral products which pass through the reflectron are collected on an in-line channeltron detector (Burle Electro-Optics, 32685) situated approximately 20 cm downstream from the last element of the reflectron. Any ionic products which pass all the way to the end of the reflectron are deflected away from the channeltron by a pair of parallel plate deflectors mounted on the rear of the reflectron. The dual charged-neutral collector arrangement enables the normalization of the time-dependent off-axis signal to the time-independent neutral signal. This dual detection allows for the reduction of fluctuations in the time-dependent ion signal due to fluctuations in the negative ion intensity or timing jitter between the ion packet and laser pulses.

2.4 Laser System

The femtosecond laser system used in these experiments has been in operation in our group for over a decade. It has therefore been fully described in previous publications,[9,15] a brief description is provided here. A Ti:sapphire oscillator (Coherent Mira Basic), pumped by a Nd:VO_4 laser (Coherent Verdi V5, $\lambda = 532$ nm), produces ~85 fs pulses at 750–850 nm, with a repetition rate of ~76 MHz and pulse energy of 7–8 nJ. Since the present experiments require higher photon fluxes than are provided by the Ti:sapphire oscillator, the pulses are amplified by a regenerative, multi-pass Ti:sapphire amplifier (Quantronix Titan), which is pumped by a Nd:YLF laser (Quantronix, model 527 DQ, $\lambda = 527$ nm). The amplifier output has a pulse energy of ~3 mJ at a repetition rate of 400 Hz. The temporal pulsewidth is measured to be ~120 fs by optical autocorrelation (INRAD, model 5-14BX) and the spectrum, centered at $\lambda = 800$ nm, has a bandwidth $\Delta\lambda \approx 10$ nm.

The photodetachment-photoionization experiments utilize the optical set-up shown in Fig. 2.3. In this configuration two-thirds of the 800 nm pulse from the amplifier is diverted into a commercial harmonic generator (CSK Optronics Supertripler, model 8315A). Second harmonic (400 nm) and third harmonic (267 nm) pulses are generated using 1 mm lithium triborate (LBO) and 1 mm β-barium borate (BBO) crystals, respectively. The remaining one-third of the 800 nm pulse pumps an optical parametric amplifier (OPA, Light Conversion, TOPAS), whose fourth harmonic output provides tunable radiation between 300 and 400 nm. The OPA and second harmonic beams passes through independent delay stages. A micrometer stage provides a fixed delay of 0.3 ps between the OPA beam and the third harmonic beam. This slight delay ensures that OPA beam comes before the third harmonic. The second harmonic beam passes through a computer controlled stage (Parker, 008-9129) providing delays up to 800 ps with a resolution of 100 fs. All the beams are combined collinearly using dichroic beamsplitters, and pass though a fused silica window into the mass spectrometer. The beams are focused to a spot of ~1 mm diameter, at the point of interaction with the ion packet, using independent telescopes. At this point, the typical pulse energies are 100 μJ for 400 nm, 60 μJ for 267 nm, and 10–12 μJ for the OPA.

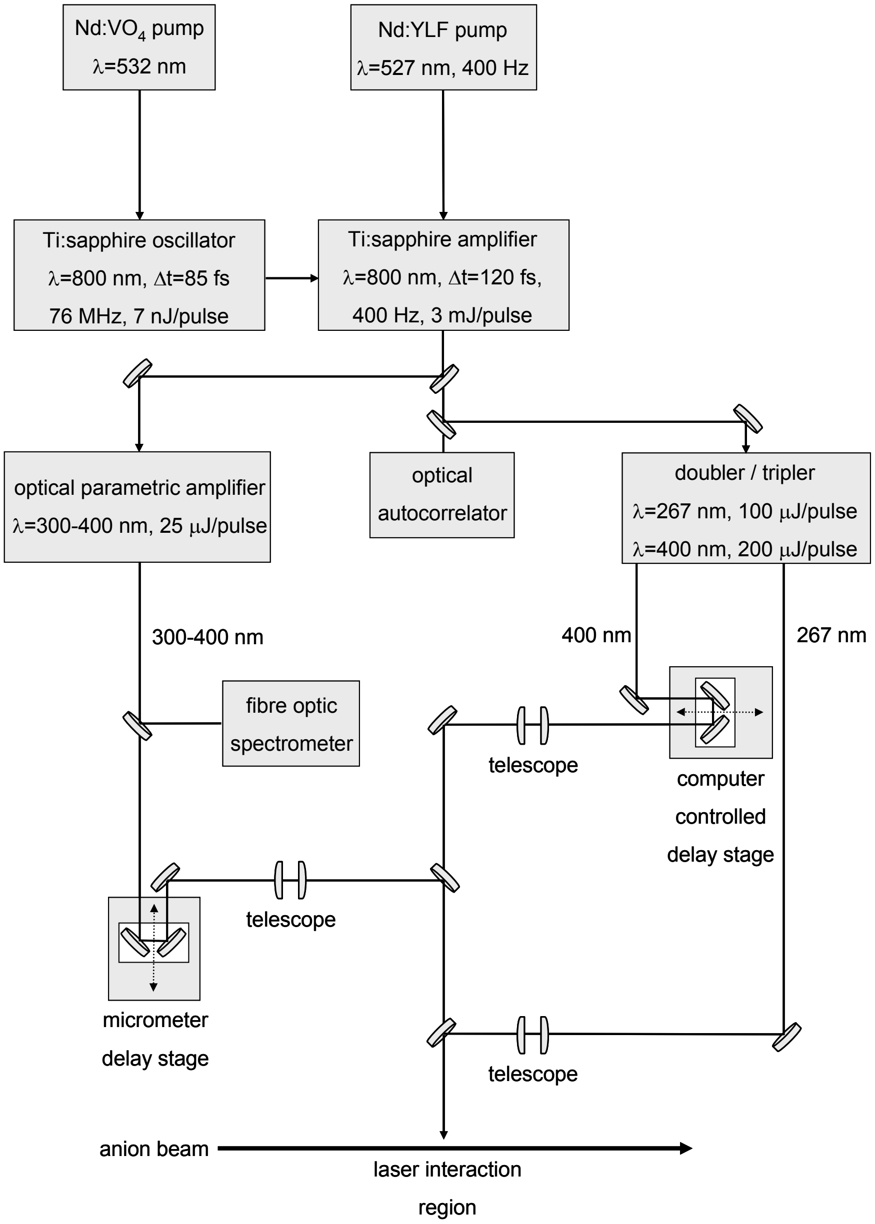

Figure 2.3 Optical set-up for photodetachment-photoionization experiments.

The one color multi-photon experiments on solvated IBr$^-$ clusters utilize the optical configuration depicted in Fig. 2.4. In this configuration half of the 795 nm output from the amplifier passes through a computer controlled delay stage (Parker, 008-9129) with a range of 800 ps, and a time resolution of ~100 fs. The remaining amplifier output travels through an optical rail delay stage with a range of 3.5 ns. Manual positioning along the optical rail leads to a precision of ~20 ps. The two beams are recombined collinearly and focused using a single telescope before passing through the fused silica window into the mass spectrometer. At the point of intersection with the ion packet the beams have a spot of ~1 mm diameter and pulse energy of ~500 μJ each.

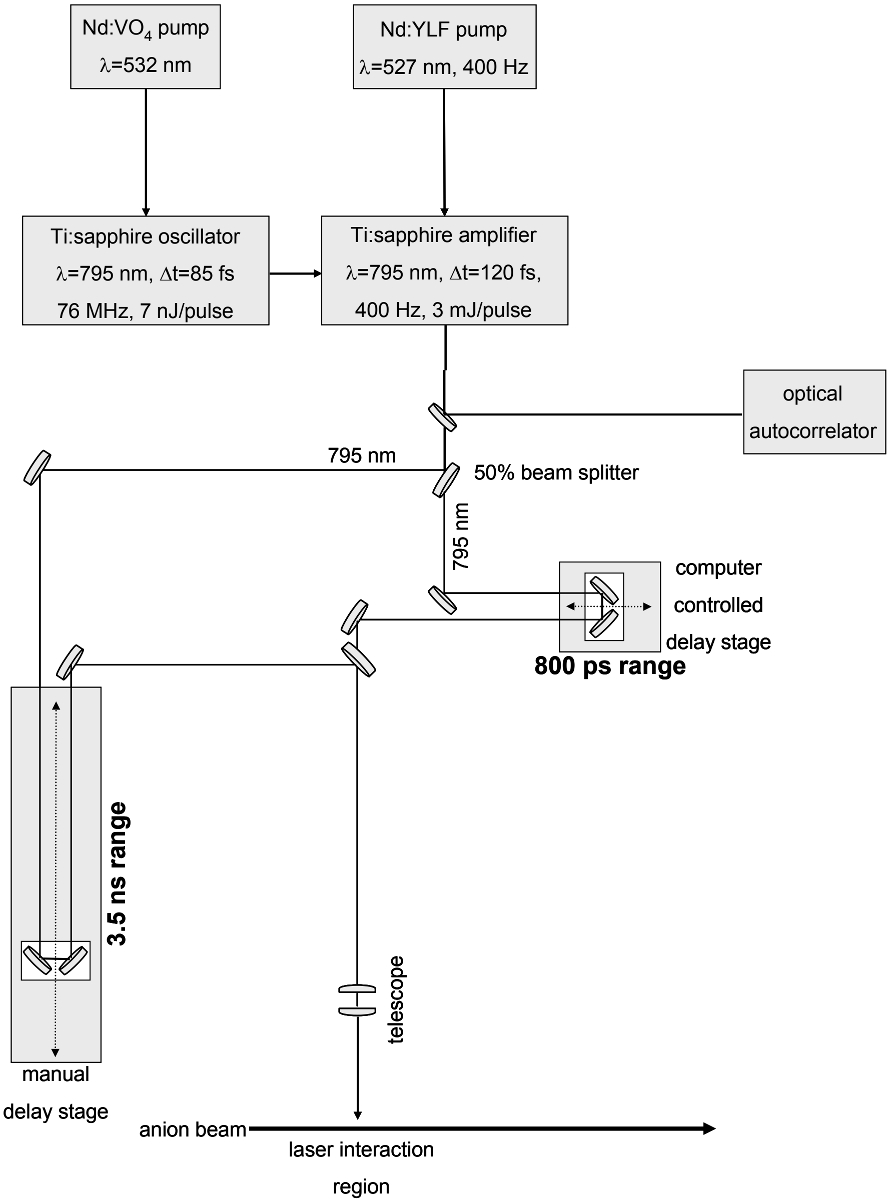

Figure 2.4 Optical set-up for one color multi-photon recombination studies.

Daily set-up for both optical configurations involves optimization of the power, shape, and overlap of the pump and probe beams. Clean homogenous beam shapes are needed in order to provide consistent overlap over the range of delays scanned during either experiment. Pulse power optimization mainly consists of daily optimization within the amplifier itself, although some power is gained through careful optimization within the OPA for the photodetachment-photoionization experiments. The optical configuration in Fig. 2.3 contains many non-linear crystals, the alignment and focusing of the beams into the crystals is critical to produce consistent beam profiles. The set-up in Fig. 2.4 only utilizes the fundamental output from the amplifier making beam shape optimization facile. Optimal pump-probe overlap is achieved in a two-step process. First, one beam is carefully overlapped with the ion beam in order to maximize the one photon signal. The remaining beam is then overlapped with the first. In this second step, carefully attention is paid to the overlap of the beams over the entire range of the computer controlled delay. Remaining beams are then overlapped using the same procedure.

2.5 Data Aquisition

A schematic diagram of the signal processing electronics for both experiments is presented in Fig. 2.5. Because the collector anode of the off-axis MCP detector is floated at high voltage, the ion signal is capacitively coupled to the signal processing electronics. This configuration allows the transient signal spikes to pass through to the amplifiers while isolating the high voltage. The signal is amplified in two stages, first by a fast 10x preamplifier (Ortec, model 9301) directly connected to the output capacitor, this stage is followed by a rack mounted bipolar amplifier (Phillips Scientific, model 771) providing an additional 10x amplification. The resulting signal is split (Minicircuits, model ZSC-2-2), with one half monitored on an oscilloscope and the other half proceeding to the particle counting electronics. Negative ion mass spectra are recorded using a 100 MHz transient recorder/signal averager (TRANSIAC, models 2101/4100), and accessed by a PC through a GPIB interface to the CAMAC crate (Kinetic Systems, model 1510-P2C), which is controlled by a GPIB crate controller (DSP, model 6001).

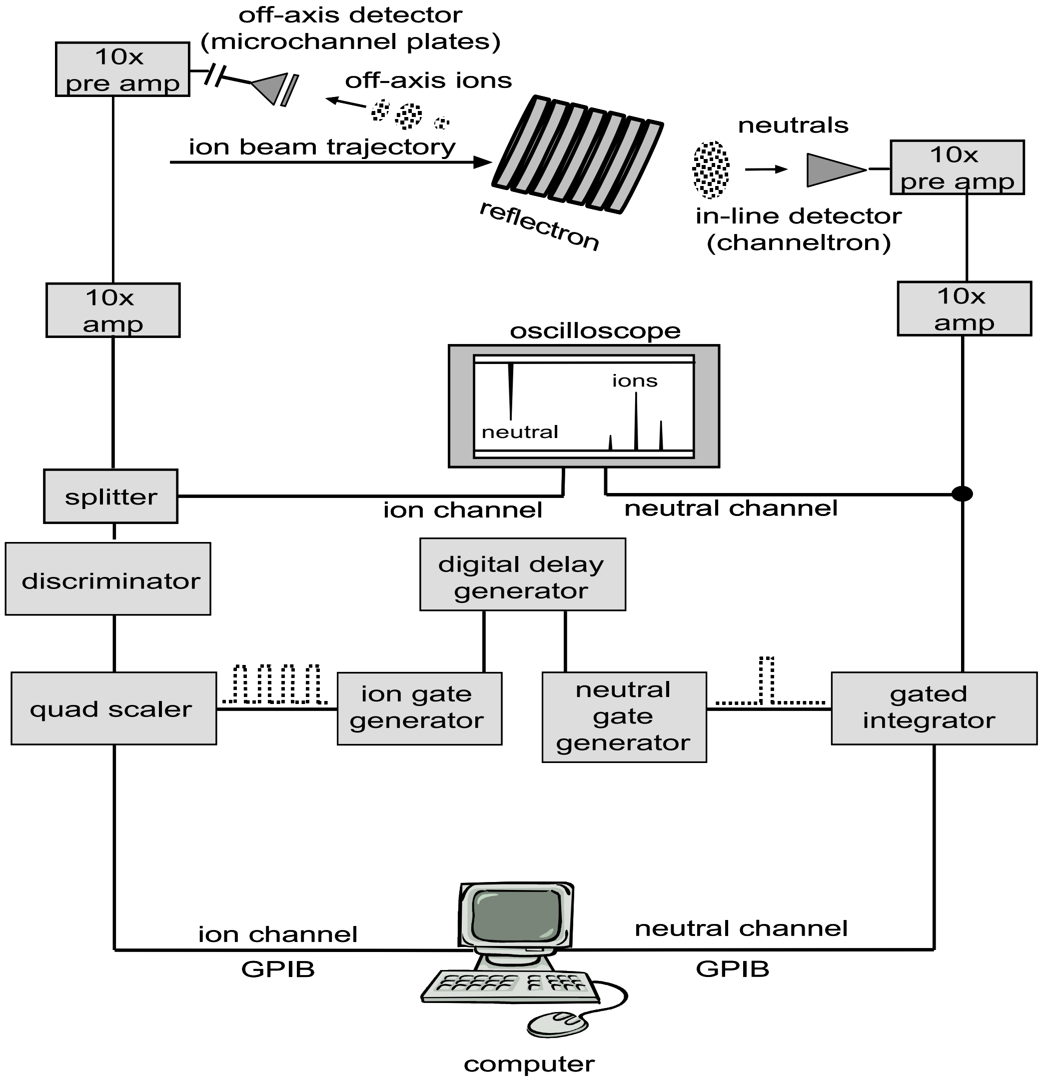

Figure 2.5 Schematic diagram of data acquisition system used in both experimental configurations.

When the experiment is being operated in ion counting mode, a 300 MHz discriminator (Phillips Scientific, model 6904, discrimination threshold ≈ 150 mV) separates detector noise from the ion signal. The ion signal is input into a quad scaler (DSP, model QS-450), which counts the pulses associated with individual ions. The quad scaler counts only the ions that arrive in one of four time-gates positioned around the arrival times of the desired photoproducts. The timing of the gates is controlled by a digital delay generator (Stanford Research Systems model DG 535). A PC acquires the signal from the quad scaler via the previously described GPIB interface and CAMAC crate.

The neutral products give rise to an analog signal at the in-line channeltron detector. This signal is amplified by a fast 10x preamplifier (Ortec, model 9301) connected in close proximity to the channeltron collector. A 10x bipolar amplifier (Phillips Scientific, model 6950) increases the total amplification to 100x, the amplified signal is split between an oscilloscope and a gated integrator (LeCroy, model 2249SG). The neutral signal is integrated in a time-gate generated by a pulse generator (Tektronix, model PG502) and timed by a digital delay generator (Stanford Research Systems model DG 535). The PC acquires the signal from the gated integrator via the previously described GPIB interface and CAMAC crate.

Two digital delay generators (Stanford Research Systems, model DG 535) control the timing of the experiments, while the master clock of the experiments is provided by the pulse train from the Ti:sapphire oscillator. A small fraction of this ~76 MHz pulse train is continuously monitored by a photodiode, and the resulting signal, divided to ~400 Hz, is used by a Pockels cell driver (Medox Electro-Optics, model DR85-A) to trigger the Ti:sapphire regenerative amplifier and the Nd:YLF pump laser. The ~400 Hz signal from the Pockels cell driver is divided down (Modulo-N divider, JILA LC022-2) to match the repetition rate needed to produce the best ionic clusters, and used to trigger the two digital delay generators.

The timing of the sequence of events in the experiments is critical for optimal ion production and detection. The first event is the relative timing between the gas pulse produced by the general valve and extraction field pulse. This timing is adjusted so that the highest density of anions is accelerated into the mass spectrometer. Once extraction has occurred, the next event is the timing of the pulsed potential switch; this timing is adjusted so that the mass range of interest is referenced to ground potential and proceeds on to the mass-gate. Next in line is the mass-gate timing itself; this is adjusted to allow maximum transmission of the parent anion packet. Timing between the extraction pulse and the laser pulse is optimized in order to ensure that the photons interact with the densest portion of the ion packet selected by the mass-gate. The last timing involves the time-gates used in the integration of the neutral and ion photoproduct signals, these gates are adjusted to collect signal corresponding to the parent anion as well as the photoproducts and neutral signal.

The photodetachment-photoionization data acquisition procedure consists of scanning a range of time delays between the pump pulse and the probe pulses, while simultaneously integrating the analog neutral signal and the individual cation photoproduct signals. One single scan consists of sweeping the entire range of time-delays while data is accumulated during 800 laser shots per time delay. Many back and forth scans are performed, for a total of ~4 x 10^4 laser shots per time delay. The final signal (after appropriate background corrections) is given by the cation signal divided by the neutral signal. Background cation and neutral signals arising from each of the one and two color combinations are measured, at a range of pump-probe time delays, using computer controlled shutters (Uniblitz, model VS14S2T0) in each of the beam paths. These measurements are used for two purposes. First, they enable analysis of the contribution that each of the three laser pulses makes to the cation signals. Second, these background measurements are typically recorded at the beginning and end of data acquisition. Subtraction of the appropriate background signals from the raw time dependent cation/neutral signal furnishes the final two or three-color signals, depending on the channel. Typical cation signals are ~0.5 cations/laser shot. Error bars for the experimental data are obtained by comparing the scatter present in multiple data sets.

The IBr^- recombination data acquisition procedure consists of scanning a range of time delays between the pump and probe pulses. One single scan consists of sweeping the entire range of time-delays while data is accumulated during 1000 laser shots per time delay. Many back and forth scans are performed, for a total of ~4 x 10^4 laser shots per time delay. Background signals arising from each of the beams are measured, at a range of pump-probe time delays using computer controlled shutters (Uniblitz, model VS14S2T0) in each of the beam paths. These measurements are used for two purposes. First, they enable analysis of the contribution that each of the laser pulses makes to the ion signals. Second, these background measurements are typically recorded at the beginning and end of data acquisition. Subtraction of the appropriate background signals from the raw time dependent ion signal furnishes the final two photon time-dependent signal. Typical two-photon ion signals are 0.2 – 0.5 ions/laser shot. The number of ions per laser shot is heavily dependent on the size of the parent anion cluster. Error bars for the experimental data are obtained by comparing the scatter present in multiple data sets.

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Chapter III

Femtosecond Dynamics of $Cu(CD_3OD)$

3.1 Introduction

As described in detail in Chapter I, the dynamics of the $Cu(CD_3OD)$ neutral complex are initiated upon photodetachment of an electron from $Cu^-(CD_3OD)$. This process produces a vibrationally excited complex which dissociates through a variety of mechanisms. In this chapter the experimental and theoretical investigation of these mechanisms is presented in the light of previous investigations of the similar $Cu(H_2O)$ complex.[1-4]

The remainder of this chapter is structured as follows. Section 3.2 describes the experimental measurement techniques. In Section 3.3 details of the *ab initio* electronic structure calculations and vibrational wave function determination are described. Section 3.4 presents the results and discussion of the experimental and theoretical work in light of the previous $Cu(H_2O)$ results. Conclusions are presented in Section 3.5.

3.2 Experimental

This section of the thesis describes the photodetachment-photoionization measurements used to investigate the dynamics of the $Cu(CD_3OD)$ van der Waals cluster. The experimental apparatus and data acquisition corresponding to this experiment were previously presented in Chapter II. The various laser pulse sequences used in the present photodetachment-photoionization experiments have been previously presented in detail,[1-3] and therefore, only a brief summary will be presented here. The radial potential energy curves in Fig. 3.1 show that neutral $Cu(CD_3OD)$ complexes are formed by electron photodetachment from $Cu^-(CD_3OD)$ using a 398 nm pulse. Monitoring the time evolution of the neutral cluster is accomplished by photoionizing Cu(CD_3OD) and its fragments in various pump-probe schemes. Figure 3.1 shows the two different pump-probe schemes used to detect the cation photoproducts. Scheme one in Fig. 3.1 is used to monitor the Cu^+ evolution as a function of the delay between the photodetachment and the excitation/ionization pulses; similarly, scheme two in Fig. 3.1 is used to monitor the Cu^+(CD_3OD) evolution. Typical Cu^+(CD_3OD) and Cu^+ signals are ~ 0.5 cations per laser shot.

The time resolution of the experimental apparatus is determined *in situ*, using three-color, three-photon photodetachment-photoionization of Cu^- (Fig. 3.1, scheme 1). The 400 nm pulse photodetaches an electron from Cu^- and a sequence of 327 and 265 nm photons resonantly ionize the $^2S_{1/2}$ Cu atom through the $^2P_{1/2}$ intermediate state.

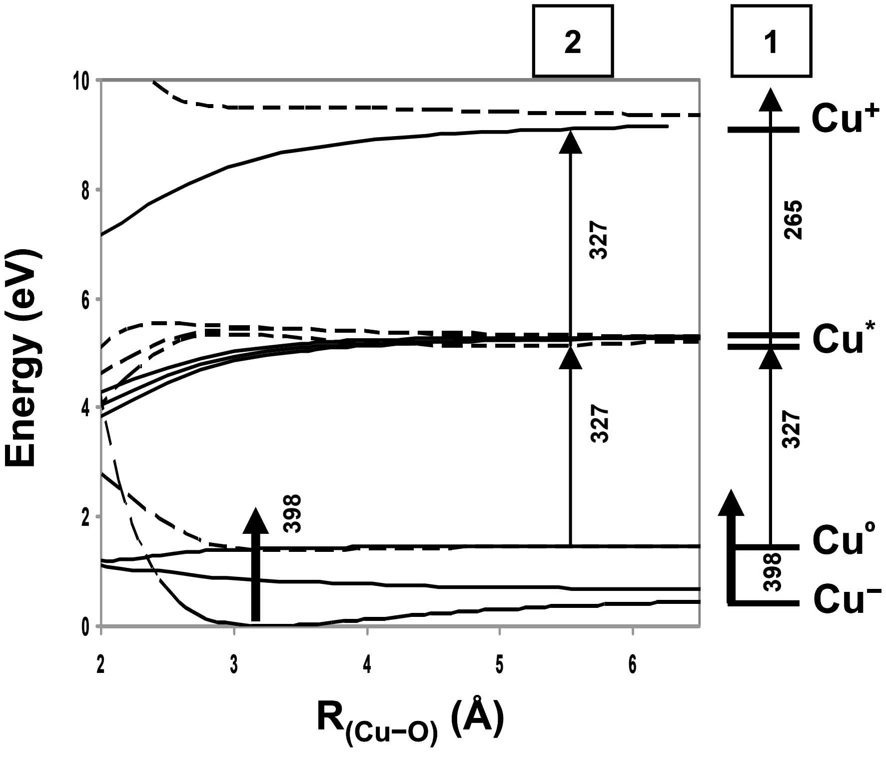

Figure 3.1 Radial potential energy curves and laser pump-probe schemes. Dashed curves represent cuts in the Cu−$DOCD_3$ C_s orientation, while solid curves represent the Cu−$ODCD_3$ C_1 orientation. The vertical arrows represent various pump-probe processes employed in the experiments reported here.

The delay between the excitation (327 nm) and the ionization (265 nm) pulses is fixed at 0.3 ps. As the photodetachment - excitation delay time (Δt) is varied, the Cu^+ signal exhibits a step function increase at $\Delta t = 0$ (Fig. 3.2) and the rise-time of this step provides a direct measure of the time resolution of the apparatus. The solid line in Fig. 3.2 is a fit of the data to the form $A(1+\tanh(t/\tau))$, and the derivative of this fit (dashed line) has a sech^2 form. The width (FWHM) of this sech^2 function provides the effective time resolution of the experimental apparatus, 260 fs.

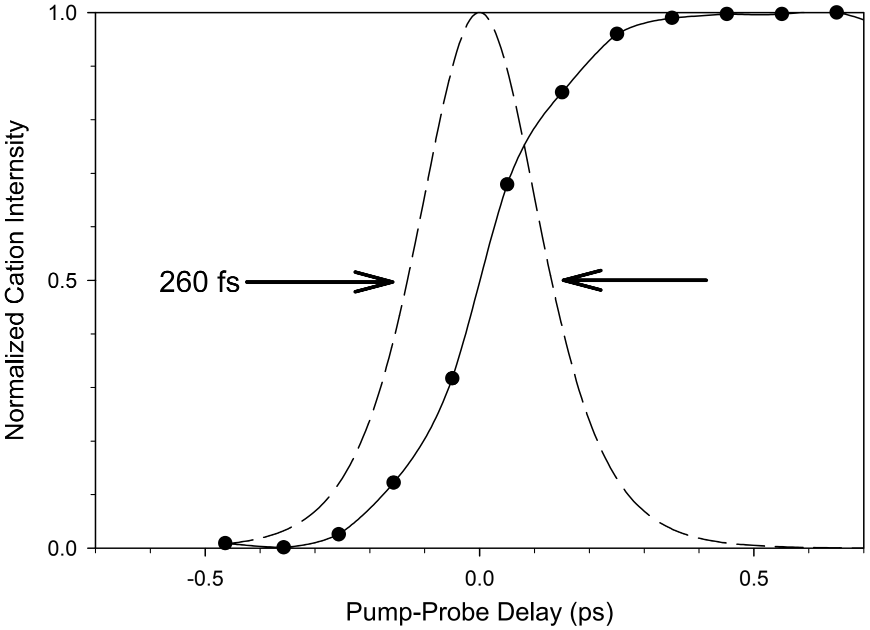

Figure 3.2 The *in situ* measurement of the time resolution for photodetachment-photoionization experiments. Rising points display rising Cu^+ signal as a function of the delay between the photodetachment and photoionization pulse sequence. Solid line represents tanh fit to points and dashed line is the derivative (sech^2) of this fit.

3.3 Theory

Previous experiments on the dynamics of $Cu(H_2O)$[1,4] focused on a three-dimensional, fully-coupled treatment that included the three intramolecular degrees of freedom of H_2O. Although the full-dimensional treatment gave useful information, it was found that many of these insights could also be borne out in analyses of three separate one-dimensional slices. Since carrying out quantum dynamics simulations on Cu(CD_3OD) in full dimensionality is impractical, we draw from our experiences with Cu(H_2O) and expect that the one-dimensional decoupled picture should hold as well for Cu(CD_3OD) as it did for Cu(H_2O). It is for this reason that we coupled the four one-dimensional motions to produce the full, four-dimensional representation.

The calculations used to characterize the Cu(CD_3OD) complex fall into two general categories. First we determine the minimum energy configurations for the anion, neutral, and cation complexes and then evaluate a series of one-dimensional slices through the potential energy surfaces, starting from these geometries. These one-dimensional potential energy surfaces are used to calculate vibrational wave functions and energies using a sinc-discrete variable representation (DVR).[5,6] The resulting energies and wave functions are used to investigate the regions of the potential surface that are sampled by Cu(CD_3OD) upon electron photodetachment. In particular we focus on the partitioning of energy among the internal coordinates and how this is reflected in the time-dependent signal and Cu(CD_3OD) photoelectron spectrum.

3.3.1 *Ab initio* calculations

All electronic structure calculations are performed using the GAUSSIAN 98 or GAUSSIAN 03 program packages.[7,8] The basis sets and level of theory used in these calculations have been described in a previous study,[2,4] and therefore, only brief details will be given here. The basis set used to represent the copper atom is an augmented form of the Stuttgart-Dresden-Bonn (SDB) relativistic core potential developed by Preuss and co-workers,[9] referred to as aug-SDB. The aug-SDB basis was developed by Wang and co-workers[10] during their investigation of anion and neutral CuX_2 (X = Cl, Br). Hydrogen, oxygen, and carbon are each represented by aug-cc-pVTZ[11,12] basis sets. Second-order

Møller-Plesset perturbation theory (MP2) was used to optimize all geometries, as well as in calculation of various potential energies. The minimum energy configurations for the anion, neutral, and cation complexes are shown in Fig. 3.3(a), (b), and (c) respectively.

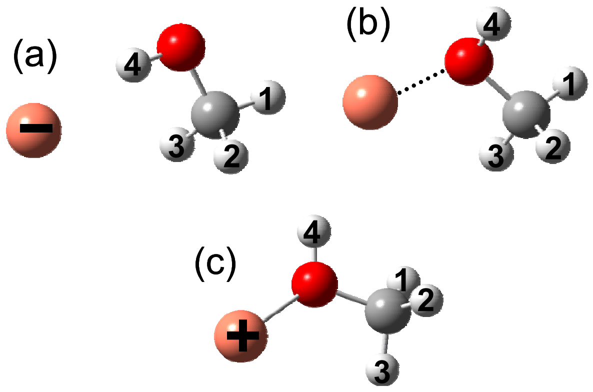

Figure 3.3 (a) Minimum energy configuration for $Cu^{-}(CD_3OD)$, used to define coordinates for the four 1-d slices employed in the simulations: Cu—O stretch; out-of-plane bend, Cu-O-C-D_4 dihedral angle; in-plane bend, Cu-O-C angle; and methyl group rotation, D_1-C-O-D_4 dihedral angle. Also shown are the minimum energy configurations for the neutral (b), and the cation (c).

Both radial and angular one-dimensional potential slices are calculated at the MP2 level of theory, beginning from the minimum energy configuration of the anion and neutral. We also calculated one-dimensional cuts starting from the vertical detachment geometry (VDG), i.e. cuts through the $Cu(CD_3OD)$ potential based on the minimum energy configuration of the anion. For example, the anion surface is calculated as a function of the Cu–O distance, *R*, ranging from 1.6 – 7.6 Å in increments of 0.1 Å. The energy of the neutral surface is calculated over a range of 1.5 – 7.0 Å while the VDG surface ranges from 1.8 – 7.2 Å; both are evaluated in increments of 0.2 Å. In all scans the O–D bond length and the Cu-O-C-D_4 dihedral angle are relaxed at every step, while all other bond lengths and angles are held constant.

Three types of angular scans were carried out, the molecular coordinates for these one-dimensional surfaces are based on the structures shown in Fig. 3.3. The electronic energy is calculated as a function of out-of-plane (OOP) motion by varying the Cu-O-C-D_4 dihedral angle over a range of ± 60° for the anion and ± 180° for the flatter, neutral and VDG surfaces. For all three surfaces, the OOP motion is evaluated in increments of 2°, and the O–D and Cu–O distances are allowed to relax at each step along the path. Variation of the Cu-O-C angle produces in-plane (IP) motion. The electronic energy as a function of this motion is calculated over a ± 60° range in 2° increments for the anion surface and from –180° to 180° in increments of 10° for the VDG surface; the O–D and Cu–O bond lengths are optimized at each step. For all three complexes, the electronic energy is calculated as a function of methyl torsion over a ± 60° range of the D_1-C-O-D_4 dihedral angle in 5° increments. In this cut, all three C–D bond lengths and O-C-D bond angles are relaxed. The ranges for each of the one-dimensional potentials are chosen such that they span the angular regions sampled by the vibrational wave functions for the states of interest.

3.3.2 Vibrational Coordinates and Hamiltonian

One-dimensional variational calculations were carried out using a discrete variable representation (DVR) technique. For the Cu–CD_3OD distance coordinate, R, we use the reduced mass of the complex. The effective masses, b_{eff}, for the angular motions are derived from the rotational constants for the associated molecular motions. In the case of the IP rotation, this corresponds to the rotation of CD_3OD about its C rotation axis, coupled to rotation of the complex about its center of mass. The OOP motion corresponds to rotation of the O–D bond about the C–O bond axis, while the methyl torsion is simply the three-fold rotation of the CD_3 group about its symmetry axis. Based on the above definitions, the values of b_{eff} for these three motions are 0.6687 cm^{-1} (IP), 9.9512 cm^{-1} (OOP), and 4.5172 cm^{-1} (CD_3), and the effective Hamiltonians for the radial and angular motions are respectively

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V(R) \tag{1}$$

$$\hat{H} = b_{eff}\hat{J}^2 + V(\theta)\,. \tag{2}$$

Here J^2 is the angular momentum operator associated with the one-dimensional motions, and as such it has eigenvalues that are proportional to j^2. The potential surfaces, V, are acquired using spline interpolations of the energies obtained from the electronic structure calculations described above. For the stretch coordinate, grid points used for the DVR calculations range from 0.5 to 15.0 Å with a grid spacing of 0.0181 Å. For the bend and torsion coordinates, the grid ranges from –180° to 180° with a spacing of 0.5°. For the stretch coordinate, grid points beyond those from *ab initio* calculations were necessary, and the *ab initio* data are extrapolated using

$$\overset{extrp}{V}(r) = \frac{C_6}{r^6} + \frac{C_8}{r^8}\,, \tag{3}$$

where the values of C_6 and C_8 are chosen to ensure that the potential and its first derivative are continuous.

Within the Condon approximation, the photoelectron spectrum can be generated from overlaps between eigenstates on the anion and neutral surfaces. Since the low-lying vibrational states on the anion surface are localized near the potential minimum, we focus on those eigenstates on the neutral surface that are evaluated using cuts near the equilibrium structure of the anion, e.g. the VDG surface. Within this treatment, the four-dimensional wave functions are approximated by products of four one-dimensional functions. The overlap integrals between the eigenstates on the anion and VDG surfaces are evaluated for each thermally populated state of the anion using the 200 K vibrational temperature as was mentioned above. The resulting spectra are summed and convolved with a Gaussian with a FWHM of 50 cm^{-1} (0.0062eV). This width is chosen to facilitate comparison with experiment.

3.4 Results and Discussion

In this section of the thesis, results from both the calculations and experiments are presented independently. Following this presentation, both sets of data are combined to present a cohesive discussion of the molecular dynamics taking place upon photodetachment of the $Cu^-(CD_3OD)$ cluster.

3.4.1 Initial State Characterization

Electron photodetachment from $Cu^-(CD_3OD)$ produces an ensemble of neutral $Cu(CD_3OD)$ complexes far from their equilibrium geometry, resulting in large amplitude solvent rearrangement and dissociation. In order to investigate the nature of this rearrangement and dissociation, we must characterize the initial state of the ion-molecule complex.

3.4.1.1 Calculations

The anion complex has a distinctly different minimum energy configuration from the neutral and cation complexes, select structural information is listed in Table 3.1. The anion structure, seen in Fig. 3.3(a), has C_s symmetry with the Cu^- positioned in the symmetry plane of methanol. We note that the interaction of methanol with the copper anion lengthens the O–D bond from 0.96 Å in isolated methanol to 0.99 Å in the cluster, and compresses the C-O-D angle from 107.98° in methanol to 105.82° in the cluster. This minimum energy configuration corresponds to a primary interaction between the copper anion and the permanent electric dipole moment of methanol molecule. In fact Cu^- interacts so strongly with the methanol that it lowers the CD_3 torsional barrier by nearly 75%. The barrier to rotation for the neutral complex is 421 cm^{-1}, but the anion has a significantly lower barrier of 110 cm^{-1}. This anion minimum energy configuration corresponds to Cu^-–$DOCD_3$. As shown in the previous study,[1,4] the $Cu^-(H_2O)$ minimum energy geometry corresponds to a C_s

configuration with Cu^- lying in the plane of the water molecule and oriented ~ 33° off the C_{2v} axis of H_2O.

Table 3.1 Select geometrical parameters of all species, calculated at MP2 level of theory.

	CD_3OD	$Cu^-(CD_3OD)$	$Cu(CD_3OD)$	$Cu^+(CD_3OD)$
$R_{(Cu—O)}$	—	3.23 Å	2.04 Å	1.86 Å
$R_{(O—D)}$	0.96 Å	0.99 Å	0.96 Å	0.96 Å
$R_{(C—O)}$	1.42 Å	1.41 Å	1.44 Å	1.47 Å
$\theta_{(C\text{-}O\text{-}D)}$	107.98˚	105.82˚	108.85˚	109.64˚

Calculations of the neutral $Cu(CD_3OD)$ cluster at the MP2 level result in a minimum energy structure with C_1 symmetry, as seen in Fig. 3.3(b). In the minimum energy structure, the neutral copper atom resides 116° off of the methanol symmetry plane at a Cu–O distance of 2.04 Å. In comparing the neutral species to methanol itself we see that the O–C bond length increases, while the O–D bond length remains unchanged, and the C-O-D angle expands slightly. In nice agreement with $Cu(CD_3OD)$, the previous characterization of $Cu(H_2O)$ shows that the minimum energy neutral geometry corresponds to a C_s $Cu–OH_2$ configuration.

Upon electron photodetachment of $Cu^-(CD_3OD)$, the resulting neutral complex is produced with an initial geometry corresponding to the minimum energy structure of the anion. Comparing figures 3.3(a) and 3.3(b) we note that this configuration is far from the minimum energy geometry of the neutral complex, described above. Given the difference in the structural parameters, it is not surprising that the frequencies are also very dissimilar between the anion and neutral complexes. The anion complex has much higher vibrational frequencies, suggesting that the Cu^-–D interaction is much stronger than that of the Cu–O interaction found in the neutral complex. Tables 3.2 and 3.3 provide the harmonic and anharmonic fundamental frequencies of several modes of interest for the anion and neutral complexes. The anharmonic frequencies were obtained from the DVR calculations described above, while the one-dimensional harmonic frequencies were obtained by replacing the potential term in Eqs. (1) and (2) with a quadratic expansion of the potential about a local minimum. In contrast, the fifteen-dimensional harmonic frequencies were obtained from a normal mode analysis at the potential minimum. There are obvious differences among the frequencies, and these frequency discrepancies arise from several sources. The contrast between the two one-dimensional results reflects the anharmonicity of the potentials. As can be seen, the stretch, IP, and OOP potentials are nearly harmonic, while anharmonicity plays a larger role in the torsion potential. The variation between the two sets of harmonic frequencies reflects the difference between the coordinates that are used to define the one-dimensional potential cuts and the normal mode coordinates.

Table 3.2 Calculated fundamental frequencies of the four vibrational modes corresponding to the 1-d potential energy slices for $Cu^{-}(CD_3OD)$ and $Cu(CD_3OD)$, which is the neutral complex in the anion configuration, i.e. the vertical detachment geometry.

Vibration	$Cu^{-}(CD_3OD)$ 15-d Harmonic	$Cu^{-}(CD_3OD)$ 1-d Anharmonic	$Cu^{-}(CD_3OD)$ 1-d Harmonic	$Cu(CD_3OD)$ 1-d Anharmonic	$Cu(CD_3OD)$ 1-d Harmonic
Cu–O stretch	138 cm^{-1}	102 cm^{-1}	104 cm^{-1}	54 cm^{-1}	57 cm^{-1}
IP bend	83 cm^{-1}	119 cm^{-1}	119 cm^{-1}	24 cm^{-1}	32 cm^{-1}
OOP bend	489 cm^{-1}	423 cm^{-1}	495 cm^{-1}	66 cm^{-1}	212 cm^{-1}
CD_3 rotation	44cm^{-1}	53 cm^{-1a}	69 cm^{-1}	105 cm^{-1}	118 cm^{-1}

[a] Due to the near degeneracy of the three lowest energy states of the torsion, this value reflects the energy difference between the third excited state and the ground state.

Table 3.3 Calculated fundamental frequencies for the four vibrational modes corresponding to the 1-d potential energy slices of $Cu(CD_3OD)$, neutral geometry.

Vibration	15-d Harmonic	1-d Anharmonic	1-d Harmonic
Cu—O stretch	230 cm^{-1}	183 cm^{-1}	193 cm^{-1}
OOP bend	298 cm^{-1}	246 cm^{-1}	265 cm^{-1}
CD_3 rotation	82 cm^{-1}	116 cm^{-1a}	123 cm^{-1}

[a] Due to the near degeneracy of the three lowest energy states of the torsion, this value reflects the energy difference between the third excited state and the ground state.

It should also be noted that no fifteen-dimensional harmonic calculations are presented for the VDG in Table 3.2. This stems from the fact that the vertical detachment geometry is not a stationary point on the neutral surface. However, the VDG does manifest itself in the one-dimensional cuts as local minima on the neutral potential energy surfaces. Therefore the one-dimensional calculations are shown in Table 3.2 for comparison to the anion and neutral frequencies.

Since the VDG is not the global minimum on the neutral surface, determining which of the calculated vibrational energy levels correspond to the ground and first excited states of the complex in the VDG can be difficult. For the OOP bend, the lowest energy state that is strongly localized in the VDG minimum is easily assigned, whereas the first excited state is more difficult to isolate. This complication reflects the fact that the barrier to free rotation of the copper atom around the OD group of methanol is only 70 cm^{-1} above this lowest energy state. As the harmonic frequency for this mode is 212 cm^{-1}, it is not surprising that the state that we identify as the first excited state has a frequency much lower than the harmonic value. In fact its energy is close to the barrier to free rotation, and it is rather delocalized over the full range for the OOP angle. The IP motion also exhibits similar difficulties, albeit to a lesser extent. We also calculated the minimum energy structure of $Cu^+(CD_3OD)$, shown in Fig. 3.3(c); key structural parameters for all three charge states are summarized in Table 3.1.

3.4.1.2 Photoelectron Spectra

The $Cu^-(CD_3OD)$ photoelectron imaging spectrum reported here was obtained using a similar instrument to that described in the experimental section. Modifications include the use of tunable radiation produced by a Coherent Infinity Nd:YAG-pumped optical parametric oscillator and the addition of a photoelectron imaging device.[13] As this spectrometer has been described previously,[14,15] only relevant details will be given here. The imaging system is operated in the velocity map imaging[16,17] mode. This photoelectron imaging spectrometer is very similar to that described by Sanov and co-workers.[17,18] Photoelectrons are accelerated onto a microchannel plate detector coupled to a phosphor screen; images are collected on a

CCD camera. The two-dimensional photoelectron images are reconstructed into the three-dimensional photoelectron velocity and angular distributions using the BASEX image reconstruction method developed by Reisler and co-workers.[19]

The $Cu^{-}(CD_3OD)$ photoelectron spectrum is displayed in Fig. 3.4.[20] For comparison, we also plot the calculated $Cu^{-}(CD_3OD)$ photoelectron spectrum, shown as a solid line. The energy scale of the calculated spectrum has been adjusted by 91 meV, such that the maxima of the calculated and experimental spectra coincide. Both the magnitude and direction of this adjustment correspond to the error found in our comparable calculation of the electron affinity of Cu atom.

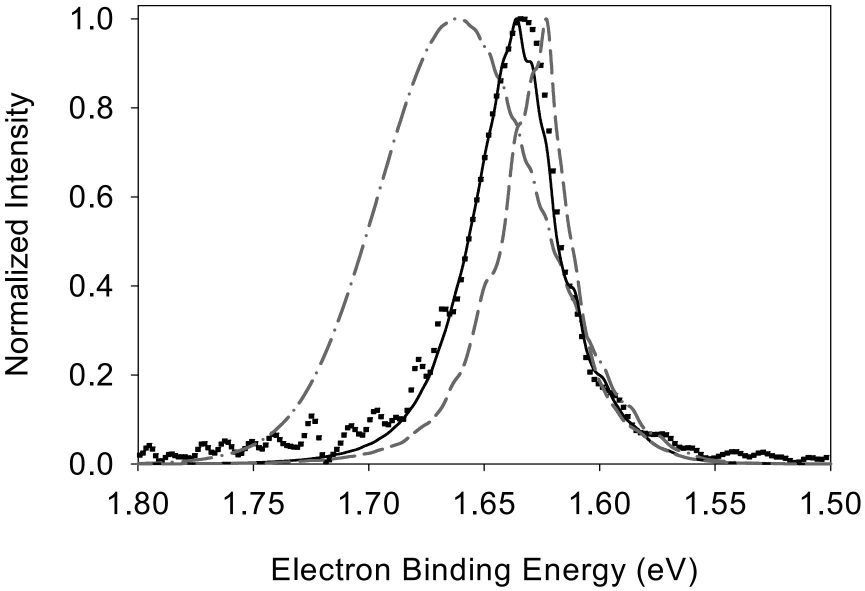

Figure 3.4 Experimental and calculated $Cu^{-}(CD_3OD)$ photoelectron spectra. The experimental spectrum is shown as black points. The three lines represent calculated photoelectron spectra with various Cu−O separations. The solid black curve gives the spectrum for R(Cu−O) = 3.42 Å, the calculated minimum energy anion geometry. The grey curves represent photoelectron spectra calculated with ± 0.18 Å changes in the Cu−O distance, with the dashed line representing 3.24 Å and the dash-dot line representing 3.60 Å.

The agreement between the experimental and calculated photoelectron spectra is remarkable. In particular, the calculated spectrum reproduces the width and contour of the experimental spectrum. This provides us with confidence in our reduced dimensional model for the Cu(CD_3OD) complex. Analysis of the calculated spectrum shows that its shape and width are captured by a one-dimensional calculation that includes only the Cu–O stretch coordinate, although the torsional motion must also be taken into account to achieve the level of agreement seen in Fig 3.4. The two dashed lines in Fig. 3.4 are spectra calculated with the Cu–O distance in the anion shifted ± 0.18 Å from the calculated minimum energy configuration. As described in Section 3.4.3. below, the lack of agreement between theory and experiment with these modified geometries gives us important additional confidence in the validity of the calculated time dependence.

3.4.2 Time Evolution of the Cu^+ and $Cu^+(CD_3OD)$ signals

The primary focus of this work is the time evolution of $Cu^+(CD_3OD)$ and Cu^+, cations that are produced by photodetachment of an electron from $Cu^-(CD_3OD)$ followed by two-photon resonant ionization after a specified delay time. The resulting signals, plotted as a function of pump-probe delay time, are reported in Fig. 3.5.

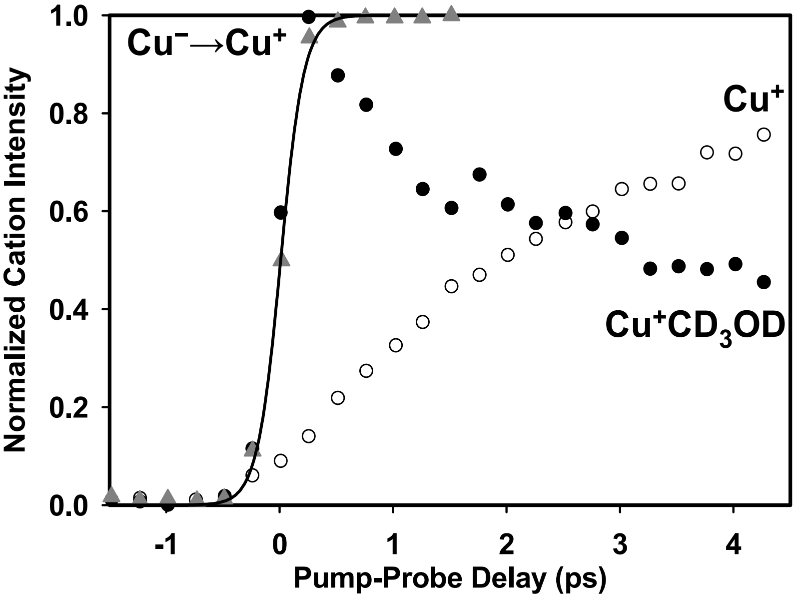

Figure 3.5 Initial experimental time dependence of cation signals. The open circles represent Cu^+ signal from $Cu(CD_3OD)$, while the filled circles represent the $Cu^+(CD_3OD)$ signal from $Cu(CD_3OD)$. The Cu^+ signal rise from Cu^- (grey triangles) indicates the instrument time resolution.

Before discussing these results we need to consider how these signals are obtained. Figure 3.1 displays the photodetachment-photoionization laser schemes superimposed on a schematic of the $Cu(CD_3OD)$ radial potential energy surface. The Cu^+ signal has primarily a three-color (398 nm + 327 nm + 265 nm) dependence, as seen in Fig. 3.1, scheme 1. The major background in this scheme is produced by a two-color (327 nm + 265 nm) contribution and is typically 10% of the maximum three-color signal. The $Cu^+(CD_3OD)$ signal has primarily a two-color (398 nm + 327 nm) dependence, as seen in Fig. 3.1, scheme 2. As in the $Cu(H_2O)_n$ experiments,[1,3] background measurements indicate that the 398 nm + (2 x 327 nm) contribution to the $Cu^+(CD_3OD)$ signal is much larger (>90%) than the 398 nm + 327 nm + 265 nm component. One-color backgrounds from both the 398 nm and 327 nm pulses contribute to both the $Cu^+(H_2O)$ and $Cu^+(CD_3OD)$ signals.

Figure 3.5 shows the initial rise of the Cu^+ and $Cu^+(CD_3OD)$ signals from $Cu^-(CD_3OD)$ following pump and probe pulses. As a point of reference, the instrument response, measured by the rise of Cu^+ from Cu^-, is plotted with grey triangles and fit with a solid line. The $Cu^+(CD_3OD)$ signal rises at the same rate as the instrument response while the Cu^+ signal rises with increasing pump-probe delay. A longer time scan is plotted in Fig. 3.6. This plot shows that both signals reach their respective asymptotic values by ~ $t = 100$ ps. If we sum these two signals, we find that their sum is nearly constant. Similar rise and decay features were also observed in the $Cu(H_2O)$ studies.[1,3,4]

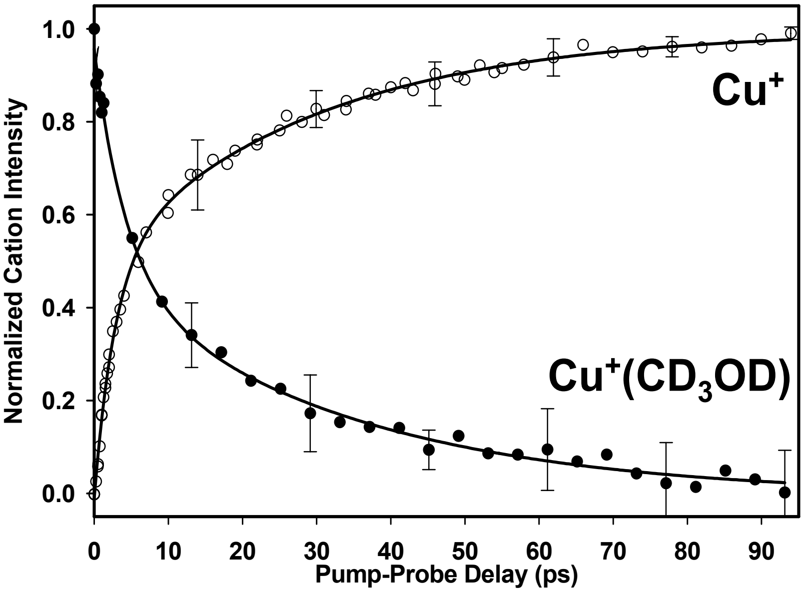

Figure 3.6 Experimental time dependence of cation signals resulting from photodetachment-photoionization of $Cu^-(CD_3OD)$. The rising Cu^+ signal (open circles) results from photodetachment (398 nm) followed by two-color (327 nm + 265 nm) resonant ionization. The decaying $Cu^+(CD_3OD)$ signal (filled circles) results from photodetachment (398 nm) followed by one-color (265 nm) resonant multiphoton ionization. Solid lines represent exponential fits to data used to extract time components.

In order to extract dynamical information from the experimental data, all data sets are summed to produce total Cu^+ and $Cu^+(CD_3OD)$ time-dependent signals. Due to day-to-day fluctuations in measured cation intensities as well as in the position of $t = 0$, special care needs to be taken when adding multiple data sets. The following procedure is used to account for these fluctuations. First, time-independent background signals are obtained at the beginning and end of each data set. If the background signals changed significantly before and after a data set, then that data set was rejected. For the accepted sets, the average background signal is subtracted from the data set. For the Cu^+ channel this background correction shows that the $t < 0$ signal is zero, while for the $Cu^+(CD_3OD)$ channel, the background correction shows that the signal is zero both for $t < 0$ and for $t > 100$ ps. The uncertainty in the determination of $t = 0$ is ± 0.25 ps. The complementary shapes of the two curves permits a simple multiplicative scaling of the $Cu^+(CD_3OD)$ channel intensity, such that the sum of the Cu^+ and $Cu^+(CD_3OD)$ signals is essentially constant at a value of 1 for all delay times greater than a few ps. The individual scaled and background-corrected data sets are averaged to obtain the Cu^+ and $Cu^+(CD_3OD)$ data shown in Fig. 3.6. Each data point is an average of $\sim 1.5\times 10^5$ laser shots. Fitting of the data to single-exponential rise [Cu^+] and decay [$Cu^+(CD_3OD)$] does not produce a satisfactory fit. Consequently a two component fit was employed. The solid lines in Fig. 3.6 were obtained by fitting the data to double-exponential rise/decay of the following form:

$$\mathrm{I}[\mathrm{Cu}^+] = a_1\left(1 - e^{-\frac{t}{x_1}}\right) + a_2\left(1 - e^{-\frac{t}{x_2}}\right) \qquad (4)$$

$$\mathrm{I}[\mathrm{Cu}^+(\mathrm{CD}_3\mathrm{OD})] = b_1 e^{-\frac{t}{x_1}} + b_2 e^{-\frac{t}{x_2}}. \qquad (5)$$

This parameterization gave a satisfactory fit; the parameters so obtained are reported given in Table 3.4. Although the fits to the Cu^+ and $Cu^+(CD_3OD)$ data were carried out independently, the corresponding derived parameters (a_1, b_1), (a_2, b_2), (x_1, y_1) and (x_2, y_2) are each within 1 σ of their counterpart. This agreement strongly suggests that both Cu^+ and $Cu^+(CD_3OD)$ signals arise from a common physical process. The fit parameters also show that each component has roughly 50% contribution to the signal. The reported error in fitting is determined by the standard deviation of the exponential fit to the averaged data sets. These errors are represented graphically in Fig. 3.6 and numerically in Table 3.4. The large uncertainty present in y_1 comes from the recurring oscillatory features present in the decaying signal, as can be seen in Fig. 3.5.

Table 3.4 Parameters of double exponential fit to the functions given in Eqs. (4) and (5); the indicated errors are ± 1σ of the least squares fit parameters.

Cu^+	$Cu^+(CD_3OD)$
$x_1 = 2.9 \pm 0.7$ ps	$x_1 = 5 \pm 3$ ps
$x_2 = 29 \pm 4$ ps	$x_2 = 33 \pm 3$ ps
$a_1 = 0.48 \pm 0.10$	$b_1 = 0.52 \pm 0.07$
$a_2 = 0.52 \pm 0.08$	$b_2 = 0.48 \pm 0.08$

3.4.3 Dissociation Time Components

In contrast to the present work, we found that three time scales were required to fit the Cu^+ signal in the $Cu(H_2O)$ study, and that the $Cu^+(H_2O)$ signal displayed more structure than was observed for $Cu^+(CD_3OD)$.[1] In $Cu(H_2O)$ the shortest timescale was ~ 1 ps. This was shown to correspond to direct dissociation of the $Cu(H_2O)$ complex upon electron photodetachment. An intermediate timescale of ~ 10 ps was associated with coupling between the hindered rotation of H_2O in the complex to the $Cu–H_2O$ dissociation channel. Finally the 100 ps component was attributed to vibrational predissociation driven by a small amount of excitation in the water bend.

3.4.3.1 Direct Dissociation

As can be seen in Fig. 3.7, after photodetachment, the neutral $Cu(CD_3OD)$ complex is in the VDG, a configuration which is far from the minimum energy configuration on the potential surface. The motions that would take the complex to the minimum energy geometry involve a combination of methanol rotation and a shortening of the Cu−O distance. At the equilibrium Cu−O distance in the VDG of $Cu(CD_3OD)$, the potential is relatively flat along the coordinates corresponding to methanol rotation. If there is sufficient energy in the Cu−O stretch coordinate, the complex should have enough time to dissociate before getting trapped near the minimum energy configuration of the complex. This mechanism is responsible for the < 1 ps, fast rise signal for Cu^+ from $Cu^+(H_2O)$.

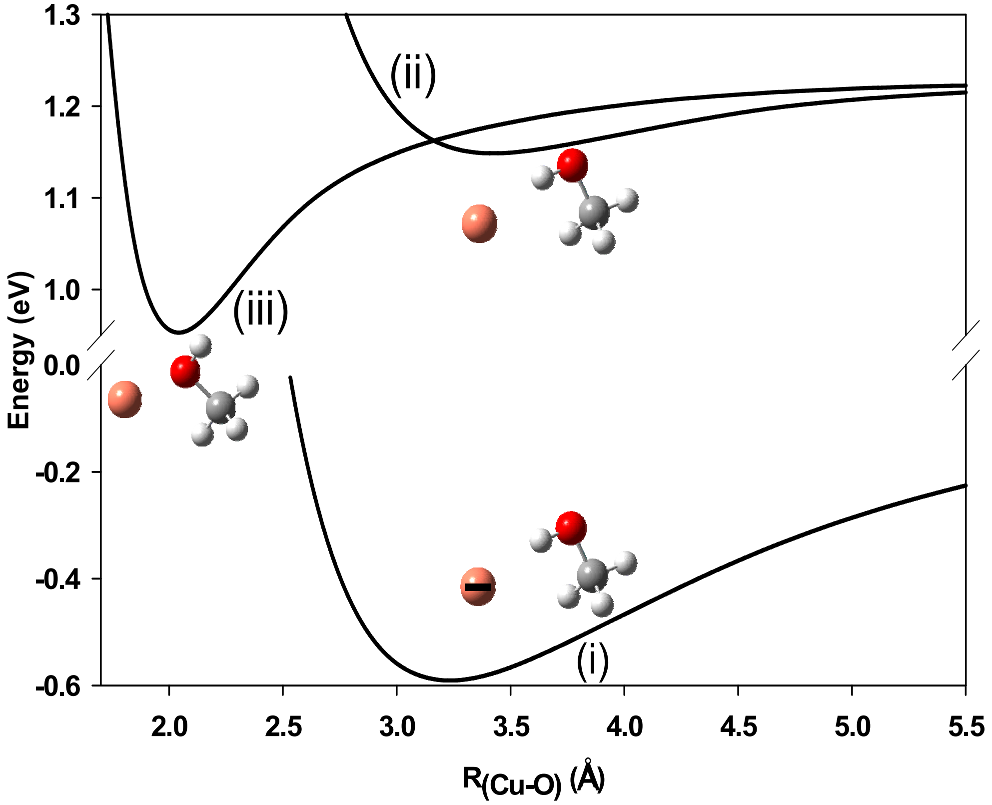

Figure 3.7 Radial [$R_{(Cu-O)}$] potential energy curves for $Cu^-(CD_3OD)$ (i), $Cu(CD_3OD)$ with other coordinates frozen at the anion configuration (ii), and fully relaxed $Cu(CD_3OD)$ (iii). The insets show the various solvent orientations for the three minima.

As seen in the results reported in Table 3.4, the parameters that describe the Cu^+ rise do not contain the fast (t < 1 ps) Cu^+ component observed in the $Cu(H_2O)$ study.[1] This direct dissociation component was also absent in the $Cu(H_2O)_2$ rearrangement studies.[3] To understand this difference between the $Cu(H_2O)$ and $Cu(CD_3OD)$ dissociation dynamics, we turn to cuts through the potentials for the anion and neutral species, plotted in Fig. 3.8.

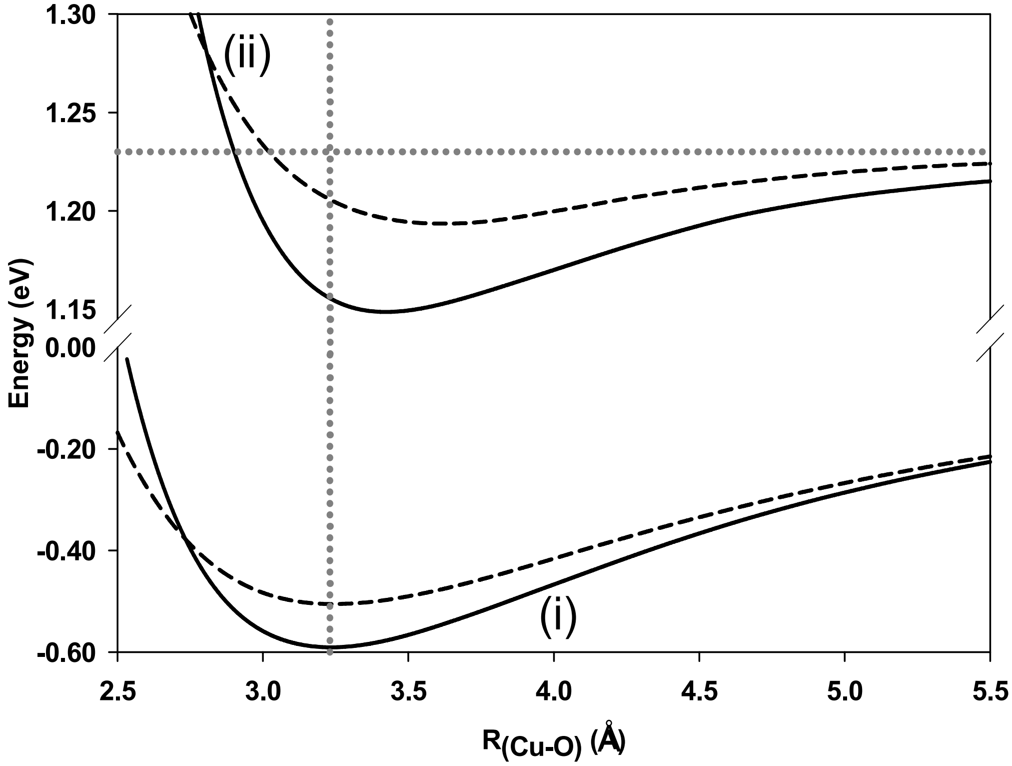

Figure 3.8 Radial potential energy curves for the anion (i) and neutral at the vertical detachment geometries (ii) of Cu(CD_3OD) and Cu(H_2O). The solid curves represent the Cu(CD_3OD), while the dashed curves represent Cu(H_2O). The vertical line is drawn at the Cu–O distance corresponding to the minimum energy configuration of both anions. The horizontal line at 1.23 eV indicates the dissociation limit of the neutral complexes.

Here the solid lines are for the Cu(CD_3OD) complexes, while dashed lines provide the potentials for the Cu(H_2O) complexes. The vertical and horizontal dotted lines represent the equilibrium Cu−O distance on the anionic surface and the dissociation energy of the neutral complex, respectively. As these plots show, upon photodetachment, the Cu(CD_3OD) complex will be in a configuration that is close to the potential minimum in the VDG, along the Cu−O stretch coordinate. Comparison of the well depths shows that the interaction energy of copper in a hydrogen-bonded configuration with methanol is much larger than the corresponding interaction energy between copper and water. These differences imply that the copper water complex will have more energy along the copper-water dissociation coordinate than will be the case for Cu(CD_3OD).

The implications of the above analysis of the potential curves, plotted in Fig. 3.8, can be quantified by considering the properties of the ground state wave functions, calculated using the lower, anionic surfaces, when they are projected onto the neutral surfaces. The average energy of these states is 148 cm^{-1} below the dissociation threshold ($D_o(C_{2v})$ = 265 cm^{-1})[4] in the copper water system, while for Cu(CD_3OD) the average energy is 586 cm^{-1} below the dissociation threshold (D_o = 628 cm^{-1}). While the greater relative energy of Cu(H_2O) compared to Cu(CD_3OD) supports the above observations, the complexes are initially at a finite temperature, and this should also be taken into account. Looking at the overlaps between the wave functions corresponding to the thermally populated states on the anion surface at 200 K and the vibrational wave functions at the VDG on the neutral surface, 18% of the probability amplitude reflects overlaps with states in Cu(H_2O) with energies above the dissociation threshold, while this value drops to less than 2% for Cu(CD_3OD). This final observation supports our inability to fit a fast time-component, analogous to the < 1 ps rise time in Cu(H_2O).

The above arguments rely on the shift between the minimum energy geometries of the slices along the Cu-O coordinate of Cu^-(CD_3OD) and Cu(CD_3OD) in the VDG. The appropriateness of this picture can be investigated by calculating the photoelectron spectrum, as described above, with the Cu−O distance dependence of the potential shifted by ±0.18 Å. The results of these calculations are plotted with dashed lines in Fig. 3.4. The best agreement in the width of the calculated and experimental spectra is obtained when the calculated vertical detachment potential surface is used. This finding, along with the calculated overlaps between the radial wave functions and the anion and VDG potential energy surfaces, supports the fact that the direct dissociation channel that was reported for the Cu(H_2O) complex is not observed in Cu(CD_3OD).

3.4.3.2 Energy Redistribution

While the above discussion shows that there is not enough energy deposited directly in the Cu–O coordinate of Cu(CD_3OD) to lead to direct dissociation, in most cases there is more than sufficient excitation in several of the other vibrational degrees of freedom to dissociate the complex. An investigation of cuts through the neutral potentials, corresponding to both the in-plane and out-of-plane motion, reveals a relatively flat landscape similar to that seen in Cu(H_2O). In the three-dimensional simulations of the dynamics of the copper-water system on the neutral surface, the 10 ps timescale obtained from the fits to the Cu^+ and $Cu^+(H_2O)$ signals are attributed to energy transfer between the hindered rotation of the water molecule and the dissociation coordinate. Comparisons of the initial internal energy in the in-plane and out-of-plane rotation coordinates in these two systems, based on one-dimensional calculations, shows that they differ by less than 10%. This, coupled to the similarity of the 3 ps time scale obtained in the present study and the 10 ps time scale for Cu(H_2O) leads us to conclude that the motions responsible for the 3 ps rise and decay times are associated with energy transfer from the methanol hindered rotation to the dissociation of the complex. The shorter timescale for methanol compared to water likely reflects the smaller rotational constants for methanol leading to a larger density of states.

In the Cu(H_2O) study, the 100 ps dissociation component stemmed from predissociation driven by vibrationally-excited bending modes of H_2O. Table 3.4 gives the longest dissociation component as 30 ps for Cu(CD_3OD). This component arises from coupling of the methyl rotor rotation into the Cu–CD_3OD dissociation coordinate. When the overlap between the thermally populated torsional levels for $Cu^-(CD_3OD)$ and the states on the neutral surface are calculated, it is found that upon photodetachment, 50% of the probability amplitude ends up in states with energy in the methyl rotor. This value of 50% matches nicely with the values of the a_2 and b_2 parameters in Table 3.4. Based on this, we attribute the 30 ps time scale to coupling of states with methyl rotor excitation to the dissociation coordinate. The difference in the dissociation time is, compared to the 100 ps component of Cu(H_2O), is ascribed to the presence of the methyl rotor and its ability to accelerate intramolecular vibrational energy redistribution (IVR).[21-23]

3.5 Conclusions

The experimental and theoretical investigations of the time-dependent dissociation dynamics of the Cu(CD_3OD) complex are reported. Experiments using photodetachment-photoionization spectroscopy provide insight to the evolution of the nascent neutral complex formed via electron photodetachment from Cu^-(CD_3OD). *Ab initio* calculations provide the minimum energy structures and one-dimensional potential energy surfaces used in determining the vibrational energies and wave functions of the complex. Analysis of both the experimental and theoretical results take place in the light of the previous detailed investigation of the Cu(H_2O) complex.

Ab initio minimum energy structures show that both Cu(H_2O) and Cu(CD_3OD) have similar hydrogen bonded anion orientations as well as similar neutral Cu–O orientations. However, the Cu(CD_3OD) complex does not exhibit the direct dissociation ($t < 1$ ps) observed in Cu(H_2O), due to the predominantly bound-to-bound transitions upon electron photodetachment of Cu^-(CD_3OD). The rising Cu^+ and decaying Cu^+(CD_3OD) signals from Cu(CD_3OD) both exhibit time components of 3 and 30 ps. The 3 ps component arises from coupling of CD_3OD hindered rotations to the Cu–CD_3OD dissociation coordinate; this time scale is comparable to the solvent reorientation coupling observed in Cu(H_2O). Angular one-dimensional potential energy slices and calculated excitation energies confirm the similarity of the two systems in these solvent reorientation coordinates. Excited methyl rotations couple into the Cu–CD_3OD dissociation coordinate on the 30 ps time scale, slightly faster than the water bend coupling of 100 ps observed in Cu(H_2O).

It has been shown in this study, as well as in the previous work on $Cu(H_2O)_2$,[3] that a dynamical analysis of larger solvent systems, where a fully dimensional theoretical investigation is impractical, is nicely interpreted using detailed results from smaller systems. This extension is important for our future investigations with more extensively solvated copper anion complexes. This work also motivates studies which investigate other solvated metal clusters. More compelling sets of experiments come in the form of producing colder anions by tagging complexes with rare gas atoms and utilizing an entrainment technique for neutral ligand addition.[24,25]

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Chapter IV

The Time-Resolved Solvent Induced Recombination of $IBr^{-}(CO_2)_n$

4.1 Introduction

As described in detail in Chapter I, excitation of IBr^{-} to the A' $^2\Pi_{1/2}$ state produces I^{-} and Br fragments. This process is altered upon addition of CO_2 solvent molecules which can lead to charge transfer products or recombination of the IBr^{-} core. The results of several experimental and theoretical investigations are presented and compared to similar work on the I_2^{-} chromophore.[1-4]

The remainder of this chapter is structured as follows. Section 4.2 explains the technique used to determine the recombination times. Section 4.3 outlines the theoretical methods used in determining minimum energy structures, radical potential energy surfaces, and molecular dynamics simulations. Section 4.4 presents the experimental results and their analysis. These results are explained in Section 4.5 using a physical picture that is based on the results of *ab initio* calculations and compared to the molecular dynamics simulations. Section 4.6 summarizes our experimental findings and suggested explanations.

4.2 Experimental

This section of the thesis describes the pump-probe technique used to investigate the solvent induced recombination of the IBr^{-} chromophore. The experimental apparatus and data acquisition corresponding to this experiment were previously presented in Chapter II. The methodology used to determine the recombination dynamics of $IBr^{-}(CO_2)_n$ clusters after excitation to the A' $^2\Pi_{1/2}$ state (Fig. 4.1) is based on the fact that the dissociated IBr^{-} chromophore regains near-IR absorption only after recombination and

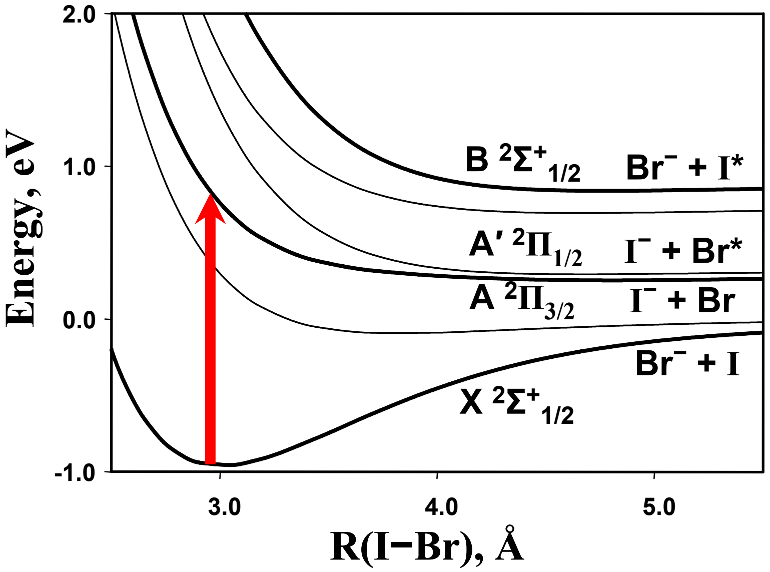

Figure 4.1 Calculated potential energy curves for the lowest six electronic states of IBr^-. The arrow indicates the pump/probe transition from the ground state (X) to the first excited state (A').

substantial vibrational relaxation on the ground electronic surface. Previous studies of $IBr^-(CO_2)_n$ A' $^2\Pi_{1/2}$ photofragmentation[5] at 790 nm demonstrated that, for clusters with $n \geq 5$, the recombination efficiency exceeds 90%, and is 100% for $n \geq 8$. The energy released in the process of bond re-formation results in evaporation of 4-6 CO_2 molecules, in accordance with the solvent binding energetics.[5] Therefore, absorption of another photon at the same wavelength by these smaller clusters leads to the formation of distinct secondary products. In order to follow the recombination process, the number of these secondary product ions is monitored as a function of the pump–probe delay time to follow the recombination process. There are considerable background signals present at delay times corresponding to small recombination signals, and these contributions were accounted for by data acquisition sequences that have been previously described in detail.[1,6,7]

The expected distribution of pump–probe product ions was obtained from sequential application of the measured[5,8] distribution of one photon ionic photoproducts, and is summarized in Table 4.1. The observed secondary product branching ratios differ only slightly from the ratios reported in Table 4.1. This, however, should be expected, since the one-photon products used to estimate the two-photon ratios were obtained at cluster temperatures of 40-70 K.[8] While parent clusters in our experiments

Table 4.1 One-photon[8] (pump only) and expected two-photon (pump/probe) ionic products for selected $IBr^-(CO_2)_n$ clusters, following 790 nm excitation. Only significant (> 5% of total) secondary products are shown. For each parent cluster size, those secondary products recorded in our experiments and used for determination of recombination time scales are shown in **bold**.

Parent cluster	**Primary (one-photon) products**	**Secondary (two-photon) products**
$IBr^-(CO_2)_5$	3% $Br^-(CO_2)_2$ 6% $Br^-(CO_2)_3$ 49% IBr^- 36% $IBr^-(CO_2)$ 6% $IBr^-(CO_2)_2$	**69% I^-** 28% $I^-(CO_2)$ 3% Minor products
$IBr^-(CO_2)_6$	4% $Br^-(CO_2)_3$ 6% IBr^- 58% $IBr^-(CO_2)$ 30% $IBr^-(CO_2)_2$ 2% $IBr^-(CO_2)_3$	**30% I^-** **58% $I^-(CO_2)$** 12% Minor products
$IBr^-(CO_2)_7$	3% $Br^-(CO_2)_4$ 16% $IBr^-(CO_2)$ 51% $IBr^-(CO_2)_2$ 22% $IBr^-(CO_2)_3$ 8% $IBr^-(CO_2)_4$	**9% I^-** **55% $I^-(CO_2)$** **10% $Br^-(CO_2)$** 16% IBr^- 10% Minor products
$IBr^-(CO_2)_8$	2% $IBr^-(CO_2)$ 26% $IBr^-(CO_2)_2$ 49% $IBr^-(CO_2)_3$ 20% $IBr^-(CO_2)_4$ 3% $IBr^-(CO_2)_5$	**42% $I^-(CO_2)$** **11% $Br^-(CO_2)$** **30% IBr^-** 17% Minor products
$IBr^-(CO_2)_{10}$	12% $IBr^-(CO_2)_3$ 38% $IBr^-(CO_2)_4$ 38% $IBr^-(CO_2)_5$ 12% $IBr^-(CO_2)_6$	7% $I^-(CO_2)$ 8% $Br^-(CO_2)_2$ **50% IBr^-** **21% $IBr^-(CO_2)$** 6% $IBr^-(CO_2)_2$ 8% Minor products

are expected to have similar temperatures, the internal energy of the recombined products may be substantially higher leading to variation in the number of solvent molecules evaporated. As the product ions are mass selected, it is possible to obtain potentially different recombination signals from each secondary product ion, as has previously been observed.[9] In the present studies, the time dependence of several different secondary products arising from a single parent ion was investigated, and no substantial differences were detected. Consequently, the time dependent data for each parent ion reported in the next section arise from the sum of those most intense secondary two photon products that are shown in bold face in Table 4.1.

4.3 Theoretical Methods

The IBr^- potential energy surfaces and associated electronic properties needed for the molecular dynamics (MD) simulations were obtained using MOLPRO 2002.6.[10] This work was performed by Matt Thompson, and a detailed description of his methods can be found elsewhere.[11,12] The energy-consistent effective core potential (ECP) of the Stuttgart-Bonn group[13] was used; specifically, the calculations employed large-core MDF ECPs based upon multi-configuration Dirac-Hartree-Fock calculations of the neutral atom. This potential also includes a core polarization potential that models the charge-induced dipole interaction of the core. The basis sets used are an augmented form, (7s7p3d2f)/[5s5p3d2f], of the stock (6s6p)/[4s4p] basis sets included with the ECPnMDF ECPs.[13,14] These calculations used the internally-contracted multi-reference configuration interaction methods developed by Knowles and Werner.[15-17] The reference orbitals and configurations were obtained from state averaged complete active-space self-consistent field calculations[18,19] that consisted of the 15 electrons in the lowest two Σ, Π_x, and Π_y states that arise from the ^2P and ^1S states of the separated atomic components. A spin-orbit calculation of all six states was then performed using spin-orbit ECPs.[20] This was performed at 42 points along the PES corresponding to bond lengths ranging from 4.5 to 100 a_0.

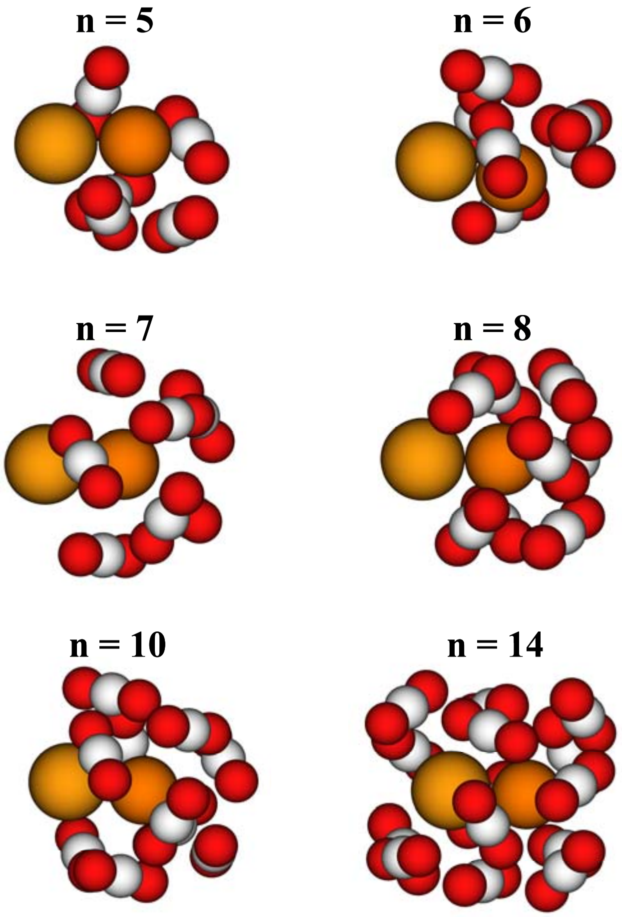

Figure 4.2 Minimum energy structures of IBr^- with various numbers of CO_2 solvent molecules, indicating asymmetric solvation around Br end.

The minimum-energy $IBr^-(CO_2)_n$ structures were constructed by sampling 201 configurations from a molecular dynamics simulation of a 1-ns trajectory on the $IBr^-(CO_2)_n$ ground state having an average temperature of 80 K.[11] These configurations were then quenched to local minima using Newton-Raphson minimization.[21] A representative sample of the resulting minimum-energy structures for relevant numbers of solvent molecules is presented in Fig. 4.2. The solvent asymmetry that leads to strong modification of the IBr^- electronic states is readily seen.

In order to more quantitatively investigate the effect of the solvent molecules on the IBr^- potential curves (Fig. 4.1), the $IBr^-(CO_2)_8$ minimum energy structure was used to construct a radial cut through the $IBr^-(CO_2)_8$ potential energy surface (Fig. 4.3) using the MD program described below. To generate the potential plot (Fig. 4.3), the iodine atom is "pulled" away from the minimum-energy configuration of $IBr^-(CO_2)_8$, and the energies of the six spin-orbit states are obtained as a function of the I−Br distance with the solvent fixed at initial configuration. This slice through the $IBr^-(CO_2)_8$ surface can rapidly change with solvent configuration.

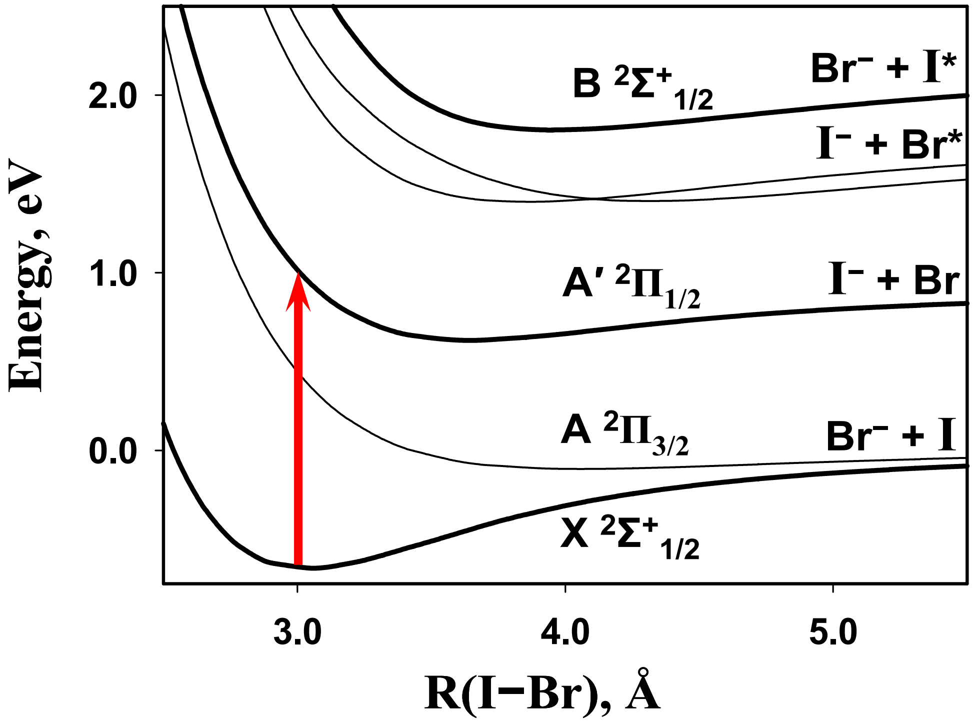

Figure 4.3 Calculated potential energy curves for the lowest six electronic states of $IBr^-(CO_2)_8$. The arrow indicates the pump/probe transition from the ground state (X) to the first excited state (A′).

The MD simulations for $IBr^{-}(CO_2)_n$ are based on the effective Hamiltonian method developed by Maslen, Faeder, and Parson[22] previously applied to $I_2^{-}(CO_2)_n$.[23-28] Briefly, the IBr^{-}-CO_2 interaction is based on an operator including electrostatic and induction terms for the solute and solvent. For the solute, distributed multipole analysis (DMA)[29] is performed during the *ab initio* calculations detailed above. More importantly, transition DMA is performed. This technique allows for calculation of the polarization response of the solute to the solvent. The solvent charge distribution and polarization is based on a condensed-phase model.[30] The short-range dispersion-repulsion interactions are described by atom-atom Lennard-Jones potentials based on high resolution photoelectron spectra[31] and from fits of CR-CCSD[T] calculations performed in GAMESS[32,33] of $Br^{-} \cdot\cdot\cdot CO_2$. At each time step in the simulation, the Hamiltonian is diagonalized to yield the energies, forces, and nonadiabatic transition probabilities needed for the next step. On a single state, motion is computed using the velocity Verlet algorithm,[34] while nonadiabatic transitions are performed according to a modified[24] version of Tully's surface-hopping method.[35,36]

4.4 Results and Analysis

The only previous measurement of the recombination time in $IBr^{-}(CO_2)_n$ was conducted for the n = 8 cluster.[5,8] Although no well-defined time dependence was recorded in that study, unambiguous evidence for recombination on a nanosecond scale was obtained. This finding was different from our expectation of rapid, picosecond-scale recombination based on studies of the similar $I_2^{-}(CO_2)_n$ system, in which the recombination times decreased from 16 ps to 5 ps as the cluster size increased from n = 8 to n = 17.[1,2,6,9]

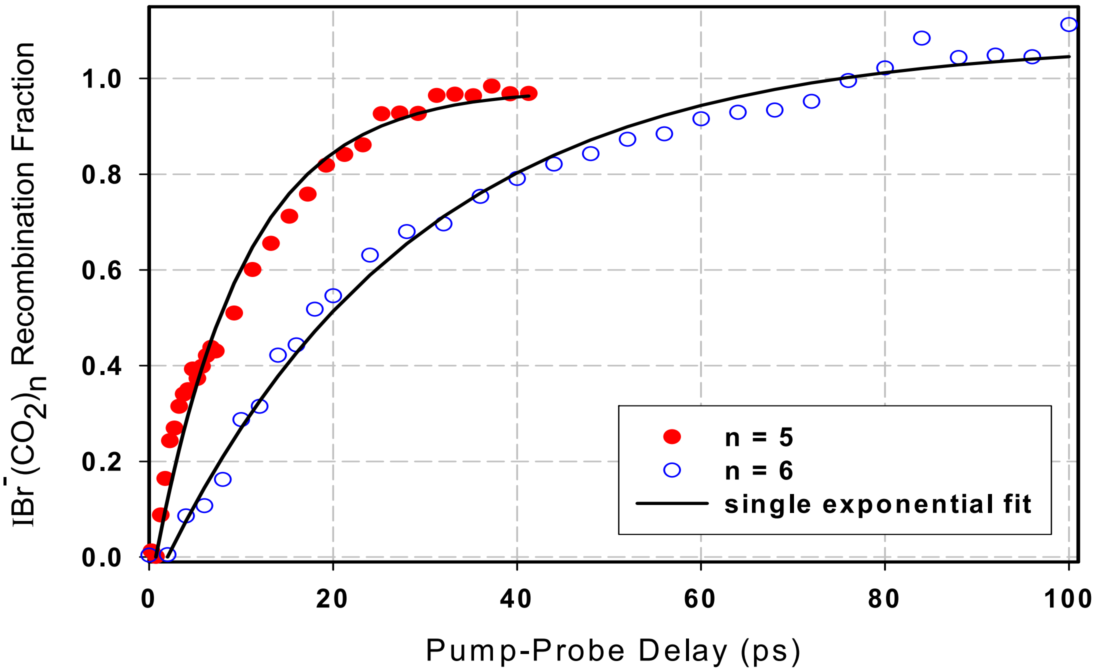

Figure 4.4 The $IBr^-(CO_2)_5$ (closed circle) and $IBr^-(CO_2)_6$ (open circle) recombination fractions as a function of time following excitation to the A′ state. Solid lines represent single exponential fits which yield recombination times of 12 ± 0.5 ps (n=5) and 30 ± 5 ps (n=6).

Figure 4.4 shows time dependent pump/probe signal obtained from the excitation of $IBr^-(CO_2)_5$ and $IBr^-(CO_2)_6$ at 797 nm. It is immediately apparent that the absorption recovery time is much shorter than that previously observed for the larger $IBr^-(CO_2)_8$ anion. In addition, the recovery time increases with additional solvation, in marked contrast to our previous experience. [1,2,6,9] Over the 100 ps time shown in this figure, there appears to be a simple functional form to the recovery, and we could fit the data to the single-exponential form $N(t)=\left[1-e^{-\frac{t}{\tau}}\right]$, with a high-quality fit and with no statistical indications for the necessity to include a second time constant. The resulting fits yield recovery times (τ) of 12 ± 0.5 ps and 30 ± 5 ps for $IBr^-(CO_2)_5$ and $IBr^-(CO_2)_6$, respectively, and are displayed as solid lines in Fig. 4.4. Unlike the previously obtained value for $IBr^{-}(CO_2)_8$,[5] the magnitude of these times is in qualitative agreement with those measured previously for $I_2^{-}(CO_2)_n$ recombination,[1,2,6,9] although the cluster size dependence is opposite to that observed for $I_2^{-}(CO_2)_n$.

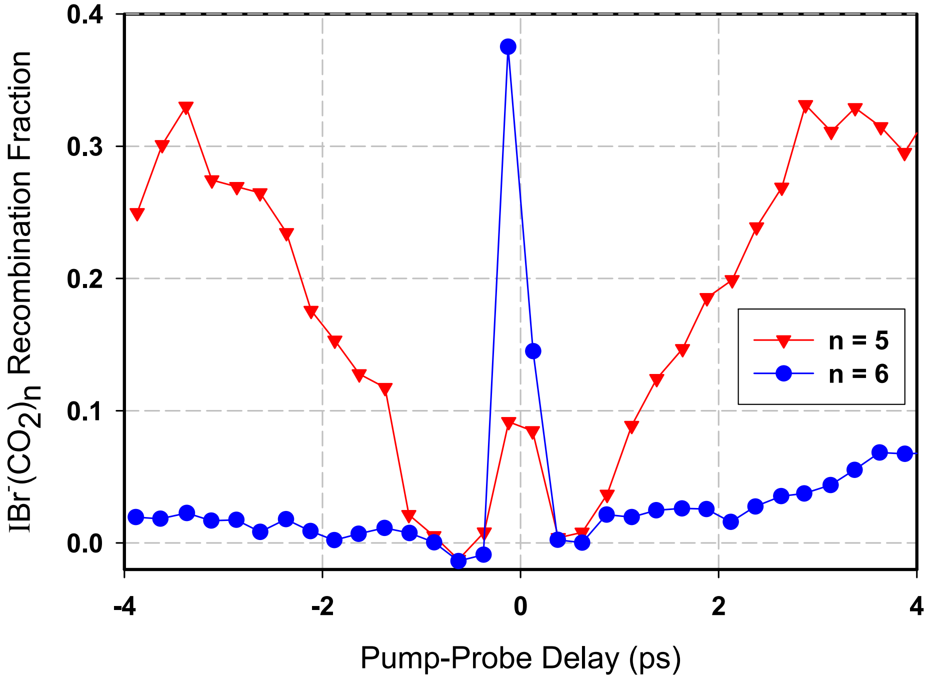

Figure 4.5 Short time recombination fractions of $IBr^{-}(CO_2)_5$ (triangle) and $IBr^{-}(CO_2)_6$ (circle) showing symmetry in data due to identical pump/probe wavelengths. The coherence peak at t=0 arises due to enhancement of two-photon background. Rising signal delayed by ~0.7 ps (n=5) and ~2 ps (n=6).

An interesting observation is emphasized in Fig. 4.5, where more detailed recombination signals at early times are presented. One can see that there is a noticeable delay in the appearance of time-dependent signal. For n = 5 this delay is ~ 0.7 ps while for n = 6 it is ~2 ps. One consequence of the long recovery times observed for the larger clusters is that the very low recombination signals at early times preclude our concluding that this delayed onset persists to larger cluster ions. However, there is no a priori reason to expect otherwise.

Due to the fact that both pump and probe laser pulses have the same wavelengths and comparable energies, the pump/probe signal in our experiment must have a symmetric shape about $t = 0$, although the unequal pump and probe intensities mean that the intensity for some $t<0$ can be different from the corresponding $t>0$ signal. Moreover, since time-independent background results from the two-photon absorption of either pump or probe radiation alone, this background doubles when pump and probe pulses overlap in time giving rise to a "coherence peak." This peak is used to determine the exact location of $t = 0$.

As more CO_2 solvent molecules are added we obtain **longer** recombination times, in contrast to those measured for $I_2^-(CO_2)_n$.[1,2,6,9] The addition of just one more solvent molecule to $IBr^-(CO_2)_6$ results in a very large change in the recombination timescale. Figure 4.6 shows the absorption recovery signal for $IBr^-(CO_2)_7$. A single-exponential fit of this data gives a time-constant of 140 ± 20 ps. Increasing the cluster size to n=8 and n=10 results in even longer recombination times. Figure 4.7 shows a single-exponential fit for n = 8 and n=10. Both of these data sets are equally well represented by the same single-exponential rise. This fit yields a recombination time of 900 ± 300 ps, in good agreement with the previous estimate for n=8.[5] Due to very low intensity of the $IBr^-(CO_2)_{10}$ parent cluster, the corresponding pump/probe signal is noisier than that of $IBr^-(CO_2)_8$.

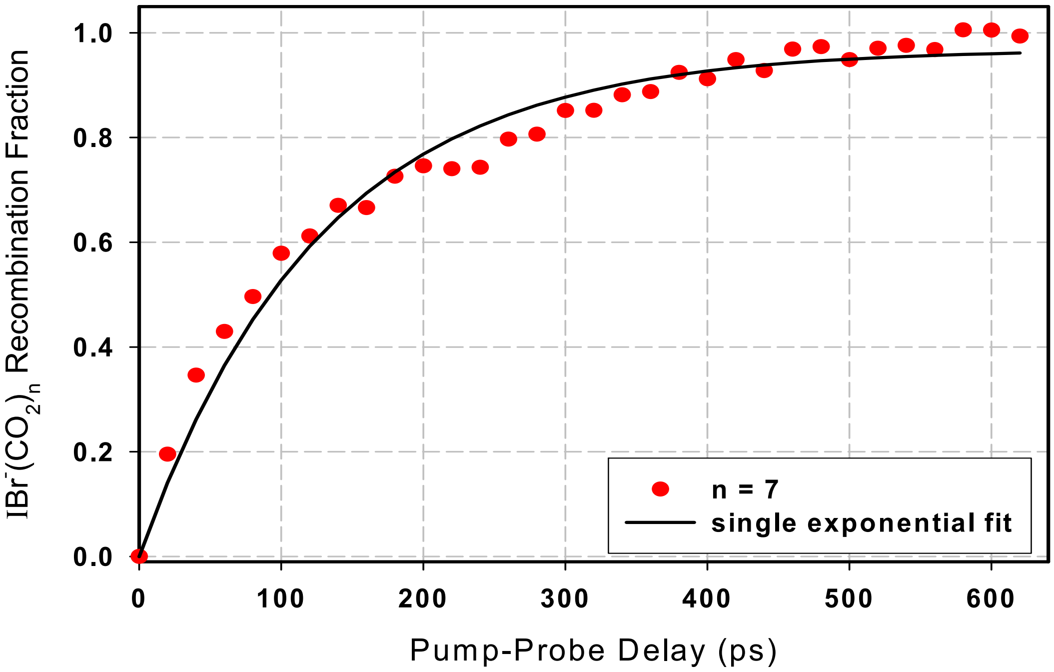

Figure 4.6 The $IBr^-(CO_2)_7$ recombination fraction as a function of time following excitation to the A′ state. The solid line represents a single exponential fit which yields a recombination time of 140 ± 20 ps.

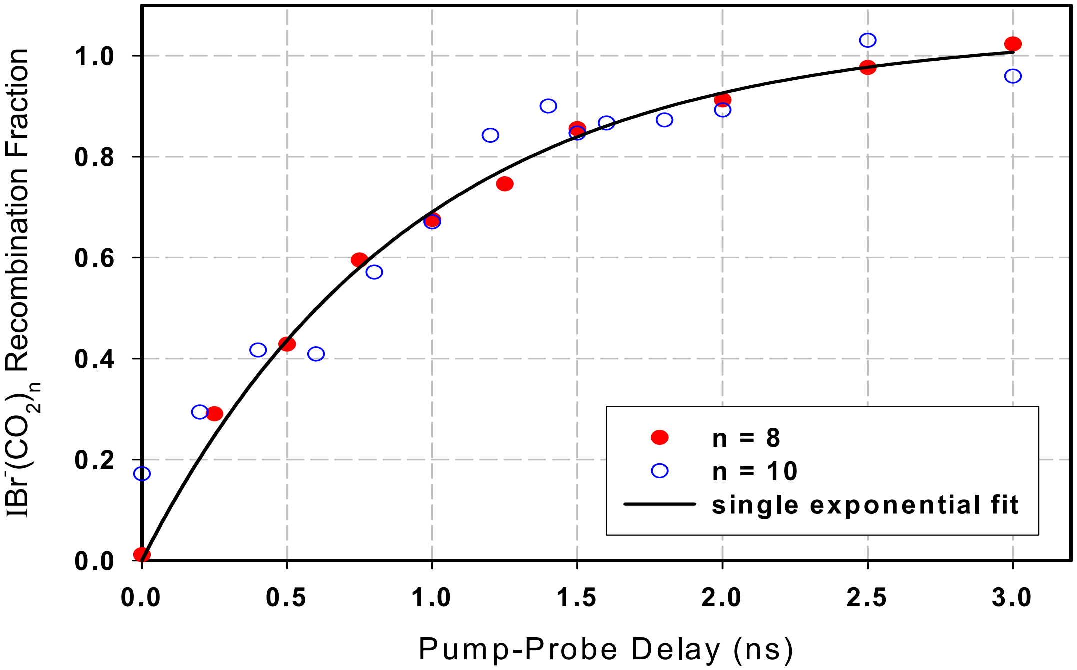

Figure 4.7 The $IBr^{-}(CO_2)_8$ (closed circle) and $IBr^{-}(CO_2)_{10}$ (open circle) recombination fractions as a function of time following excitation to the A′ state. The solid line represents a single exponential fit which nicely describes both data sets and yields a recombination time of 900 ± 100 ps. The n=10 data exhibit more noise due to very low ion signals.

Preliminary experimental data shows that the trend of recombination times lengthening with the addition of CO_2 molecules ends when we reach the n = 12 level. Figure 4.8 shows a single exponential rise for n = 12 with a time-constant of 9 ± 0.7 ps. This recombination time is faster than that seen for the n = 5 case and is on par with the $I_2^{-}(CO_2)_n$ recombination measurements. Experiments are underway to confirm this n = 12 measurement as well as to obtain a recombination time for n = 14.

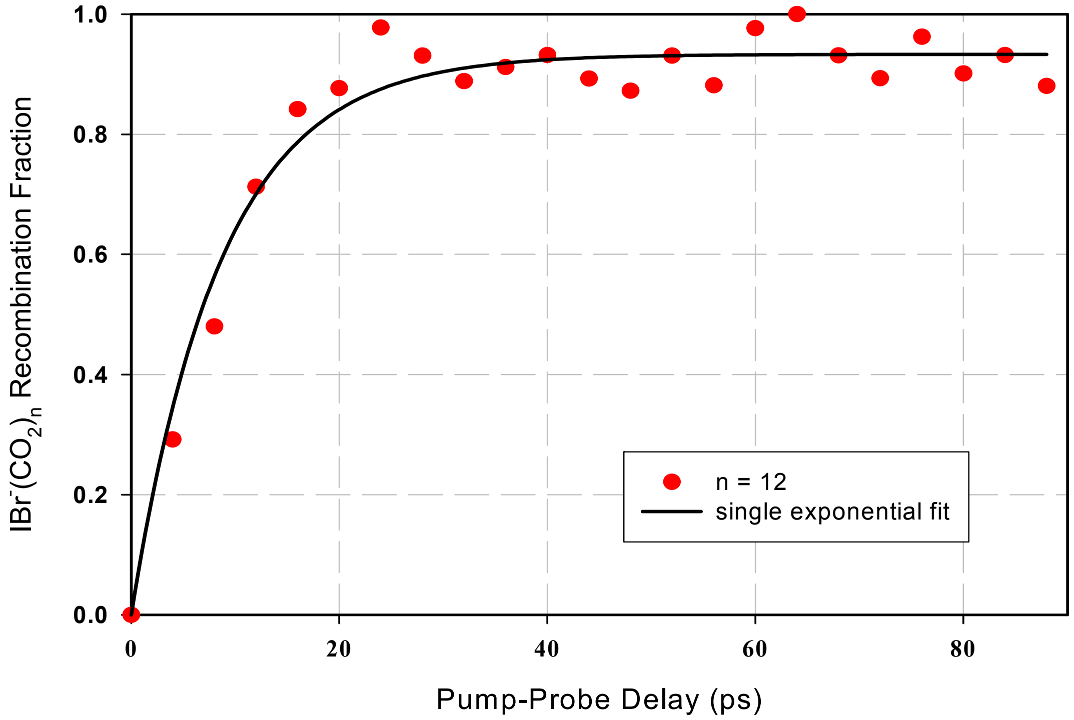

Figure 4.8 The $IBr^-(CO_2)_{12}$ recombination fractions as a function of time following excitation to the A′ state. The solid line represents a single exponential fit which yields a recombination time of 9 ± 0.7 ps.

4.5 Discussion

The experimental results obtained in this study and presented in previous sections can be rationalized using a physical picture based on calculations[37] and on comparisons to similar $I_2^-(CO_2)_n$ and $ICl^-(CO_2)_n$ systems.[6,38] According to *ab initio* calculations and other experimental investigations, there is a major qualitative difference between the shape of the A' $^2\Pi_{1/2}$ curve in I_2^- [1,9,39,40] and those in IBr^- [37]and ICl^-.[38] While the A' state of I_2^- is essentially repulsive,[41] the corresponding state of IBr^- exhibits a detectable well[42] at an internuclear separation of ~ 4.5 – 5 Å (see Fig. 4.1). Addition of asymmetrically placed solvent molecules increases the depth of this well until it reaches a maximum depth for $IBr^-(CO_2)_8$ and changes its radial location (Fig. 4.3). According to our structure calculations, this is the most asymmetric solvent configuration, based on the solvent electric field at the center of the solute ion. In this solvent size range, the well depth is comparable to the binding energy of a single solvent molecule and could readily slow the evaporative cooling process, the mechanism whereby the recombined solute anion returns to near its initial energy. We will argue that this well is responsible for “trapping” the IBr^{-} solute on the A' surface and leads to the slow recombination observed over a small range of partial solvation.

Nonadiabatic MD simulations of $IBr^{-}(CO_2)_{5-13}$ were carried out to obtain the time dependence for the recombination process described above. All simulations used a time step of 1 fs, while the length of simulations ranged from 20 ps for $IBr^{-}(CO_2)_5$ to 2000 ps for $IBr^{-}(CO_2)_{10}$, with ensemble sizes ranging from 35 trajectories for $IBr^{-}(CO_2)_{10}$ to over 1700 for $IBr^{-}(CO_2)_5$. The ensembles of trajectories gave no indication for the necessity of a fitting form more complicated than the simple exponential form employed to fit the experimental data. Consequently, the MD simulations were summarized by a functional form consisting of a single-exponential fit to the fraction of total recombined trajectories over time. The resulting time constants increased rapidly with increasing solvation, from 5 ps for $IBr^{-}(CO_2)_5$ to 5000 ps for $IBr^{-}(CO_2)_{10}$. For $IBr^{-}(CO_2)_{10}$, only 10 recombination events were observed in 2 ns for an ensemble of 35 trajectories. Due to the substantial calculation time required, these 35 trajectories were not propagated beyond 2 ns. The reported 5000 ± 1000 ps recombination time constant was obtained by augmenting the simulation data with the experimental observation[5] that all of the photoexcited $IBr^{-}(CO_2)_{10}$ ions eventually return to the ground state surface, providing an unambiguous long time asymptote for the fit. As the number of solvent molecules is further increased, the recombination time constants dramatically shorten, with $IBr^{-}(CO_2)_{12}$ showing 70 ps recovery and $IBr^{-}(CO_2)_{13}$ showing a 30 ps recovery time!

More detailed inspection of the individual trajectories in the MD simulations supports this mechanism of trapping on the A′ excited state. The long recombination times appear to arise from the presence of a configurational transition state, where achieving a narrow range of solvent and solute geometry is necessary for nonadiabatic transition to the ground electronic state of the solute. The results of molecular dynamic simulations are shown in Fig. 4.9 in comparison to the experimental results. The simulations produce recombination times with slight variances to those measured, by a factor of 3-5, however, they are in excellent qualitative agreement with experiment, with the exception of n=10. The magnitude of the experimental error bars in Fig. 4.9 reflects the range of recombination times observed for each cluster size. The details of the simulations and the nature of the solvent-induced excited state trap will be explored more deeply in a future publication.[37]

Finally, the simulations suggest that for clusters with $n \geq 10$ recombination time becomes short again (see n = 12, 13 in Fig. 4.9). To date, one data set shows this trend to faster recombination times. This data shows that for n = 12 the recombination time is now < 10 ps, in stark contrast to the previous n = 10 point of Fig. 4.9. This rebound to fast recombination time nicely matches the calculated trend. Efforts are underway to confirm this measurement as well as to obtain recombination times for clusters with n >12.

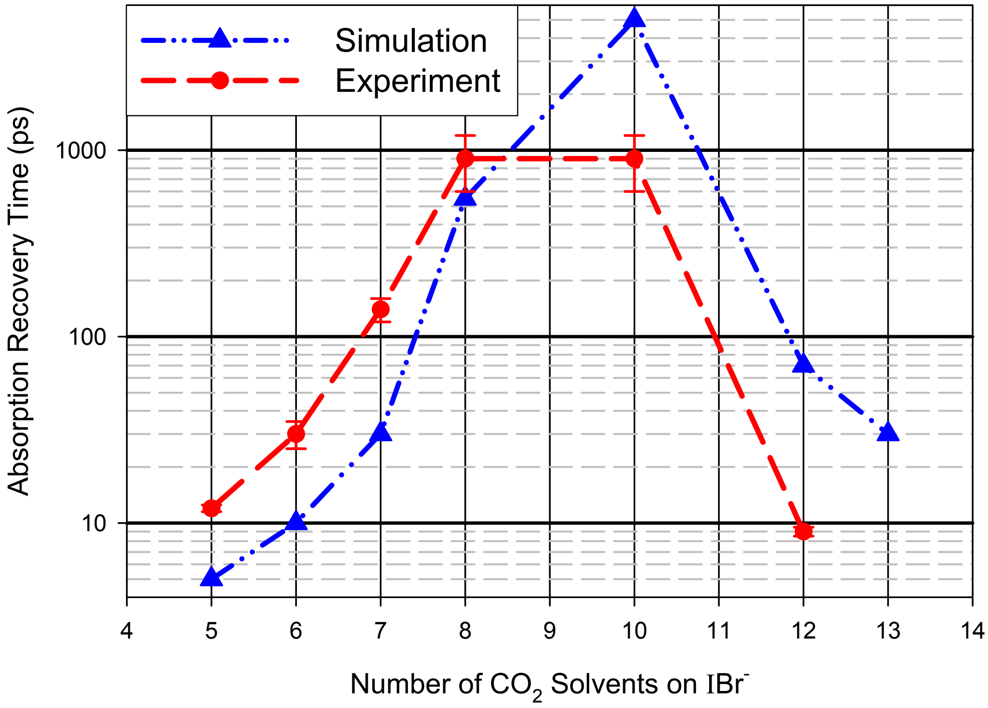

Figure 4.9 Comparison of absorption recovery times for experiment (closed circle) and molecular dynamics simulations (closed triangle). Dashed lines are provided to guide the eye.

In addition to the qualitative agreement between theoretical and experimental timescales, the simulations for clusters with 5 and 6 CO_2 molecules also display initial delays in product appearance similar to those observed in Fig. 4.5. Although the exact origin of these delays is not completely clear, we assume that they reflect the time required for dissociation, nonadiabatic relaxation to the ground state and partial vibrational relaxation, all in the absence of an excited state trap.

4.6 Conclusion

Time-resolved experimental studies of the recombination of size selected $IBr^-(CO_2)_n$ anionic clusters following excitation to the A' $^2\Pi_{1/2}$ state was carried out using tandem time-of-flight mass spectrometry combined with an ultra-fast laser system. The IBr^- chromophore near-IR absorption recovery was observed and the timescales of the recombination were extracted from the experimental data. The recombination rates exhibit a very strong dependence on the number of solvent molecules. For clusters with n = 5-7, recombination occurs on a picosecond timescale, similar to that of $I_2^-(CO_2)_n$ clusters. Clusters with 8 and 10 CO_2 molecules exhibit strikingly longer nanosecond timescales. Such changes in the recombination rates are explained in terms of the solvent-induced potential well that is especially deep for configurations involving solvent surrounding primarily the Br atom. Molecular dynamics simulations confirm this picture and are in excellent qualitative agreement with experimental data. The simulations (along with preliminary experimental data) predict an increase of the recombination rate for larger $IBr^-(CO_2)_n$ ($n>12$) cluster ions; experiments are currently in progress to further test this conclusion.

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Chapter V

Chemical Education Introduction

5.1 Towards an understanding of student learning

The traditional lecture format, in which a professor talks and students listen, has been the mainstay of teaching for centuries. Issues of what to teach and how to teach within the chemistry discipline date back as far as the early 1920s with a report that appeared in the first issue of the Journal of Chemical Education.[1] However, it was not until the mid-1980s that educators started to question the format in which students were taught. One bulletin by the American Association of Higher Education (AAHR) reports that the traditional lecture format still dominates college and university classrooms and suggests "Seven Principles for Good Practice in Undergraduate Education"[2] as a start to changing the way students are taught. Several studies after this bulletin have shown that students need to do more than just listen to truly learn, they must read, write, discuss, or be engaged in solving problems.[3-5] Despite these many calls for education reform in the sciences,[6-8] changes to the way we educate undergraduate students continues to be the topic of many publications.[9,10]

In response to these ongoing calls for change, this portion of the thesis addresses issues of student learning and education reform in undergraduate chemistry. The work presented here focuses on two aspects within this broad topic, namely, student beliefs about learning chemistry and the use of interactive tutorials as a supplement to traditional lectures. While many studies focus on gains in students' content knowledge through various teaching practices,[11] very little work has been done in studying how these practices affect the equally important topic of students' beliefs. In addition to addressing student beliefs as part of an effective learning environment, an educator must also address how students learn the content within their course. The use of guided inquiry methods has been shown to aid students in developing deeper connections with difficult concepts.[12,13]

5.2 Measuring student beliefs about chemistry and learning chemistry

After many years of reports on the ineffectiveness of the lecture format, chemical education researchers began to change their focus from the "content" of chemistry courses to the "delivery" of this content to the students. This shift in focus has placed students at the center of learning. This "student-centered" approach has been the basis of reform efforts in courses from environmental science to physical chemistry.[13-15] With these important changes occurring, the need for easy, effective evaluations of the impact of these changes becomes pertinent. In addition to any evaluation of the effects on students' content knowledge of chemistry, there is a need to monitor and evaluate the impacts on students' beliefs about chemistry and learning chemistry. Distinct differences exist between novice and expert learners concerning their beliefs about science and learning science, Table 5.1 summarizes these differences in three main areas. An individual's beliefs shape their own personal experiences on a daily basis. Several studies have shown that students' expectations can be a better predictor of college science performance than previous math or science experience.[16-18] Student beliefs can affect how they learn new information; in turn, a student's experience can shape their beliefs.[7,19,20] The measurement of student beliefs has been an area of investigation in the physics community for some years,[21-25] but studies in chemistry are more limited.[26]

Table 5.1 Contrast of novice and expert beliefs on several dimensions of science (adapted from David Hammer27).

Novice		Expert
Isolated pieces of information	**content and structure**	Coherent framework of concepts
Handed down by authority. No connection to the real world	**source**	Describes nature. Established by experiment
Pattern matching to memorized arcane recipes.	**problem solving**	Systematic concept-based strategies. Widely applicable.

In order to investigate students' beliefs about chemistry and the learning of chemistry we have modified the Colorado Learning Attitudes about Science Survey (CLASS), originally designed for use in physics.[21] The survey is designed to be used in a wide range of undergraduate chemistry courses (from survey courses for non-science majors to graduate level courses); therefore, student interviews were conducted with a broad population of students to ensure clear concise wording and meaning of all statements. The CLASS-Chem survey contains 50 statements to which students respond using a five-point Likert scale (strongly agree to strongly disagree). For example, "I think about how the atoms are arranged in a molecule to help my understanding of its behavior in chemical reactions". A complete list of statements can be found in the appendix of chapter VI. Student responses are scored in comparison to expert chemists' responses and grouped into nine categories. In contrast to other survey instruments, our groupings of statements into categories are not predetermined but emerge from student response data and reflect various aspects of student thinking. The statements are grouped and categorized using the modified principal component analysis method (similar to factor analysis) developed during creation of the original CLASS survey.[21]

5.3 Tutorials for undergraduate physical chemistry

Teaching and learning are not synonymous. An individual can teach well without having their students learn.[28] There is an old Chinese proverb which nicely summarizes the theme of this portion of my work. "Tell me and I forget. Show me and I remember. Involve me and I understand." Students need to do more than just listen to truly learn: they must read, write, discuss, or be engaged in solving problems.[5] The practice of "student-centered" learning provides many formats for actively engaging students in the learning process. The active engagement of students has been shown to improve learning and knowledge retention in science education.[29-32] I propose to use hands-on models and computer simulations in concert with learning tutorials to engage students in an undergraduate physical chemistry lecture course. The hands-on models provide an easy lecture format for students to test the physical chemistry concepts under investigation. Previous research has shown that computer simulations can help students develop conceptual models of physics phenomena.[33] Computer simulations facilitate knowledge construction by providing evidence to assist in the formulation and development of explanatory models.[34] Otero states in her studies of computer simulations that "students tend to treat this type of information more like phenomenological evidence than like "the right answer" or dictums from authority because they actually perform the computer experiments in order to obtain it."[34]

5.4 Dissertation overview: Chemical Education

The work presented in this section of the dissertation is divided into two chapters. Chapter VI presents the modification and validation of the Colorado Learning Attitudes about Science Survey to measure students' beliefs about chemistry and the learning of chemistry. Chapter VII presents the development and testing of three learning tutorials for use in an undergraduate physical chemistry lecture. Due to the diverse nature of the work presented in this dissertation, each individual chapter will present conclusions and outline future directions.

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Chapter VI

Measuring Student Beliefs About Chemistry and Learning Chemistry

6.1 Introduction

As described in Chapter V, we have developed the Colorado Learning Attitudes About Science Survey (CLASS-Chem), a survey instrument designed to measure students' beliefs about chemistry and about the learning of chemistry. In this chapter the development of the survey is presented along with the validation studies performed on the completed instrument.

The remainder of this chapter is structured as follows. Section 6.2 describes the design of the survey instrument. Section 6.3 details the administration of the survey and the scoring of the data collected. In section 6.4 the validation studies are discussed in detail. Applications of the newly developed and validated instrument are presented in section 6.5. Section 6.6 presents conclusions and possible future uses of the instrument.

6.2 Instrument Design

While there are many surveys available for probing student beliefs in the physical sciences,[1-3] there is only one other instrument designed specifically for chemistry, the Chemistry Expectations Survey (CHEMX).[4] While both the CHEMX survey and the CLASS-Phys survey (which is the basis for the CLASS-Chem) are originally based on the Maryland Physics Expectation survey (MPEX),[3] they diverge in their goals and methodologies as discussed below.

Since the design of the original CLASS-Phys survey has been described previously,[5] only brief details will be given. Statements in the CLASS-Chem survey are written to be meaningful for a range of students and designed to address a wide variety of beliefs about:

(1) learning chemistry
(2) the content of chemistry knowledge
(3) the structure of chemistry knowledge
(4) the connection of chemistry to the real world

The design of the CLASS surveys differs from the MPEX and CHEMX in three main areas. First, wording is carefully selected and tested with students with a range of backgrounds to provide clear concise statements with a single interpretation; MPEX claims only to be valid for use with calculus based courses. Next, CLASS statements do not prompt students' beliefs or expectations about a specific course, but about chemistry in general; many of the CHEMX statements measure students' views about a particular course, including laboratories. We set out to design an instrument for use in all courses, regardless of whether they have a laboratory component. Finally, the grouping of CLASS statements are determined and validated using reduced basis factor analysis, which creates empirically determined groupings of statements based on student responses, the MPEX and CHEMX surveys categorize statements based on predetermined, author-defined groupings.

In creating a chemistry version we first tried merely switching "physics" to "chemistry" in the CLASS survey to create the CLASS-Chem v1, but subsequent interviews (covered in chapter 6.4.1) with chemistry students revealed that three of these modified statements required some minor wording changes and three other statements were not valid. Student interviews also revealed that with the change of context some statements could not reliably distinguish between novice and expert learners. For example when responding to the statement, "There is usually only one correct approach to solving a chemistry problem," even the most novice students disagree stating that "there are many different reactions which lead to the same products." Therefore, in a chemistry context this statement does not provide a useful distinction between learners. The largest modification done when creating version two is the addition of 11 new chemistry-specific statements. Many of the added statements investigate views of chemical reactivity and molecular structure which we consider additional important characteristics of expert thinking about chemistry.

Education in both physics and chemistry challenges students to develop problem solving skills and to form cohesive networks of conceptual ideas. Difficult, and major, components unique to chemistry curriculum involve visualization, reactivity, and molecular structure. All of these concepts are introduced in introductory courses and are developed throughout a wide range of chemistry classes. The visual nature of this material poses unique challenges in learning. Investigations of the beliefs connected to this visual component are a motivating factor in preparing a chemistry specific version of the CLASS survey.

A series of interviews with a range of students produced the additional chemistry-oriented statements for the CLASS-Chem v2 survey. These statements appear in Table 6.1. All statements, including the 42 modified statements from the physics version, have undergone reliability and validation studies (described below) in order to produce the 50 statements currently used in the CLASS-Chem v2. All 50 statements appear in the appendix.

Table 6.1 Chemistry statements added to the CLASS-Chem v2.

2. To understand a chemical reaction, I think about the interactions between atoms and molecules.

11. I think about how the atoms are arranged in a molecule to help my understanding of its behavior in chemical reactions.

12. If I have not memorized the chemical behavior needed to answer a question on an exam, there's nothing much I can do (legally!) to figure out the behavior.

17. I can usually make sense of how two chemicals react with one another.

21. Why chemicals react the way they do does not usually make sense to me; I just memorize what happens.

29. When I see a chemical formula, I try to picture how the atoms are arranged and connected.

33. The arrangement of the atoms in a molecule determines its behavior in chemical reactions.

37. In learning chemistry, I usually memorize reactions rather than make sense of the underlying physical concepts.

44. Thinking about a molecule's three-dimensional structure is important for learning chemistry.

48. Spending a lot of time understanding why chemicals behave and react the way they do is a waste of time.

50. When I'm solving chemistry problems, I often don't really understand what I am doing.

6.3 Scoring and Administration

The scoring and administration is identical to that previously described for the CLASS-Phys survey.[5] Brief details will be given here. Students respond to each statement using a five-point Likert scale (strongly agree to strongly disagree). An individual student's 'Overall % favorable' score is the percentage of responses for which the student agrees with the expert's response (including only those statements where experts have consistent views – 45 of 50). Similarly, the 'Overall % unfavorable' score is the percentage of responses for which the student disagrees with the expert. A choice of neutral is neither grouped as favorable nor unfavorable. These individual scores are averaged to determine the 'Overall % favorable' and 'Overall % unfavorable' score for all participating students. Scores and averages are also determined for groupings of statements within categories. Each category contains a number of statements which portray an aspect of student thinking, the determination of this categorization will be addressed in chapter 6.4.3.

While we ask students to respond to statements on a five-point Likert scale, we collapse this scale to a three-point scale (agree/neutral/disagree) during scoring. We have found that utilizing a five-point scale for student responses is important for two reasons.[5] First, student interpretations of agree vs strongly agree are not consistent, the same belief may elicit a strongly agree response for one student and only an agree response for another. Second, students state that without this distinction they would have chosen neutral more often. We believe that we may lose some definition within the responses by grouping strongly agree with agree (and strongly disagree with disagree), however, this collapsed scale still provides us with comparisons to 'expert' responses.

The CLASS-Phys survey has been administered since fall 2003 and the CLASS-Chem survey since fall 2004 (v1) and summer 2005 (v2). To date, over 5000 students in over 30 courses at CU-Boulder have taken the CLASS-Chem. Currently, two other universities are also using the survey. We administer the survey online and have been successful in maximizing student responses by utilizing the following approach: (1) the survey is announced in class by the instructor and the HTML link is posted on the course web site; (2) students are contacted via email and given a 5-7 day window to submit their survey, a follow-up email is sent a few days from the end of the window to those who have not submitted; (3) whenever possible, a small amount of credit is offered for participation as we have seen that the small credit increases participation significantly (e.g. matched data, defined below, increased from 40% to 60% of enrolled students in a large (>800 student) 1st term chemistry course). Students may receive this credit for simply submitting their name and ID number, but very few choose this option.

The number of responses actually scored is less than the total number of submissions for many reasons. A number of scoring controls are either built into the on-line survey or utilized during the scoring protocol. Two controls are imbedded in the on-line survey itself. First, a timer records the amount of time each student spends at the web site. We have determined that students spending less than 3 minutes at the site could not be reading and understanding each statement before clicking on an answer. Therefore, a student's submission with a time of less than 180 seconds is flagged and not counted as "good". There is one statement in the survey used to gauge if the students are actually reading the statements or simply clicking answers at random. Statement 31 is used to identify these students, "We use this statement to discard the survey of people who are not reading the statements. Please select agree (not strongly agree) for this statement." During the scoring process we eliminate any duplicate submission, we find that a handful of students take the survey twice either because they do not remember they took it or hear about the deadline reminder and retake it just to be sure they get course credit. We also look for repetitiveness within students' submissions as well as the number of statements answered. We do not want to include a student's submission if they clicked the same answer for the entire survey or only answered a small percentage of the statements.

On average, we have about a 75-85% response rate on the survey with roughly 10-15% of these responses being dropped for the above reasons; the remaining responses provide useful pre and post data. In order to evaluate shifts in beliefs from pre to post, we compile a subset of data, "matched data" which consists of only students who have successfully completed both pre and post surveys. This approach ensures that the calculated changes reflect shifts in student thinking rather than changes in populations. We have seen increases of ~20% in participation, both pre and post as well as in "matched" data sets, when the instructor offers some form of course credit for taking the survey.

6.4 Validation

The CLASS-Chem survey has undergone extensive validation studies. It is important to point out the criteria we believe an instrument must meet in order to be considered valid. First, the wording and meaning of the statements within the survey must be clear to the target population. In addition, students' responses (either 'expert' or 'novice') must be consistent with their explanation for why they chose that response. Second, the statement answers must be agreed upon by experts, providing face validity to the survey. Next, the grouping of statements into categories used to characterize the thinking of the student population must be statistically robust – that is, responses to the individual statements are reasonably correlated with one another. Lastly, the instrument must demonstrate the ability to distinguish between groups that should be distinguishable in theory – for example, between the beliefs of non-science majors and chemistry majors. The statements in CLASS-Chem v2 are validated through interviews with chemistry students as well as with chemistry faculty. The faculty responses are also used to establish the expert opinion. Statement groupings are validated using Principal Component Analysis[6] on student responses.

6.4.1 Interviews

During development of the original CLASS survey, over forty students were interviewed.[5] This series of interviews with students in various physics courses, many of which were concurrently enrolled in chemistry courses as well, established the wording and content for the initial statements used on the survey. In addition to these interviews, ten students in a range of courses – from chemistry for non-majors to junior level organic chemistry – were interviewed during development of the chemistry version. Students were selected to provide a diverse group in terms of gender, race, and major. The interview process consisted of three parts. First, the students completed a pencil and paper version of the survey. Once completed, students were asked about their major, course load, educational interests, good/bad class experiences, and future goals. These statements provided information to characterize the students and their interest as well as put them at ease by engaging in familiar conversation. The bulk of the interview consisted of the interviewer reading the statements while the student looked at a written version. Students were asked to respond to each statement using the five-point Likert scale and then to reflect on any thoughts prompted by the statement. Most students freely provided thoughts and comments on all statements; those that did not were prompted to explain their answer choice. If questions were asked by the student about a statement or the interview itself, they were not addressed until the very end of the interview session.

6.4.1.1 CLASS-Phys Statements

Student interviews resulted in minor wording changes in two statements (#'s 27 and 32) and the complete removal of only 3 out of the original 42 CLASS-Phys statements (one was not scored in the CLASS-Phys and the other two were scored but not included in any specific CLASS-Phys category). Students expressed some confusion as to the original context of statements 27 and 32. The confusion was due to the fact that the words "equation" and "formula" are readily interchangeable in physics and have the same mathematical meaning; in chemistry, however, these words do not have the same meaning and hence are not interchangeable. An "equation" in chemistry can be either the mathematical type, as in physics, or the chemical type. A "chemical equation" is a format for writing a chemical reaction[7] and differs from a "chemical formula" which is a format for listing the number and kind of constituent elements in a compound.[7] If a statement did not obviously indicate which form of the words was being used, then the prefix "chemical" or "mathematical" was attached. For example in the statement, "spending a lot of time understanding where formulas come from is a waste of time," the word "formula" was replaced with "mathematical formula." This provided unambiguous interpretations for most of the statements.

Based on the student interviews, the three statements below were removed from CLASS-Chem v1.

--*There is usually only one correct approach to solving a chemistry problem.*

--There could be two different correct values for the answer to a chemistry problem if I use two different approaches.
--It is possible for chemists to carefully perform the same experiment and get two very different results that are both correct. (Not scored on CLASS-Phys)

The first statement was removed because in a chemistry context it is readily obvious to even the most novice students that there are many approaches to solving a chemistry problem, for example, students learn a number of various reaction pathways to produce the same product. In the case of the physics version, the novice learners tended to agree with the statement and 'experts' disagreed, providing a measure of discrimination between 'novice' and 'experts'. The second statement had similar problems with students referring to reaction pathways. The third statement, which is scheduled for revision or replacement in the physics version due to lack of a consistent expert response, posed difficulties with the less experienced students. Many students stated that there may be "unconsidered variables" or that there were "a lot of twists in chemistry that break the rules." During interviews students would also reflect on past laboratory experiments where "everyone followed the same procedure" but the results were very different. Based on these comments, and the fact that these specific statements were not grouped into any of the eight categories in the physics version, we removed all three statements. Dropping these statements also made room for more additional statements as we did not want to exceed a total of 50 statements.

6.4.1.2 Chemistry-specific Statements

Using student interviews, we tested over twenty candidate statements to probe the additional chemistry-specific areas of students' beliefs, including some statements selected from the CHEMX and some inspired by or revised through student interviews. Seventeen statements proved to be valid in interviews and we kept the 11 we felt were most informative. Many statements were revised based on vocabulary problems. It was discovered that words such as "intuitive," "theories," and "structure" do not have unambiguous definitions for introductory students. It was found that the word “structure” must be associated with either molecular or electronic in order to have singular meaning to many students.

6.4.2 Faculty Surveys

The 50 statements selected for the CLASS-Chem v2 survey were given to over 20 chemistry faculty at four different universities. This data was used to confirm the expert response and also to provide additional feedback about the statements themselves. Forty-five of the statements had consistent expert responses. These responses (agree or disagree) are included in the appendix. Using these responses to define the ‘expert’ view, we scored the individual faculty surveys using the same approach as used for student responses. Figure 6.1 plots the faculty’s average ‘% Favorable’ vs ‘% Unfavorable’ scores for ‘Overall’ and each category. For the 45 statements which comprise the ‘Overall’ score, the faculty surveyed score 89.2% favorably and only 3.2% unfavorably.

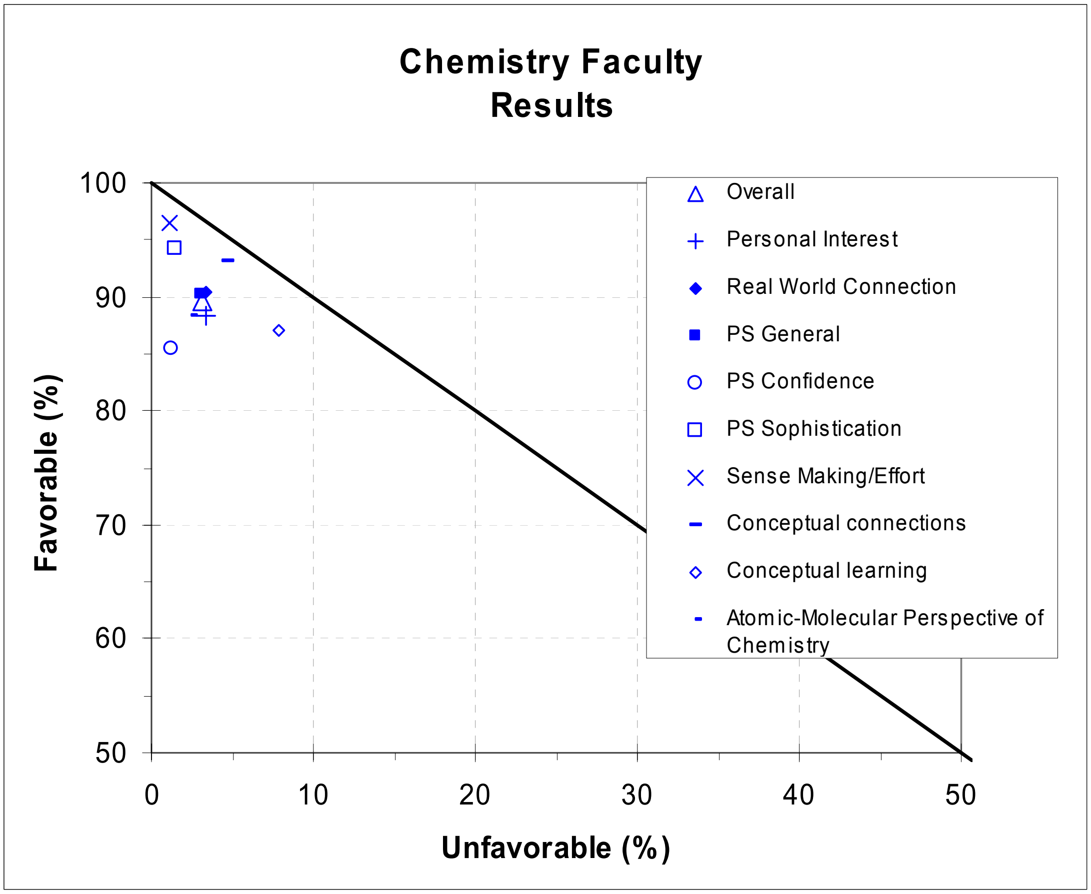

Figure 6.1 % Favorable vs % Unfavorable plot of faculty responses.

Four of the five un-scored statements do not have consistent faculty responses and gauge either nature of science (#8) or learning style aspects (#s 5,10,39). We include these learning style statements in the survey because they provide useful information about student approaches to learning. Developing suitable nature of science statements is an ongoing area of investigation; statement #8 will be revised or replaced in a future version. The last un-scored statement is number 31; this statement, as described earlier, is used during the scoring process to reject surveys submitted with random guesses.

On the faculty version of the survey, participants were asked if they had any comments or concerns about each statement. A free response box was incorporated into the on-line version to collect this information. Roughly 35% of the statements received comments from the faculty. Some of these responses reflect the importance of the statements or topics in the faculty member's mind. A list of some of these statements along with a sample response is presented below.

Statement #3. When I am solving a chemistry problem, I try to decide what would be a reasonable value for the answer.
-"Knowing how to 'guesstimate' is important"
-"After we "calculate" our value we ask if it seems reasonable"

Statement #20. Understanding chemistry basically means being able to recall something you've read or been shown.
- Students "must be able to apply info"

Statement #36. Reasoning skills used to understand chemistry can be helpful to me in my everyday life.
- "That's why I teach chemistry!!! My purpose is not just to impart chemical knowledge but rather to teach and encourage students to think and reason for themselves. By tackling chemistry, students are learning how to learn because chemistry is usually something they're not too familiar with."

Statement #42. There are times I solve a chemistry problem more than one way to help my understanding.
-"This is really when you understand a concept!"
-"And to double check an answer! Arriving at the same result via two or more independent methods increases the confidence level I have in the result."

In interviewing a few of the faculty about their courses and how they interpret the results from their course, we found that many choose to focus on a few key statements which they find important. One such professor prides himself on providing a strong foundation in problem solving during his course; therefore, he focuses on how the students' responses to the problem solving statements change over the course of the semester.

6.4.3 Categorization of Statements

A significant difference between the CLASS surveys and MPEX or CHEMX is the method by which the statement groupings are determined. The categories in the MPEX or CHEMX surveys are defined a priori by the developer without the use of statistical methods to ensure their validity. During the development and validation of the physics version of CLASS, a substantial number of students were given the MPEX survey. Upon statistical analysis, it was found that some groupings were made up of statements with very weak correlations (<0.05). If statement groupings are to be used in characterizing facets of student thinking, then the student responses to the statements within that grouping should be reasonably correlated (>0.15), if in fact the groupings represent student thinking. If statistical analysis is not used to determine correlated student responses, it is very unlikely that predetermined categories will be made of statements which reflect student thinking.

6.4.3.1 Categorization Philosophy and Approach

The details of our categorization are presented in the previous CLASS-Phys validation paper;[5] a brief summary will be given here. Categories can be established using two different philosophies, either "raw statistical" or "predetermined." In the raw statistical approach, no constraints are in place and categories emerge from the data via exploratory factor analysis.[8-10] In contrast, a predeterministic approach bases categories on expert perspectives about how statements should be grouped. Both of these approaches have strengths and weaknesses.[5]

Exploratory factor analysis ensures that all categories are statistically valid. This categorization procedure has been shown to provide insights into student thinking.[5,11] An example of this is the category labeled as "sense making and effort," where student responses show a strong correlation between statements involving how a student makes sense of chemistry and statements concerning the amount of effort needed to solve problems. A substantial drawback to defining categories simply using exploratory factor analysis is that many statement groupings are not very useful to an educator.

It is the apparent connection with particular aspects of instruction that make predetermined categorization so widely used. From a statistical standpoint however, predetermined categories are not a valid characterization of an aspect of student thinking if little or no correlation exists between respondents answers. An additional drawback to predetermined categories is the fact that statements are designed to fit into a single category.

It was found throughout our factor analysis that statements routinely group into more than one category and more importantly in some cases statements do not group into any categories.

Our approach combines the strengths of both methods, providing an optimum set of valid categories. Figure 6.2 (courtesy of Adams *et al.*) summarizes the iterative process used in choosing categories; a detailed description of the process can be found in the work of Adams *et al.*[5] The parameters of the factor analysis performed using the SPSS program[6] are as follows: Extraction Method: Principal Component Analysis, Rotation Method: Direct Oblim, Missing Values: Excluded pairwise.

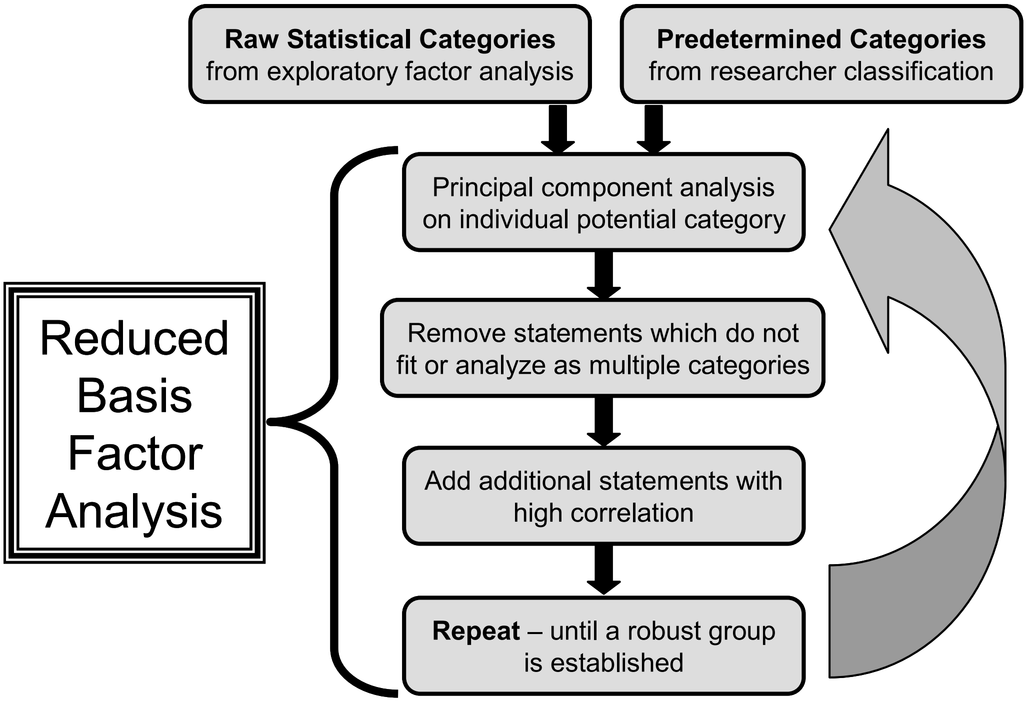

Figure 6.2 Flow chart depicting reduced basis factor analysis.

Several indicators of statistical validity are evaluated in determining the strength of each statement grouping. To facilitate comparison between various groupings, a robustness calculation is used to assign a value for each group. Optimization of this value provides a robust, statistically valid grouping of statements. The robustness calculation looks at the output of doing a factor analysis on each set of statements in a category. This criterion is determined by evaluating various indicators of statistical validity including the correlation coefficients between statements, the percent of variance explained by the weighted combination of statements represented by the first factor and the factor loadings for each statement in that first factor. (A factor analysis always produces as many factors/components as statements in the basis.) The robustness number for a grouping is calculated using the following equation:

$$\text{Robustness} = (2cc + fl + 5|\Delta E|/N) \times 3R^2$$

where cc is the average absolute value of the correlation coefficients between statements, fl is the average absolute value of the factor loadings for the category, ΔE represents the shape of the scree plot (see Fig. 6.3 for details), N is the number of statements in the category, and R^2 is the Pearson product moment correlation, which represents the linearity of the scree plot components beyond the first component. The coefficients (2, 1, and 5) are chosen to give the terms in the sum the relative weightings that we believe are the most appropriate. The shape of the scree plot accounts for 45%, and the factor loadings and correlation coefficients are equally weighted at 27.5%. The factor of 3 sets the maximum value for the robustness at 10. Values used to calculate robustness for the ‘Real World Connection’ category can be found in Table 6.2; reports for all categories appear in the appendix. The total variance calculations are based on the slopes of the scree plot in Fig. 6.3.

Table 6.2 Data from optimized 'Real World' Category

Statement Correlation Matrix					Category Values	
	S34	**S36**	**S41**	**S43**	**Robustness**	9.68
S34	1.00	0.45	0.43	0.35	**cc**	0.39
S36	0.45	1.00	0.35	0.42	**fl**	0.74
S41	0.43	0.35	1.00	0.33	**ΔE***	-1.37
S43	0.35	0.42	0.33	1.00	**N**	4
Factor Loadings			Total Variance*		**R^{2*}**	0.99
S34	0.76		**Slope 1-2**	-1.47		
S36	0.76		**Slope 2-4**	-0.09		
S41	0.71		*Based on scree plot (A) in Fig. 3			
S43	0.71					

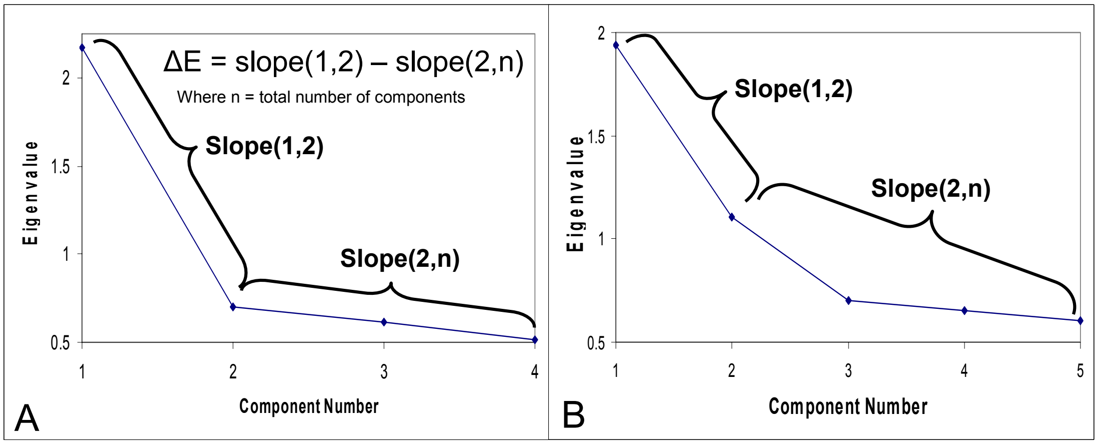

Figure 6.3 Scree plots from a good category (A) and a poor category (B).

6.4.3.2 Unmodified Physics Categories

The initial implementation of the CLASS survey in chemistry courses consisted of simply changing the word "physics" to "chemistry" in all the statements. Before modification of any categories proceeded, the robustness of the eight original categories was measured and compared to those published.[5] From the comparison of post semester data in Table 6.3, we see that the statement groupings produce nearly equal robustness values for each category regardless of the statement context (physics vs chemistry).

Table 6.3 Comparison of robustness values for the eight categories of the CLASS-Phys survey with both physics and chemistry students.

Category	**CLASS-Phys**	**CLASS-Chem v1**
Personal Interest	8.20	7.74
Real World Connections	7.32	9.68
Problem Solving-General	6.50	6.44
Problem Solving-Confidence	7.39	6.60
Problem Solving-Sophistication	8.25	8.00
Sense Making/Effort	5.91	4.94
Conceptual Connections	5.57	4.31
Applied Conceptual Understanding	5.71	5.30

In validation of the physics version,[5] the lowest acceptable robustness value was set at five. The consistent robustness of the categories between these two populations is a strong affirmation of the universality of the statements and our grouping procedure. With these categories and values as a start, we set out to investigate the series of additional statements.

6.4.3.3 CLASS-Chem Categories

The iterative process using reduced basis factor analysis depicted in Figure 6.2 was used to optimally incorporate the 11 additional statements into the chemistry survey. The final CLASS-Chem v2 categories and robustness factors are listed in Table 6.4. These categories are quite similar to the original CLASS-Phys categories.

Table 6.4 CLASS-Chem v2 categories, statement numbers, and robustness values. **Bold** indicates added statements to v2.

Categories	Statement Numbers	Robustness
Personal Interest	4,13,16,28,34,36	7.74
Real World Connection	34,36,41,43	9.68
Problem Solving: General	15,18,19,**21**,28,30,40,47,49,**50**	7.16
Problem Solving: Confidence	18,19,40,47	6.60
Problem Solving: Sophistication	6,24,25,28,40,47,**50**	8.48
Sense Making/Effort	13,**21**,26,27,38,42,46,**48**,49	6.17
Conceptual Connections	6,7,15,24,**37**,38,**50**	6.01
Conceptual Learning	1,6,7,**12**,24,25,47	6.71
Atomic-Molecular Perspective of Chemistry	**2**,**11**,**17**,**29**,**33**,**44**	7.13

The additional statements are spread over five original categories and one new category not in the physics version. Statements 1 and 9 were removed from the 'Conceptual Connections' and 'Conceptual Learning' categories, respectively, because of poor correlation with the other category statements. The remaining original statements all strengthened each category to the same degree, or more, as in the physics version.

With the addition of these statements, the category names were reviewed. It was found that in all but one instance, the names chosen for the physics categories reflected the overall theme of the statements grouped within them, the exception being that the 'Applied Conceptual Understanding' category was renamed 'Conceptual Learning.' One new category named 'Atomic-Molecular Perspective of Chemistry' was added and contains six of the additional statements. Only 36 out of the 45 statements with 'expert' responses are factored into one or more of the categories. This demonstrates the usefulness of the categorization scheme used. For example, we expected that statement #35: "To learn chemistry, I only need to memorize how to solve sample problems," would fit into one of the problem solving categories, but the analysis revealed it did not correlate with the other statements in these categories and hence did not describe student thinking in these areas.

6.4.4 Concurrent Validity

The CLASS survey is designed to measure students' beliefs about chemistry and the learning of chemistry. Therefore, an appropriate concurrent validity test would be to show that the instrument can measure a difference in beliefs between populations which should have different beliefs. Figure 6.4 shows the percentage of favorable responses for the 'Overall' statements and those in the 'Personal Interest' category. It is expected that students' 'Overall' and 'Personal Interest' scores should correlate with course selection. For example, one would not expect a student taking an introductory course for non-majors to have a strong personal connection to the discipline, in contrast to a chemistry major taking a junior level physical chemistry course. Not only does the survey distinguish between these different populations, but it can also differentiate student populations within the same course as shown in Figure 6.4. Students in both general and organic chemistry who are chemistry majors show more "expert-like" beliefs than the non-chemistry majors (made up of biology majors, non-science majors, or other science majors) in these same courses.

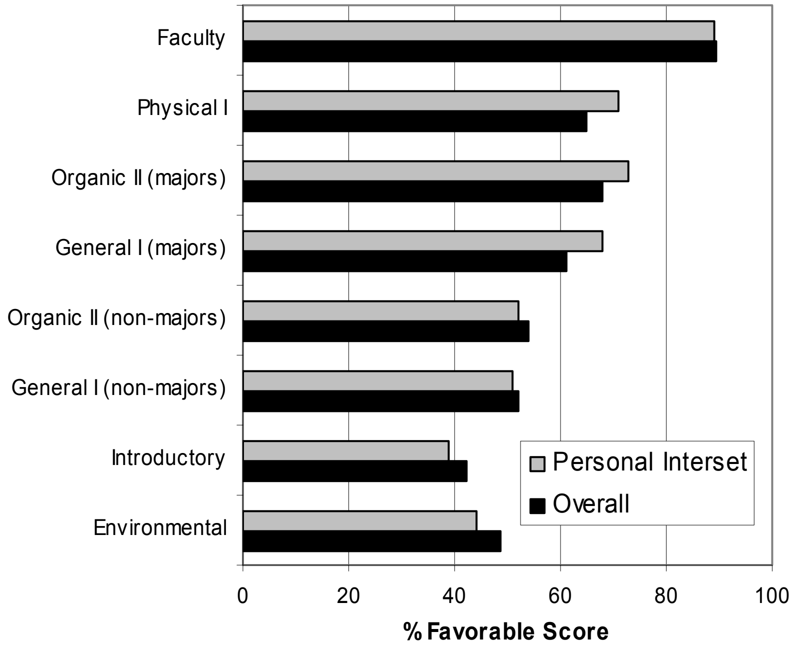

Figure 6.4 Comparison of percent favorable scores for 'Personal Interest' and 'Overall' categories for a range of courses and majors including faculty.

6.4.5 Test-Retest Studies

In order to gauge the reliability of the CLASS instruments we use the test-retest method.[12,13] Reliability was measured using pre responses from two general chemistry I courses during the fall 2005 and fall 2006 semesters. Since it is reasonable to assume there is little variation in these large (N>800) student populations from year to year, this provides a good direct measure of survey reliability. The correlations shown in Table 6.5, of the percent favorable, percent neutral, and percent unfavorable scores for all statements on the CLASS-Chem v2, show that student responses between the two years are very similar. Data from the physics version is also presented in Table 6.5 for comparison.

Table 6.5 Correlation of percent favorable, neutral, and unfavorable scores from fall 2005 to fall 2006 general chemistry I courses and fall 2004 to spring 2005 algebra-based physics I.

	%Favorable	%Neutral	%Unfavorable
Chemistry	0.99	0.95	0.99
Physics	0.98	0.88	0.98

We feel that this is a better measure than calculating a Cronbach alpha value[12,13] for this type of instrument for two reasons. First, because we have large and very consistent student populations from one year to the next in these large courses, the retest-approach provides the most direct test of reliability. Second, the Cronbach alpha test relies on correlations between statements, and we intentionally exclude statements with a very high degree of correlation, in order to obtain the maximum amount of information from a given number of statements. We did calculate the average Cronbach alpha value, using fall 2006 data from nine chemistry course at two different universities, for CLASS-Chem v2 to be 0.89. While this value is high and falls into the 'good' range,[14] it is not so high that it suggests repetition within the survey statements. Streiner *et al.* state in their work on measurement scales that "if alpha is too high, then it may suggest a high level of item redundancy; that is, a number of items asking the same question in slightly different ways."[15]

6.5 Applications

The breadth of data collected with the CLASS survey can be analyzed in a variety of different ways to extract specific results. Using physics data, our group has studied the correlation of students' self-reported interest in physics to their surveyed beliefs[16] as well as differences in beliefs with gender[5] and correlations between beliefs and content learning.[17] Using the common statements between CLASS-Phys and CLASS-Chem we compared how biology majors view each discipline (see 6.5.2 below).[18] In addition to characterizing students' beliefs, shifts in beliefs over the course of a semester can be correlated to various teaching methods.

6.5.1 Semester Shifts

The general trend in shifts for both physics and chemistry are in the negative direction, meaning the students score more favorably at the start of a semester than at the end. Table 6.6. shows pre and post scores along with calculated shifts for a general chemistry I course. This trend is a current topic of investigation as its cause can stem from a variety of sources. We do have data from two physics courses which do not show a decline in beliefs. These instructors made modest efforts to address student beliefs over the course of the semester, suggesting that such undesired impacts of instruction are relatively easy to change. Obtaining large positive shifts in beliefs has been challenging and is an area of ongoing research in the physics community.[19]

Table 6.6 General chemistry I: Results show decline in percent favorable scores over one semester.

Category	PRE	POST	SHIFT	Std. Error*
Overall	53	48	-5	1
Personal Interest	53	44	-9	2
Real World Connection	58	46	-12	2
Problem Solving: General	59	53	-6	2
Problem Solving: Confidence	64	56	-8	2
Problem Solving: Sophistication	44	40	-4	2
Sense Making/Effort	66	56	-10	1
Conceptual Connections	55	51	-4	2
Conceptual Learning	42	40	-2	2
Atomic-Molecular Perspective of Chemistry	52	51	-2	2

6.5.2 Comparison Between Chemistry and Physics

We have collected CLASS-Physics responses in a first-term, algebra-based Physics I course (Phys I) and CLASS-Chemistry responses in a first-term, introductory general chemistry course (Chem I). In prior research, we have found differences in students beliefs correlating with choice of major;[17,20] thus, in this study, we focus on just the biology majors.[21] We choose first-term courses because college physics courses have been shown to alter student beliefs.[3,17] With these data, we are able to compare two large and similar populations of students because there are a large number of biology majors and the students are required to take both courses to fulfill their majors.

From Table 6.7, we see that both courses were large lecture courses (over 500 enrolled) with a large number of biology majors, the majority of whom are women. The results presented here are for the 156 (Chem I) and 212 (Phys I) biology-majors for which we collected matched pre- and post- surveys. The instructor for the Phys I course is very familiar with research findings in PER and incorporated many research-based practices into the course, including: in-class concept questions where student-student discussions are highly encouraged and reasoning/sense-making is emphasized; interactive feedback in lecture where students use H-ITT "clickers" to vote; conceptual questions on homeworks and exams; and labs revised to incorporate more discovery. In implementing

Table 6.7 Demographics of introductory courses surveyed.

	Chem I	**Phys I - Alg**
Total # students	812	553
Total # bio majors	362	330
Total # bio majors with matched surveys	156	212
% women bio majors	70.3	72.2
% men bio majors	28.4	27.4

these practices, the instructor explicitly worked to promote expert beliefs. Although the Chem I course used concept tests and clickers, the course was comparatively traditional, with less emphasis on peer discussion, reasoning, and conceptual learning.

Students' responses on the pre-course surveys were compared to identify difference between biology majors' view of physics and chemistry prior to any college instruction in the discipline. Statistically significant differences ($p<0.01$) between their responses to the CLASS-Physics and CLASS-Chemistry surveys were measured for the 'Overall' score and for three categories – 'Real World Connection', 'Conceptual Connections' and 'Applied Conceptual Understanding', note: the 'Applied Conceptual Understanding' category was renamed 'Conceptual Learning' on the second version of the CLASS-Chemistry. In figure 6.5, we see that biology majors have consistently more expert-like beliefs (denoted as points closer to upper-left corner of plot) about physics and learning physics than about chemistry across these categories. The most dramatic difference is observed in the 'Real World Connection' category where the % favorable scores are 69.3% for physics and only 56.8% for chemistry, indicating that these biology majors see physics as substantially more connected to the real world – as both describing and being useful to understand real world experiences.

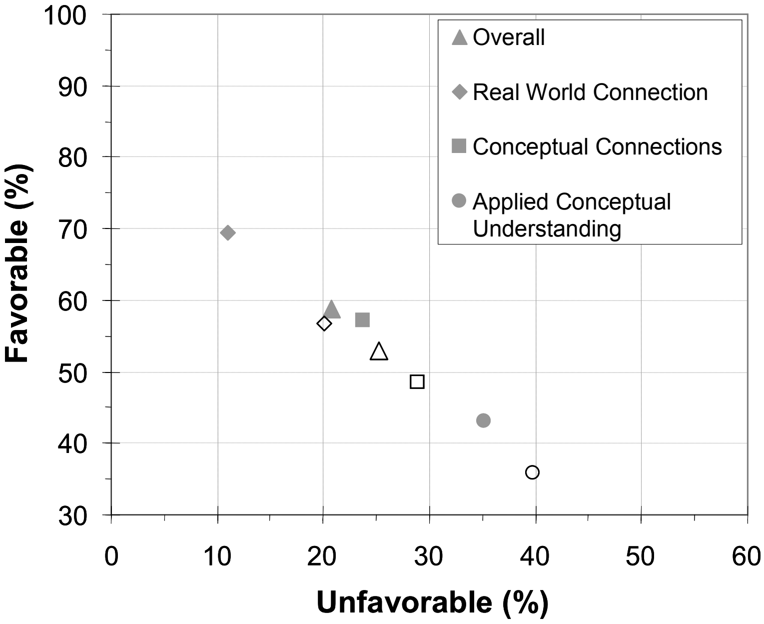

Figure 6.5 CLASS survey scores for biology majors at the start (pre) of Phys I (solid) and Chem I (hollow). The students were consistently more expert-like in their view of physics, with differences beings statistically significant ($p<0.01$) for both 'Overall' and the 3 categories shown.

Figure 6.6 shows the shifts in CLASS scores over the course of the term (pre-to-post) for the biology majors in the Phys I and Chem I courses. Only categories for which the shifts are statistically different ($p<0.01$) are included. In Chem I, we see the biology majors shifting to be much more novice-like in their beliefs about chemistry – a result consistent with the typical shifts observed in introductory physics courses.[3,17] In the Phys I course, however, we observe students beliefs holding steady in most cases. We attribute this to the Phys I instructor's emphasis on conceptual understanding and reasoning, his infusion of real world examples, and his use of concept tests and peer discussion in class.

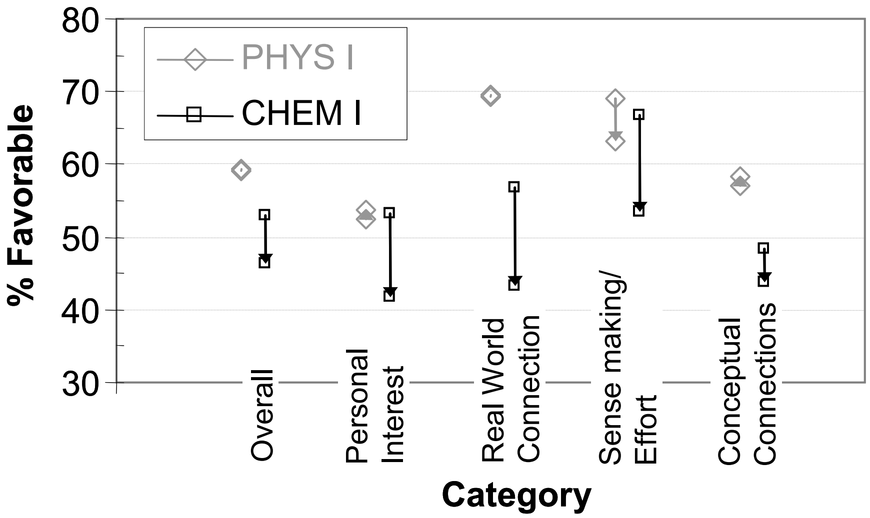

Figure 6.6 Pre-post shift for CLASS-Chemistry and CLASS-Physics scores where there is a statistically significant difference in the shifts ($p<0.01$).

We observe significant differences in biology majors' beliefs about physics and their beliefs about chemistry. In all measures, these students have more novice-like beliefs about chemistry, specifically seeing chemistry as *more* about memorizing and *less* about the real world. Since these differences are present at the *start* of these first-term introductory courses, these differences in beliefs were established by some combination of prior experiences. As with many physics courses, we see that introductory chemistry courses, even those that use concept tests and clickers, may lead to significant declines in students' beliefs about chemistry and learning chemistry. Physics courses where reforms have succeeded in avoiding this typical decline may serve as a useful model for reforming chemistry courses.

6.6 Conclusions and Future Directions

This chapter describes the modification and validation of the CLASS-Phys survey for use in chemistry courses. The CLASS-Chem v2 consists of 50 statements, 39 slightly-modified statements from the CLASS-Phys survey plus eleven additional statements. Validation has been performed for all statements to ensure clarity in wording and meaning for a wide group of students. Statements are categorized into statistically robust groupings which are useful to educators in evaluating various aspects of student thought.

This work establishes an instrument which can be used to study student beliefs about chemistry and the learning of chemistry. This instrument is a useful tool for evaluating the impacts of teaching practices. The impacts of instruction on reducing interest in chemistry are particularly worth noting if one is concerned with increasing the number of students majoring in chemistry.

This survey instrument can be combined with a conceptual exam in order to provide an educator a wealth of knowledge about how their teaching practices affect students' beliefs and conceptual understanding. This combination would greatly enhance the decision of what to teach and how to teach it for any course.

Extending the beliefs survey into the high-school setting would allow researchers to investigate broader trends in science education. Are students more 'expert-like' in high-school? Does the 'novice-like' behavior begin in high-school or at the freshman level in college? Can we implement curriculum change at the high-school level that will impact the number of incoming science majors?

An additional extension of the beliefs survey would be a laboratory specific version. A great deal of time and effort is placed on developing "new and exciting" chemistry experiments for undergraduate teaching labs. Is there a benefit to these labs? Do inquiry based labs have an impact on students' beliefs about chemistry? Do students believe that they are actually learning chemical concepts in a lab setting or simply gaining tactile lab skills?

Copies of the CLASS-Phys and CLASS-Chem surveys can be found online and in PDF format at http://CLASS.colorado.edu. Excel scoring templates are also available from the same address.

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[21] *including students majoring in Molecular, Cellular, and Developmental Biology, Ecology and Evolutionary Biology, and Integrative Physiology as well as the now-discontinued majors of Kinesiology and Environmental, Population, and Organismic Biology*.

Chapter VII

Tutorials for Undergraduate Physical Chemistry

7.1 Introduction

As described in Chapter V, we have developed learning tutorials for use in a first semester undergraduate physical chemistry course. These tutorials integrate a physical model or computer simulation into the standard pencil-paper tutorial format. The models allow students to make direct observations and predictions connected to the concepts being addressed. The three tutorials covered in this chapter address concepts of the First Law of Thermodynamics, the Second Law of Thermodynamics, and Reaction Kinetics.

The remainder of this chapter is structured as follows. Section 7.2 describes the design of the study itself including observed student misconceptions and an outline of potential models to address these problems. In section 7.3, the developed tutorial material is tested and results are presented. Section 7.4 addresses the implementation of these tutorials into a classroom setting and compares results from this course to a control group. Lastly, section 7.5 presents conclusions of this work and provides ideas for future directions with these and other tutorials.

7.2 Study Design

The purpose of the current research is to develop learning tutorials to address difficult or often misunderstood concepts within the thermodynamics and kinetics curriculum of a physical chemistry course. This section outlines the procedures used to identify these problem areas and presents potential tutorial models to address these areas. The tutorial design is based on these findings and covered in the last section (7.2.3). Copies of the tutorial worksheets can be found in Appendix B.

The study of student misconceptions has been an area of investigation in chemical education for over 4 decades.[1] An investigation of the literature reveals more than a hundred studies which address student misconceptions in chemistry.[2] In this thesis I will limit these misconceptions to those directly pertaining to the First Law of Thermodynamics, the Second Law of Thermodynamics, and Reaction Kinetics.

As a chemistry major I have heard the same quote from people when they ask me what I study, "I hate chemistry." It is not surprising to me now that so many people have a dislike for the area of science to which I have dedicated myself. Many students taking chemistry at the high school and college level struggle to learn the material and most do not succeed.[3] Research shows that many students taking an introductory chemistry course do not correctly understand the fundamental chemistry concepts covered in these formal courses.[4] This lack of understanding at the fundamental level provides a blockade for these students when they attempt to learn more advanced concepts which build upon these fundamentals. This lack of conceptual understanding has also been shown to hinder students' problem solving capabilities in chemistry.[5] These learning tutorials are designed to aid students in connecting to often difficult or misunderstood fundamental concepts within the physical chemistry curriculum.

7.2.1 Student Observations and Interviews

Since the summer semester of 2005 we have been observing the first semester undergraduate Physical Chemistry I courses (Thermodynamics and Kinetics) at the University of Colorado in Boulder. In addition to these classroom observations we have conducted a series of informal interviews with students enrolled in these courses. These informal interviews came in the form of either problem solving sessions or small group activity sessions. These observations and interviews were used to decide which concepts to target and which tools would best address student problems.

Classroom observations began as part of an initiative to modify the way physical chemistry is taught at the University of Colorado. One or two observers attended every class period and recorded field notes about the topics covered and the depth of the coverage. These observations also included students' questions about the material being addressed. The initial use of this information was to simply get a baseline for how the course was taught and what information was covered in a typical semester. Sitting in on the class also provided the needed background information about the class so that the observers could participate in problem solving sessions. These sessions were held once a week for two hours, usually scheduled toward the end of the week before problem sets for the class were due, and were not mandatory. On average only 2-3 students attended these sessions at any given meeting time.

One direct conclusion from the classroom observations was that the instructor was covering too much material and not spending enough time addressing any one topic to provide the students with a depth of understanding. This "teaching to the text" mentality is a common problem arising when instructors feel the need to cover a wide range of topics because that is what the book presents.[6-8] A portion of the transformation of the physical chemistry course addresses this issue; however, addressing this issue is not covered in this thesis. The results of this modification have implications on the material covered in the course and so a brief summary is given. In a typical physical chemistry textbook there are roughly 30 chapters.[9] About one half of these chapters make up the first semester (Thermodynamics and Kinetics) material. In order to determine which topics the faculty who regularly teach this material deem important, the syllabi from 6 schools (~ 10 courses) were reviewed and comparisons made.[10] These results were presented to the physical chemistry faculty member who was involved in transforming the course. From this information, a list was generated of the 5 main core areas for which a physical chemistry student should have a solid fundamental understanding.

1. First Law of Thermodynamics
2. Second Law of Thermodynamics
3. Chemical Equilibrium
4. Simple Mixtures
5. Reaction Kinetics

Part of the transformation of the course was to limit the number of topics covered but provide an in-depth coverage of the chosen material. Therefore, this short list was used to define target areas for students' fundamental understanding.

With these five target areas in mind, a review of student questions from the class as well as from the problem solving sessions was used in determining the individual concepts from each area that needed the most attention. Individual concepts were deemed as needing "the most attention" if they were fundamental in nature and were needed to build further understanding within the larger concept area (i.e., an understanding of heat and/or work on which to build other First Law concepts). Due to the amount of time needed in fully investigating any one of these five areas, this thesis work only covers the First Law, Second Law, and Kinetics sections of the course.

The course under observation began the semester with the First Law of Thermodynamics. This material typically spans two chapters in the text and is covered in about two weeks. The instructor (and the text) immediately introduces heat, work, and internal energy, giving these topics about one class period (2 pages). After this brief introduction, the material turns to the various conditions under which changes can be made to a system (i.e., isothermal, adiabatic...). By the end of the first of these two chapters, the students are immersed in partial differential equations and the focus of the material is mainly mathematical manipulation.

Student responses to in-class questions, as well as student questions themselves, revealed that most of the class struggled with basic fundamental concepts presented in the first few class periods. Students did not have a clear understanding about how work and/or heat affect the internal energy. Nor did they understand the sign conventions associated with these forms of energy transfer (i.e., work done ON a system is positive with reference to the system itself). In working with students during problem solving sessions, it became clear that in addition to "minor" problems many students did not believe that there was a difference between "heat" and "temperature." This "major" problem has been addressed in many publications[11-13] and has particularly devastating consequences in a thermodynamics course. Students' misunderstandings of the differences (or lack thereof) between heat (q) and temperature (T) hinder their development of many fundamental concepts in thermodynamics. For example, consider the following question from the point of view of a student who believes that $q = T$.

An insulated cylinder containing an ideal gas undergoes an adiabatic (q=0) compression, how does this compression change the temperature of the gas?

This student would likely respond that $\Delta T = 0$ because the problem states that the compression is adiabatic meaning $q = 0$, when in reality, $q \neq T$ and when the gas is compressed $\Delta T > 0$.

The two chapters following the First Law cover the Second Law of Thermodynamics. This material is again given approximately two weeks of lecture time. Students are initially introduced to the concept of entropy and use the mathematical definition of entropy in deriving the fact that entropy is a state function. This classic derivation involves the Carnot cycle which is built of four reversible processes. Once this material is covered, the course/text begins to build on this introductory material eventually leading to derivation of the Gibbs energy equation ($G = H - TS$). The entire second chapter on the Second Law material covers the Maxwell relations and various derivations which can be used to describe thermodynamic systems.

Due to their lack of fundamental understanding of the First Law concepts presented above, many students struggle to understand the Carnot cycle and state function derivation. Not only do students struggle with the equations and definitions associated with the Carnot cycle, but students could not connect to a physical picture of what this “cycle” represented. This material is generally presented solely in terms of a pressure versus volume plot where the four stages are graphed.

The fundamental concept of Gibbs energy is introduced to chemistry students in freshman level general chemistry courses; this concept is built upon in physical chemistry and used to derive many different relationships. Very little attention is paid to students’ “understanding” of Gibbs energy and what it means for a process/reaction to be spontaneous. When students are asked to evaluate if a process/reaction is spontaneous or not, many students only focus on one part of the picture; similar results were found by Granville in 1985.[14] For example, students state that an endothermic processes ($\Delta H > 0$, where the process takes in thermal energy) can not occur spontaneously because energy is being added, or that reactions where the entropy decreases ($\Delta S < 0$) can not be spontaneous because this too requires energy. However, these students are failing to consider all the variables and how they are combined in the Gibbs energy ($\Delta G = \Delta H - T\Delta S$) when determining spontaneity.

Towards the end of the semester, the course material turns towards kinetics. About four weeks (and four chapters) are typically dedicated to this topic, including a section on the kinetic molecular theory of gases. This material is independent of all of the previous thermodynamic material presented; in fact, many courses reverse the order of topics and begin the semester covering the kinetic molecular theory and kinetics. In the kinetic molecular theory students learn about molecular speeds, collision rates, and diffusion. This material is tied up in one chapter before beginning the kinetics sections. In learning kinetics, students are reintroduced to rate equations, rate constants, and other fundamental concepts first presented in general chemistry. After this reintroduction, students begin various derivations of rate laws and methods of determining rates and rate constants. The last two chapters (of the three kinetics chapters) solely address the kinetics of “complex” reactions and molecular reaction dynamics, respectively. Many courses either do not cover these sections or plan to cover them but run out of time in the semester.

The temperature dependence of reaction rates is addressed in general chemistry when students are introduced to the Arrhenius equation ($k = Ae^{-Ea/RT}$). Students learn that a reaction rate which obeys the Arrhenius equation increases with increasing temperature. At the general chemistry level, very little effort is placed on explaining WHY this is true. However, in covering the kinetic molecular theory of gases in physical chemistry, students learn about velocity and energy distributions and how these scale with temperature. Despite the additional chapter of material, and week of class time, when asked to explain WHY a given reaction rate increases with temperature many students present flawed responses. The most candid of these responses is simply “because that is what we were taught in general chemistry,” others respond mathematically by explaining the Arrhenius equation itself and why k increases as T increases. Two typical responses involve the potential energy profiles (see Fig. 7.1) common in all general and physical chemistry text books. Students state that either the reactant potential energy raises or the transition state potential energy lowers as temperature is increased. To clarify what was meant by this many students were asked to sketch how the profile changed, a typical sketch is seen in Fig. 7.2.

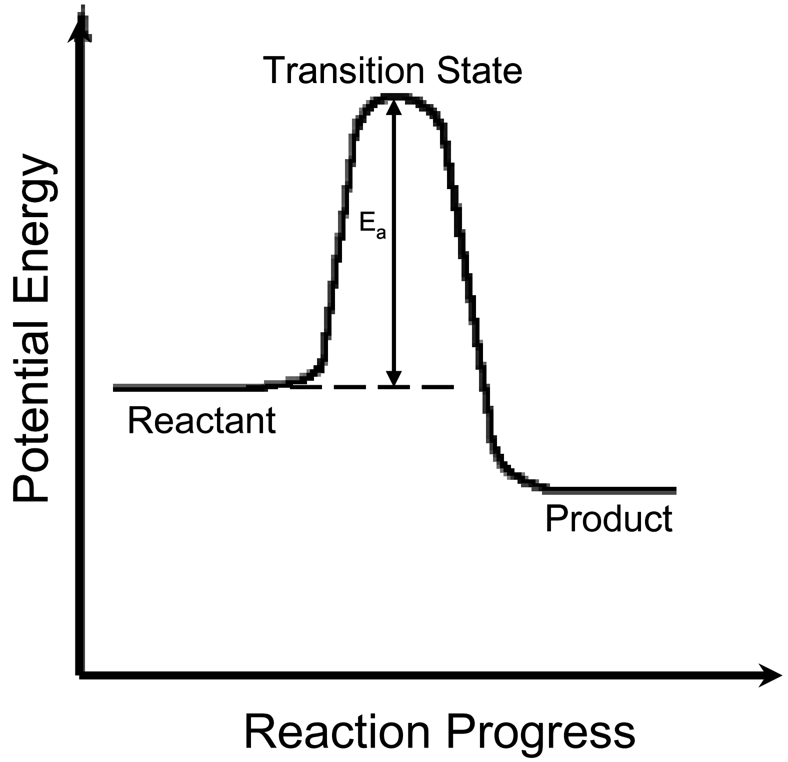

Figure 7.1 Typical reaction energy profile showing potential energies for the reactant, product, and transition state.

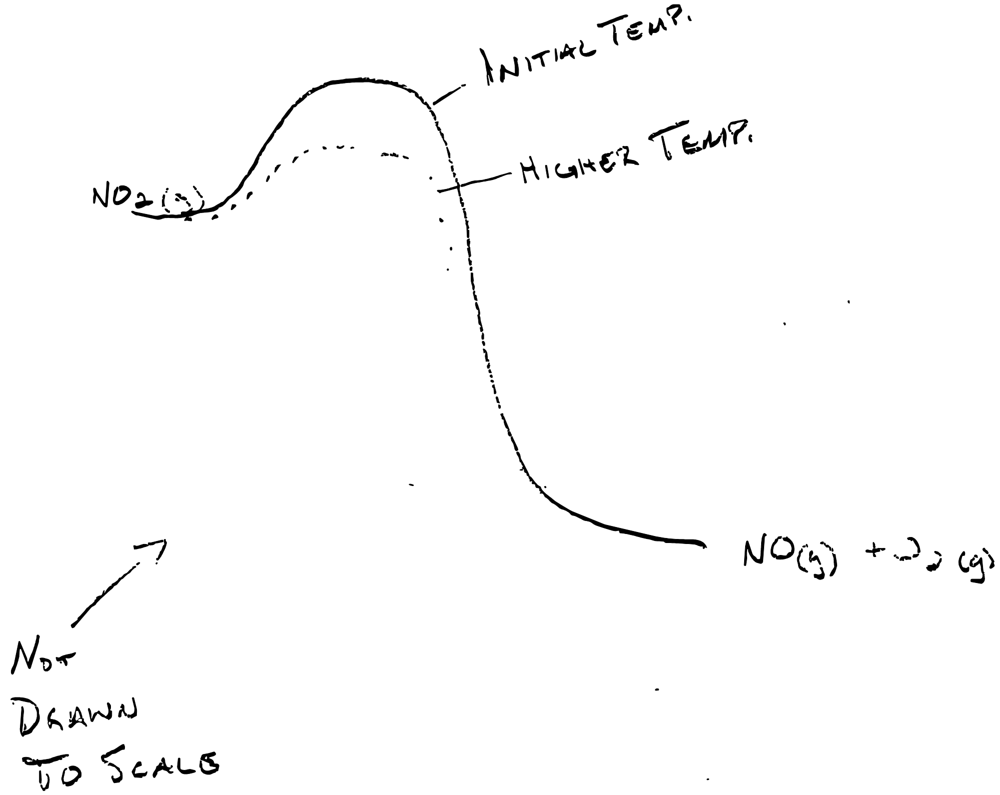

Figure 7.2 Student sketch of how potential energy of transition state varies with temperature.

As one can imagine, there are many other misconceptions and difficulties associated with a first semester physical chemistry course. However, as stated in the introduction above, only a select few will be addressed here. In the light of the problems presented above, the next section will pinpoint the various student misunderstandings and present models which can be used to address these issues.

7.2.2 Physical Models

All of the examples presented in the previous section involve concepts first presented to students during introductory general chemistry. Therefore, when presented during the physical chemistry course, all students have had some previous exposure to the material. It is likely that students either did not fully understand these concepts when they were first confronted with them or they learned them in such a way that after several semesters they no longer have a working knowledge set. In either case, our goal is to develop a model to help the students understand the concepts at hand and gain some connection which they can access at later times. To do this, we set out to provide active learning strategies which have been shown to improve learning and knowledge[6,8,15,16] while at the same time providing the student with some "real world" connection to the material. This "real world" connection will be addressed further for each individual model in the next section.

7.2.3 Tutorial Design

Tutorial use is on the rise in both Chemistry and Physics. The two most popular published tutorial series in these disciplines are the Process Oriented Guided Inquiry Learning (POGIL)[17] series and the Tutorials in Introductory Physics.[18] Both of these series were reviewed and fundamental structures of each were utilized in our work. The three tutorials presented here differ from both of these published series in that our tutorials are designed around a physical model or computer simulation.

7.2.3.1 First Law of Thermodynamics

Throughout the classroom observations and student interactions presented in section 7.2.1 above, it was clear that many students either possess a very weak understanding or no understanding at all of the fundamental concepts of the First Law of Thermodynamics. There are many stock demonstrations and everyday experiences that can be used as a model to help students connect with these fundamentals. One common classroom demonstration is the Fire Syringe. This demo consists of a glass cylinder and piston sealed with o-rings. A piece of flash paper or tissue paper is placed inside the cylinder and the piston is quickly depressed. Students observe that the piece of paper ignites due to the increased temperature of the gas trapped inside the cylinder. This model provides a great visual connection of an adiabatic compression for students as they can readily observe the fire ball. However, the cost of these instruments is around $30 each and no student will have access to these models outside of the classroom setting.

The same adiabatic compression can be performed using a simple bicycle tire pump with the outlet hose blocked off. In this case students can feel the barrel of the pump get hot as the plunger is depressed. This does not have the visual effect of the fire syringe but students still get a hands-on evaluation of what happens during the change. One main advantage of using the bicycle pump model is that most students have access to a pump outside of the classroom environment. In addition to models for adiabatic compressions, any compressed air can may be used as a model for adiabatic expansions. In this model students can feel the can getting cold as the gas is expanded out of the container. At some point in every student's life they have used some sort of compressed gas can, many students report that they have indeed noticed that the temperature decreased. We feel that this model provides the best "real-world" connection of an adiabatic process for many reasons. First, almost every student has already made this observation but most have never thought about it in terms of a thermodynamic process. Second, most students have some sort of compressed gas readily available to them outside of the classroom environment; therefore, once this phenomenon is put into thermodynamic terms many students will recall this each time they experience the phenomenon in their daily life. Lastly, we want to provide in class models that all students can experience and use. This model provides the most cost effective way to provide many duplicates for individual groups to use.

7.2.3.2 Second Law of Thermodynamics

The physical chemistry course sequence has long had the reputation as being the hardest chemistry course one will take as an undergraduate. This reputation stems both from the abstractness of the concepts presented during this series and the rigorous mathematical content of the material. Traditionally taught physical chemistry courses tend to focus on the mathematical aspect of the material and students' "understanding of the material" is based primarily on their calculations. This mode of instruction and evaluation does not provide the instructor or student any insight about the content knowledge of a specific topic. One example of this is the Second Law of Thermodynamics and its connection with Gibbs energy.[14,19,20]

A widely used model in both general and physical chemistry courses to teach students about Gibbs energy and its dependence on Enthalpy and Entropy is the rubber band demonstration. A typical example can be found at this address:

http://www.usm.maine.edu/~rhodes/Goodies/RubBandThermo.html

In this demonstration each student is given a rubber band and they are prompted through a series of "experiments" in order to determine the change in Gibbs energy, Enthalpy, and Entropy during stretching and relaxation. This model provides a nice every day example to gain insight to these thermodynamic properties. An added advantage to using this "real world" model, instead of a typical chemical reaction, is that in determining the Entropy change students must consider the change in Gibbs energy and the change in Enthalpy. In the typical chemical equation example students can simply evaluate any change in the number of moles or phase in making a determination about Entropy changes.

An additional model similar to the rubber band demonstration is to use protein folding as an example. However, this model does not provide a "hands-on" system to study but may help biochemistry students gain a strong connection to the material. In using this example students must be focused on the Enthalpic and Entropic changes and not the hydrophobic/hydrophilic effect.

7.2.3.3 Reaction Kinetics

Traditionally students are introduced to reaction kinetics during the second half of the general chemistry series. Very early in this kinetics material students are presented with the idea of the reaction coordinate and shown reaction potential plots similar to that of Fig. 7.1 above. Students are also introduced to the concept of the temperature dependence of a reaction rate and are frequently asked to perform calculations using the Arrhenius equation ($k = Ae^{-Ea/RT}$). However, throughout our student interactions it became clear that students do not have a robust fundamental picture for how the temperature change actually affects the reaction on a molecular level. As pointed out above, students try to use the only knowledge to which they have access when struggling to explain the temperature dependence. This leads to false explanations of how the increased temperature alters the potential energy of the system.

Despite the additional coverage of the Kinetic Molecular Theory of Gases in physical chemistry, students still struggle in applying molecular collisions to reaction rates. This material is traditionally presented with multiple equations and plots followed by some 2D graphics in a text. This format does not provide students with a visual picture of what is actually happening at the molecular level during a reaction. To aid in this molecular level understanding we intend to use a reversible reaction simulation developed by the physics education technology (PhET) group at the University of Colorado.

The reversible reaction simulation (http://phet.colorado.edu/web-pages/index.html) allows students to monitor the collisions which take place between reactant molecules and gain a visual picture of how these collisions provide the energy needed to react, see Fig. 7.3. The simulation provides a variety of additional information to the students as well. As students raise the temperature of the reaction, they can directly see this impact on the distribution of kinetic energy and speed in two independent plots. In addition to providing a visual picture for the students to connect molecular motion to reaction rate, the simulation also provides a format for collecting temperature dependent data. A built in stop watch and count of reactant and product molecules allows students to record number of molecules and time data. These data can be used find the rate constant (k) of the reaction. Rate constants at various temperatures can be measured and used to generate the Arrhenius parameters (A and E_a) generally given on problem sets and homework.

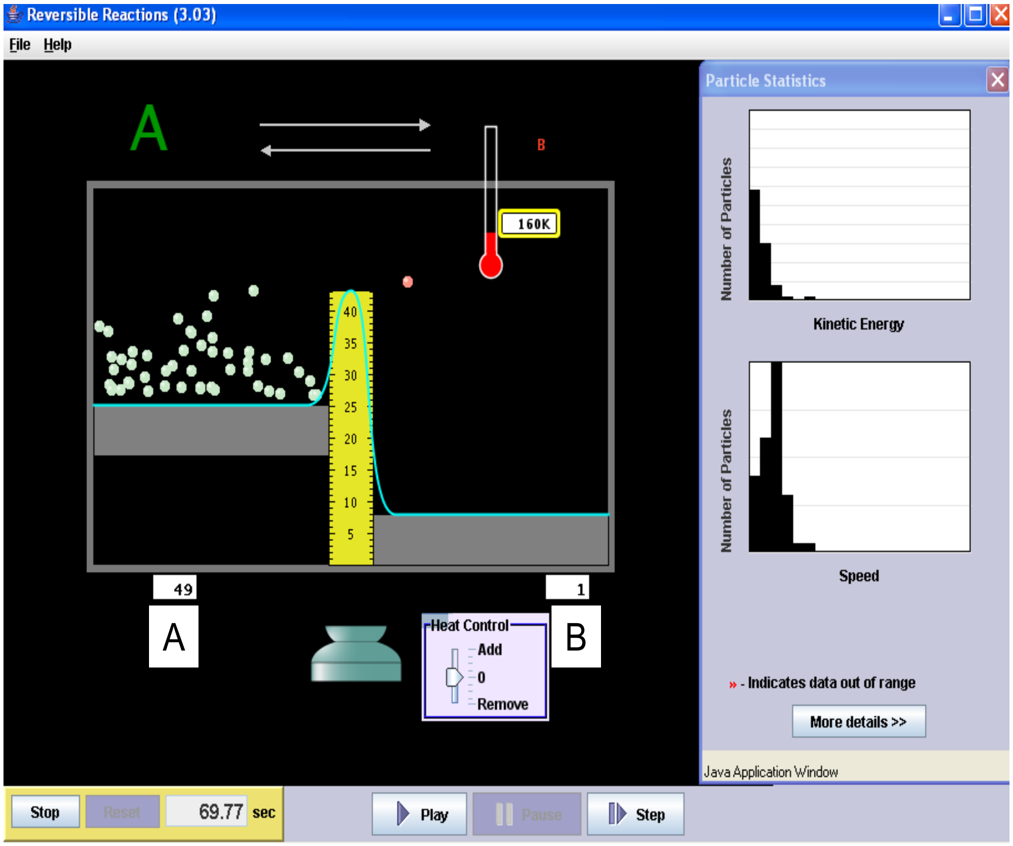

Figure 7.3 Screen image of reversible reaction simulation showing a potential energy plot with several reactant molecules. Kinetic energy and speed distributions are also plotted for the molecules shown.

Other kinetics simulations exist for student use; however none clearly display the actual molecular motions leading to reaction. Several examples are presented below.

http://www.chem.uci.edu/undergrad/applets/sim/simulation.htm http://cheminfo.ou.edu/~mra/Kinetics/HBr.htm

http://jchemed.chem.wisc.edu/JCEDLib/WebWare/collection/reviewed/WW007/index.html

http://www.jce.divched.org/Journal/Issues/2002/May/abs638.html

http://www.chm.davidson.edu/ChemistryApplets/kinetics/ReactionRates.html

In many of these simulations, molecular collisions are shown and students can vary the temperature in order to observe its effect. However, this increase is not visually tied to a reaction rate. Other programs allow students to make changes in the initial concentrations or temperature of the reaction and follow the change in reaction rate; however, this is done with graphical means only.

7.3 Testing

Based on the issues uncovered during classroom observations and student interviews tutorial worksheets were developed. As stated above, these worksheets are centered around a physical model or computer simulation. Each individual tutorial is designed to assist students in building up an understanding of several concepts which ultimately tie into a larger concept. The prepared tutorials were tested on a volunteer basis with students enrolled in the physical chemistry course. Students met in small groups (3-4 total) and each session was audio recorded. The tutorial sessions were scheduled after the course instructor covered all the material pertaining to the individual topic. Each session was placed before the class exam covering the material; this placement provided incentive for student participation as they were told that it would be a good review of the material they had covered.

The testing phase of the tutorial development began during the Summer 2005 semester and has continued through the Fall semester 2006. During each semester modifications were made based on student feedback and our observations. This section reviews the testing phase and addresses the individual components of the tutorial separately.

Each portion of the tutorial will be outlined in detail and examples of observations and student discussions will be provided.

7.3.1 Scoring Rubric

All of the pre, post, and exam questions used in the testing and implementation phases are scored using one of two rubrics. The pre and post quizzes contain two different types of questions. There are initial questions which are used to gauge student understanding of the basic concepts underlying the main concept being addressed. Each quiz contains one detailed question which asks students to explain the thermodynamic or kinetic reasoning behind some process or observation. The initial questions on the pre/post quizzes are scored with the rubric presented in Table 7.1 below. This rubric provides a three-point scale (from zero to two) to determine the correctness of the student response. The detailed pre/post quiz questions as well as all of the exam questions (covered in 7.3.5) are scored using the rubric presented in Table 7.2 below.

Table 7.1 Grading rubric used for introductory quiz questions.

Rubric Score	Criterion
0	Student has no idea or student response is totally incorrect.
1	Student responds correctly to question but provides incorrect reasoning.
2	Student responds correctly to question and provides correct reasoning.

Table 7.2 Grading rubric used for detailed quiz questions.

Rubric Score	Criterion
0	Student has no idea or student response is totally incorrect or irrelevant as compared to the expert response on the central concept(s).
1	Student response includes some aspects of the expert response on the central concept(s) but major aspects of the expert response on the central concept(s) are missing or incorrect.
2	Student response matches expert response on the central concept(s) but with one important aspect of the central concept(s) missing or incorrect.
3	Student response essentially matches expert response on the central concept(s) but some of the details concerning the central concept(s) are missing or incorrect.
4	Student response matches the expert response on the central concept(s).

This rubric scores each response on a five-point scale from zero to four. A high numerical value indicates that a student's response closely matches an expert response on the central concept(s) addressed in the question. A low numerical value indicates a poor match with an expert response.

7.3.2 Pre Tutorial Quizzes

In order to gauge the incoming knowledge base of the students as well as any learning gains associated with performing the individual tutorials we administer a pre-tutorial quiz. Students are given about 10 minutes to complete the quiz individually before beginning group work on the tutorial. In the early testing phases the pre quiz was used as an introduction to the material being covered as the tutorials were not tied directly to the course itself. These quizzes mainly addressed the introductory material and definitions that students would need to perform the tutorial itself and were not used in measuring learning gains associated with the tutorial. Beginning with the Fall 2005 semester, the tutorials were tied to the course material. Tutorials were scheduled after the specific material was covered in lecture but before the exam covering the material. This allowed us to gauge the students' incoming knowledge after completing the lectures, reading, and problem sets.

7.3.2.1 First Law of Thermodynamics

The pre-quiz for the First Law of Thermodynamics tutorial assesses students' incoming knowledge about work, heat, and their connection to internal energy. A copy of the quiz appears in Appendix B1. The first question appears in two parts; the first part is designed simply to gauge the students understanding of the sign or wording conventions associated with work. Students are asked whether work is done ON or BY as gas that is being compressed. The second part of question one addresses the thermal energy exchange during the same compression. Here students are asked if there is a transfer of thermal energy during the compression, the question states that the cylinder in non-insulated. The data from this first question (covered below) is used to ensure that students understand these individual components so that when we review responses to more detailed questions we can analyze the overall concept itself. In the second question, students are given a scenario of an insulated cylinder containing an ideal gas. Students are asked how the internal energy and temperature of the gas are affected by a compression of the gas.

The results of the pre-quiz are presented in Table 7.3. Here we see that over 85% of the students correctly respond that work is done ON the gas in question 1a. In question 1b student scores are split at ~40% between students who correctly respond that thermal energy is transferred out of the system and students who do not respond correctly for a variety of reasons. This first question tells us that most of the students can correctly identify when work is done ON or BY a gas during a process but less than one-half understand the thermal energy transfer associated with this compression. In question 2 we see that nearly 50% of the student responses are scored as a one on our rubric (Table 7.2). This indicates that students are missing many of the important aspects of the First Law concepts associated with this ideal gas compression after typical course instruction, reading, and problem sets.

Table 7.3 First Law of Thermodynamics pre-quiz results. Data reflects percentage of students with each individual rubric score. Questions 1a and 1b are scored using Table 7.1, question 2 is scored using Table 7.2.

Question N = 28	Rubric Score				
	0	1	2	3	4
1a	10	4	86		
1b	39	18	43		
2	0	46	32	18	4

Additional important findings during the scoring of question 2 are the misconceptions held by the respondents. Greater than 30% of the responses show some indication that the student does not distinguish between heat (q) and temperature (T), this misconception has been observed in many previous research studies.[11-13,21] The majority of these responses contain statements equivalent to the following quote: “this is an adiabatic compression, therefore $q = 0$ and the temperature remains constant”. In addition to the misconception that heat and temperature are equivalent, greater than 40% of the responses reflect student reliance on the Ideal Gas Law equation ($PV = nRT$) in addressing the temperature change upon compression. A similar reliance on the Ideal Gas law has been observed in previous studies.[19,22] The conclusion of many of these responses is that “the pressure and temperature are directly related and when pressure increases so does the temperature of the gas”. Many students add in that temperature and volume are also directly related (indicating that temperature should decrease as volume decreases) but that “volume changes less than pressure so the temperature still increases”. Some combination of these two main misconceptions make up the reasoning behind the majority of the low rubric scores presented for question 2 in Table 7.3.

7.3.2.2 Second Law of Thermodynamics

The pre-quiz for the Second Law of Thermodynamics tutorial assesses students' incoming knowledge about heat, entropy, and the temperature dependence of the Gibbs energy. A copy of the quiz appears in Appendix B3. The quiz uses an example of an ice pack consisting of two chemicals which when mixed together get cold. In the first question students are told that the pack feels cold to the touch, they are then asked if this means that thermal energy (heat) is going INTO the reaction mixture or OUT OF the reaction mixture. We ask this question knowing that many students struggle with the concept of heat. The second question asks the student to determine the Entropy change as the reaction proceeds. In this question students are instructed to use the sign of the Gibbs energy (the reaction is spontaneous) and Enthalpy (endothermic reaction) along with the Gibbs equation in solving for the Entropy change. This question provides information about how students connect the individual thermodynamic properties together. The last question asks students about the temperature dependence of the reaction based on the information they have about the thermodynamic properties. This question provides information about a students understanding of the balance between Enthalpy and Entropy when considering a reactions spontaneity.

The results of the pre-quiz are presented in Table 7.4. We see in the results from the first question that ~25% of the students still incorrectly address the thermal energy transfer. The significance of this result is heightened when we consider that this quiz was given nearly halfway through the course and yet one-quarter of the students still struggle with the concept of heat. In question 2 we see that more than 50% of the students scores (rubric score = 1) reflect major conceptual aspects missing in their understanding of entropy change.

Table 7.4 Second Law of Thermodynamics pre-quiz results. Data reflects percentage of students with each individual rubric score. Question 1 is scored using Table 7.1, questions 2 and 3 are scored using Table 7.2.

Question	Rubric Score				
	0	1	2	3	4
1 (N=31)	23	3	74		
2 (N=31)	0	52	16	13	19
3(N=14)	0	43	36	7	14

Question 3 was added to the quiz after the Spring 06 semester in order to gain more detailed information about the temperature dependence; it is for this reason that the total number of responses is less than the previous two questions. In this question we see that more than 75% of the students (rubric score ≤ 2) have a weak understanding of the effect of temperature on the spontaneity of the reaction.

In scoring the pre-quizzes we also observe two main misconceptions held by the students. First, many students (>15%) relate the reactions overall spontaneity solely to the increase in Entropy ($\Delta S > 0$) and not the Gibbs energy. This is true only when considering $\Delta S_{universe}$, not ΔS_{system}.[14] This belief can lead students to a misunderstanding of the temperature dependence of the Gibbs energy (hence, the reaction spontaneity) because they do not view spontaneity as a balance between Enthalpy and Entropy. In addition to the spontaneity misunderstanding, more than 15% of the students state that "because the ice pack is cold it must be giving up heat (thermal energy)". This misunderstanding of the thermal energy transfer leads to an incorrect determination of the Enthalpy change for the process.

Many of the low scores on questions 2 and 3 are mainly due to some combination of the two issues presented here.

7.3.2.3 Reaction Kinetics

The pre-quiz for the Reaction Kinetics tutorial assesses students' incoming knowledge about what conditions effect reaction rate and how the reaction rate is dependent on temperature. A copy of the quiz appears in Appendix B5. This quiz is designed to gauge the students understanding of reaction rate at the molecular level. The first question asks students what conditions are required in order for a reactant molecule to become a product molecule. This question provides information about what each student finds important for a reaction to occur. In the second question, students are asked specifically if the energy barrier height, on the figure provided, changes as a function of temperature. This question came directly out of our observations that students use this line of reasoning when explaining the change in reaction rates. In the last question, students are asked to explain why a specific reaction rate increases with increasing temperature.

The results of this pre-quiz are presented in Table 7.5. Here we see that according to question 1, 75% of the students (rubric score = 2) have a good understanding of what is required for a reactant molecule to become a product molecule. Most responses reflect that students understand that the reactant molecules must surmount the reaction barrier (activation energy, Ea) at the transition state in order to produce products. However, in question 2 student responses are split at 46% between those that believe the energy barrier itself lowers as temperature increases (rubric score = 0) and those that state that the barrier is independent of temperature (rubric score = 2). Question 3 shows that nearly 90% of the responses (rubric score ≤ 2) reflect a poor understanding of why a given reaction rate increases with increasing temperature. Many of these students do make some connection to an increase in energy but fail to connect this energy increase to the reaction rate correctly.

Table 7.5 Reaction Kinetics pre-quiz results. Data reflects percentage of students with each individual rubric score. Questions 1 and 2 are scored using Table 7.1, question 3 is scored using Table 7.2.

Question N = 24	Rubric Score				
	0	1	2	3	4
1	25	0	75		
2	46	8	46		
3	0	42	46	12	0

The main misconception addressed in this quiz is the belief that a reaction barrier (activation energy) or transition state is temperature dependent. While 46% of the student responses reflect this belief, it is not surprising after talking with students. While chemistry students are introduced to the reaction energy profile (Fig 7.1) in general chemistry and use this type of diagram often, it is clear that few students actually understand what the diagram represents. Many students state that, "as temperature is increased the energy of the reactants is increased". They then go on to explain that this "increased energy raises the left side of the graph (reactant potential energy) essentially lowering the activation energy". Despite past instruction in both general and physical chemistry few student correctly connect the temperature increase to an increase in the kinetic energy of the molecules.

7.3.3 Tutorial Worksheets and Models

Each individual tutorial worksheet and associated model is designed to help a student gain a stronger connection with the concepts at hand. To do this, the individual components which make-up the concept as a whole are addressed separately. This structure allows students to uncover the principles associated with each component before tying them together in understanding the larger concept. In contrast to the pre and post quizzes, students work in groups of 3-4 on the tutorials. Groups are encouraged to discuss all opinions concerning the individual questions and concepts before writing their answers. Each tutorial is designed to take about 40 minutes so that they will fit within one 50 minute class period.

7.3.3.1 First Law of Thermodynamics

The First Law tutorial is designed to assist students in learning the fundamentals of work and heat and how these two components are related to the internal energy of a system. The tutorial begins with a prediction section designed to help engage the students. The tutorial worksheet then goes on to individually address both work and heat for an expanding gas before asking students to connect these together in explaining changes in internal energy. The entire tutorial worksheet can be found in appendix B2.

To begin, students are shown a figure of a can covered with a balloon. Students are told that the can contains a gas at high pressure and that the gas will be expanded into the balloon. Students are asked to predict, and explain, what will happen to the temperature of the gas inside the can during the expansion. Once students come to an answer, each group is given a can and balloon to test their prediction. Through observation of the individual groups, most students easily predict that the gas, and the can, will get cold. Some students qualify their answer with the simple fact that they have felt this before. Despite their correct predictions, many groups struggle to correctly explain WHY the gas gets cold. Nearly every group begins their explanation using the ideal gas law. Individual students will point out how a decrease in pressure will lead to a decrease in temperature. Other students will counter these explanations with the fact that the volume of the system (can AND balloon) also increases. It is at this point when groups begin to realize that the ideal gas law may not fully explain this situation. A few groups make the leap to using the First Law with no outside advisement; most groups require some assistance to start down that path.

After testing their predictions, groups start their investigation of work. The tutorial worksheet shows two cylinders sealed with pistons which contain the same ideal gas. Each piston has a block sitting on top. One cylinder is insulated and the other is not. The block is removed from both pistons and the groups are asked if work is done ON the gas or BY the gas after removal of the block. Observations show that it does not take much time (<1 minute) for all groups to conclude that with the reduced external pressure the piston moves up as the gas expands. All students correlate this expansion with the gas DOING work. Very little discussion takes place in any group and no group members express a belief that work was done ON the gas.

After coming to a consensus on the work question, students are asked about the transfer of thermal energy in the two systems after the blocks are removed. If there is a transfer of thermal energy, students are asked to draw an arrow on the diagram indicating the direction of the transfer. It is at this point that we see students really starting to discuss their own beliefs and trying to defend those beliefs. The two cylinders are labeled as isothermal and adiabatic, many students begin their explanation by defining what these terms mean. Students immediately point out that there is no thermal energy transfer for the insulated cylinder, the one labeled as adiabatic. In most groups a few minutes of discussion surround the isothermal case. It is usually pointed out by one group member that there must be a transfer of thermal energy and the discussion centers around the direction of this transfer. Groups eventually decide that if the gas is DOING work (reducing the energy of the gas) then the transfer of thermal energy must be counter to this and thermal energy ENTERS the gas. At this point, very few groups or individuals have connected any of these changes with the temperature of the gas.

The last two questions ask the groups to explain how the heat and work involved in these expansions affect the internal energy of each gas. Question 3 first asks about the internal energy of gas A, the isothermal expansion. All groups tend to start out by one of two methods. The first method is when one of the group members simply states that in an isothermal process the change in internal energy should be zero, at this point usually no explanation is provided other than they know this is true. The second method has group members looking back at questions 1 and 2 and writing down their previous results for the heat and work associated with gas A. In either case, all groups tend to discuss how if the gas is DOING work after the block is removed than this will tend to lower the internal energy. They then go on to state that the temperature will also lower. This line of discussion leads groups to state that in order for the temperature, and internal energy, to remain constant (it is an isothermal process) then the thermal energy entering the gas must be equal to the energy lost due to work.

The last question on the tutorial (question 4) asks about the internal energy of gas B, the insulated (adiabatic) system. Most groups quickly reach consensus on this question. All groups begin by pointing out the fact that in this system the energy lost due to the work done BY the gas can not be "replaced" by thermal energy entering because the cylinder is insulated. This leads to the conclusion that the internal energy must be reduced because the gas is doing work and that this "loss of internal energy", means the temperature of the gas is less.

During the discussions surrounding the last question most groups connect the internal energy and temperature reduction of the adiabatic system back to the air can that they originally made a prediction on. This connection ultimately leads to some brief discussion that a process can be adiabatic even if the container (cylinder or can in this case) is not insulated. It seems that before this discussion, most students simply relied on being told that a given process occurred adiabatically or isothermally and never really considered what that meant. In section 7.3.4 (post-quiz), we will see how the discoveries made during this tutorial affect the individual student scores.

7.3.3.2 Second Law of Thermodynamics

The Second Law tutorial is designed to assist students in learning the fundamentals of Gibbs energy, Enthalpy, Entropy, and how these components are related to the spontaneity of a process. The tutorial begins with a prediction section designed to help engage the students. The tutorial worksheet is designed around using a simple rubber band to determine these thermodynamic properties. The entire tutorial worksheet can be found in appendix B4.

To begin, students are shown a figure of a rubber band being stretched by a weight. Students are asked to predict what happens to the height of the weight as the rubber band is heated. Instinctively all groups and individual students respond that the weight will lower because "as you heat the rubber band it will stretch". When asked how they "explain" this, three general responses are given. Many students state that the rubber molecules can "move around more when heated and therefore the band can stretch", or that "when you heat the band the rubber gets soft and the weight stretches it more". A large fraction of students simply state that, "I don't know why the band should lengthen I just feel that it should". Once the groups come to some conclusion they are allowed to test their prediction using a model set-up exactly like the diagram, students use a heat gun to warm the rubber band. All students are impressed and confused when they observe that the rubber band contracts and the weight is lifted as heat is applied. Immediately students begin to ask WHY this happens. At this point students are told that once they work through the tutorial they should be able to answer that question of WHY for themselves.

For the tutorial, each student is given their own rubber band and students work in groups of 3-4. The tutorial begins by asking the students if a stretched rubber band relaxes spontaneously when released. All students come to the same conclusion that yes, the relaxation is spontaneous. Next students are asked, based on their response about the spontaneity, if the Gibbs energy of the rubber band increases or decreases in going from the stretched to the relaxed position. This first question begins brief discussions about the sign of ΔG for a spontaneous process. Most students quickly remember that ΔG is less than zero for a spontaneous process, so "the Gibbs energy decreases as the band is relaxed".

In the next step of the tutorial students determine the Enthalpy change during the stretching/relaxing of the rubber band. Students are instructed to place the rubber band flat against their lip and to note any change in the temperature as they stretch and relax the band. As each student performs this procedure, discussions begin about if the band is hot or cold when stretching and relaxing. After a few minutes all groups conclude that the band is warmer when it is being stretched and cooler when it is being relaxed. The second question on the worksheet asks if thermal energy is entering or leaving the rubber band as it is relaxing. Students begin to state that, "when I relax the band I feel that it is cooler on my lip, this means that thermal energy is leaving my lip and entering the rubber". One or two students struggle to understand how feeling the band is cooler means that thermal energy (heat) is entering. This confusion was also present during the air can tutorial but to a larger extent. In all cases, the correct explanation was discussed with another group member before continuing on.

Question 3 now asks about the sign of the thermal energy transfer for the relaxation. With little discussion, groups conclude that "if thermal energy is entering the rubber band then the sign of q (thermal energy exchange, heat) for the band is positive". They are then asked in the same question whether the enthalpy of the rubber band increases ($\Delta H > 0$) or decreases ($\Delta H < 0$) for the process. This portion of the question sparks discussion in all groups as they try to connect the transfer of thermal energy to the change in Enthalpy. Students search their brains to remember equations which relate the two variables; others try to reason out connections by thinking about endothermic and exothermic reactions. Ultimately all groups conclude that if $q_{band} > 0$ than $\Delta H > 0$. Before continuing on, the worksheet prompts students to tabulate their data about the changes in both Gibbs energy and

Enthalpy for both stretching and relaxing. Most students realize that for the stretching process they simply need to flip the sign for the Gibbs energy and Enthalpy determined for relaxation.

At this step the student are asked about the change in Entropy for the rubber band for both stretching and relaxing. Unlike other chemical examples, students do not have a chemical equation to refer, which allows them to view a change of state or calculate the number of moles. Here they must use the Gibbs equation ($\Delta G = \Delta H - T\Delta S$) to determine how the Entropy changes. The students are now forced to look at the equation for Gibbs energy and relate the signs of the variables they know to what the sign for entropy should be. Student discussions begin with either the stretching or relaxing case. The results of one such discussion are summed up by an individual's statement that "for relaxation the Gibbs energy is negative (spontaneous) and the Enthalpy is positive (Endothermic) so the only way to get a negative Gibbs energy is if the Entropy is positive". A few groups also concluded that in addition to ΔS being positive, $T\Delta S$ must be larger than ΔH. Other groups needed to be asked if the sign of ΔS was the only requirement, only one group needed more than this simple hint.

The last portion of the worksheet asks students if they can create conditions under which a rubber band will spontaneously lengthen (ie: without being pulled on). In doing this students are told to consider the values of ΔH and ΔS to be temperature independent. With this task at hand, groups begin to discuss how they can change the sign of ΔG for stretching from positive to negative, which would indicate a spontaneous process. With the Gibbs equation in front of them as well as the signs for all of the variables, most groups quickly decide that at room temperature (for stretching) the $T\Delta S$ term was larger than the ΔH term making ΔG positive. Therefore, if they lower the temperature (T) to the point where ΔH is larger than $T\Delta S$ the sign on ΔG will be negative. With this conclusion students begin to discuss how this relates to the opposite effect seen when the rubber band was heated and contracted raising the weight.

7.3.3.3 Reaction Kinetics

The Reaction Kinetics tutorial is designed to assist students in learning the fundamentals of reaction rates and their temperature dependence. The tutorial uses a computer simulation depicting a potential energy plot and a variable number of reactant molecules. Students are informed that this reaction model simulates a *cis-trans* isomerization. The tutorial worksheet provides basic simulation instructions (shown in **bold** on worksheet) as well as guided observations and questions. The entire tutorial worksheet can be found in appendix B6.

To begin, students are instructed to insert a given number of A molecules (reactants) into the simulation and observe how an A molecule becomes a B molecule (product). Working in groups of 3-4 students begin to note that the A molecules undergo many collisions and a few occasionally jump up to the height of the reaction barrier but do not cross to become a product. After about 2 minutes of observation, students begin to observe that a few A molecules reach the reaction barrier and are traveling in the correct direction to become B molecules. These observations spark discussion that it is not simply that the A molecules have enough energy (ie: they are higher than the barrier) but they must move in the proper direction (ie: the *cis-trans* isomerization requires twisting about the central bond axis).

In the next step the effect of raising the temperature is investigated. The simulation easily allows students to raise the temperature and observe the effects. All students state that "the molecules begin moving faster and colliding more often; this makes them jump over the barrier faster". Students are asked specifically if raising the temperature had any effect on the height of the reaction barrier itself. Some students raised the temperature again just to be sure of their answer but ultimately all students' state that the barrier height does not change.

In the next step students use the built-in stop watch to record how long it takes for the first B molecule to be formed when 50 A molecules are inserted at 350 K. This provides a number for comparison in a later step. With molecules inserted at 350 K students are instructed to sketch and discuss the plot of the Number of Particles versus Kinetic Energy shown on the screen of the simulation. Most groups spend on average about 5 minutes discussing what the plot means and eventually come to the conclusion the most of the molecules have a small range of energies and only a few vary from that range, shown as a small tail to the right on the plot.

Following this procedure at 350 K the students are asked to predict if the first B molecule will be formed faster at 750 K (compared to 350 K). Groups then run the simulation at 750 K and make their observations. The tutorial now asks how the time to form B compares between the 350 and 750 K cases as well as how the collision rate of molecule A changes. Groups quickly conclude that B molecules form faster at 750 K and the collision rate of the A molecules is higher at 750 K. Question 10 helps to focus the students at this point. The tutorial points out that, for the forward reaction, the equation for the rate of formation of molecule B is $d[B]/dt = k_f[A]$. Students are then asked how the rate coefficient (k_f) varies from 350 K to 750 K, and to explain this difference in terms of the molecular motions. During the discussion of these questions students begin to start connecting all the pieces together. Students state that “both times we added the same number of A molecules so [A] is the same but at 750 K B formed faster, so this must mean that k_f is bigger at 750 K”. Others point out that “the molecules start going crazy and colliding a lot at 750 K so they get over the barrier faster”. After several minutes some groups start to connect collision frequency to the rate coefficient, others need a little assistance and are asked about the relationship between collision frequency and k_f.

At this point the students are asked to sketch the Number of Particles versus Kinetic Energy plot from the simulation at 750 K and compare this to their predicted plot. Here students begin to discuss why the plot gets wider and the peaks at the lower energies decrease in height. Students’ comments reflect that they are beginning to connect the increase in temperature to a “larger range of kinetic energies”. Lastly the tutorial asks how the plots at 350 and 750 K compare and what this indicates about the TOTAL energy at each temperature. Most students have already discussed the similarities and difference in the plots during the previous question and tend to focus on the total energy difference. A few students ask, “what do you mean by total energy, you mean kinetic plus potential energy?” Once clarified, all groups conclude that the total energy is greater at 750 K than at 350 K and that the potential energy at both temperatures is identical.

It is during these final discussions that many groups begin to see the connections between the kinetic energy, molecular collisions, and increased rate. The understanding of these connections as well as the belief that the reaction barrier height changes with temperature will be investigated on the post-quizzes in the next section.

7.3.4 Post Tutorial Quiz

In order to quantify any changes in student understanding of the topics covered in the tutorials we administer a post-tutorial quiz. The questions on these quizzes are identical to those administered on the pre-quiz. This allows direct comparison of student scores and filters out any bias due to question wording or context. Students were given the quiz immediately after finishing the tutorial worksheets, quizzes were not part of the group work. Each group of students was given as much time as necessary to complete the post-quiz, however, no student took more than 5 minutes to complete their quiz.

7.3.4.1 First Law of Thermodynamics

The pre-tutorial quiz in section 7.3.2.1 reflected the level of understanding of several fundamental topics connected with the First Law of Thermodynamics. Here we will outline the effect on students’ understanding, using the same topics and questions, after use of the tutorial designed to cover these topics. A copy of the post-tutorial quiz can be found in appendix B1.

For the first part of question 1 on the pre-quiz (see Table 7.6), 86% of the responses reflect students' understanding that as a gas is compressed it has work done ON IT. This number drops to 82% (a change of one student) on the post quiz. In looking at how the individual students move from pre to post we see that 2 of the three students who initially scored zero remain at zero, the third moved from zero up to two. The one student who scored one on the pre-quiz moved down to zero on the post. Two of the students scoring two on the pre-quiz drop down to zero on the post. A review of field notes from the various tutorial sessions reveals that the three students showing declines down to zero on the post-quiz were all in the same work group. This group was one of the first to participate in the tutorial and there was a significant language barrier component associated with all three members. On subsequent tutorial sessions these students did not all work together. In lieu of these few declines, the post-scores reflect that most of the students understand that a compression does work ON a gas.

Table 7.6 First Law of Thermodynamics post-quiz results and pre-post gains. Data reflects percentage of students with each individual rubric score. Questions 1a and 1b are scored using Table 7.1, question 2 is scored using Table 7.2. Average gain is calculated for question 2 only.

Question N = 28		Rubric Score					
		0	1	2	3	4	Avg. Gain
1a	Pre	10	4	86			
	Post	18	0	82			
1b	Pre	39	18	43			
	Post	10	4	86			
2	Pre	0	46	32	18	4	40%*
	Post	0	7	10	29	54	

*Note: Each individual student gain is calculated as post score minus pre score; average gain reflects the entire sample group.

The second half of question 1 shows a large increase in students' understanding of thermal energy transfer during the compression example. The percentage of students who correctly answer question 1b has doubled after performing the tutorial. Here we observe no declining scores and note that two of the three students scoring zero on the post are from the group mentioned above. This dramatic increase suggests that the tutorial design and group discussions do indeed help students in understanding the concept of thermal energy transfer.

Finally, on the second question we calculated an average gain of two points (40%) on our scoring rubric (see Table 7.2). These average gains reflect the gains achieved by all students sampled, where individual student gains are calculated as their post score minus their pre score. Table 7.6 shows that on the pre-quiz, 78% (rubric score ≤ 2) of the responses reflect some significant misunderstanding of the First Law concepts. This number drops to only 17% on the post quiz. No declining scores were calculated and 6 of the 28 responses reflected no change (4 of these students scored either 3 or 4 on the pre-quiz) after using the tutorial. The size and direction of these rubric scores nicely displays the effect of the tutorial construction in helping students gain an understanding of the fundamentals of the First Law of Thermodynamics.

In addition to the rubric score gains, we see significant changes in student misconceptions after using the tutorial. During the pre-quiz, 42% of the responses showed that students were relying on the ideal gas equation when considering the temperature change upon compression. This number drops to zero after the tutorial session. The percentage of students who equate heat (q) and temperature (T) drops from 32% to 10%, this reflects the difficulty in students grasping the concept of thermal energy.

7.3.4.2 Second Law of Thermodynamics

The pre-tutorial quiz in section 7.3.2.2 reflected the level of understanding of several fundamental topics connected with the Second Law of Thermodynamics. Here we will outline the effect on students' understanding, using the same topics and questions, after use of the tutorial designed to cover these topics. A copy of the post-tutorial quiz can be found in appendix B3.

In the first question we see that on the pre-quiz (see table 7.7) nearly 75% of the respondents correctly address the transfer of thermal energy which takes place during the chemical reaction, this percentage increases to 94% after the tutorial. A bigger jump is seen if we compare the scores from the similar First Law question (pre/post question 1b) where only 42% responded correctly before the tutorial and 86% afterwards. While there is a decline of roughly 10% between the post-score on the first activity quiz and the pre-score on the second activity quiz, the population contained 5 students (12%) who did not participate in the first activity.

Table 7.7 Second Law of Thermodynamics post-quiz results and pre-post gains. Data reflects percentage of students with each individual rubric score. Questions 1 is scored using Table 7.1, questions 2 and 3 are scored using Table 7.2. Average gain is calculated for questions 2 and 3 only.

Question		Rubric Score					
		0	1	2	3	4	Avg. Gain
1 N = 31	Pre	23	3	74			
	Post	3	3	94			
2 N = 31	Pre	0	52	16	13	19	30%*
	Post	0	6	10	16	68	
3 N = 14	Pre	0	43	36	7	14	20%*
	Post	0	7	29	14	50	

*Note: Each individual student gain is calculated as post score minus pre score; average gain reflects the entire sample group.

Question 2 asks students about the change in entropy for the given reaction, to correctly address this question; students must connect the change in both the Gibbs energy and Enthalpy using the Gibbs equation. Table 7.7 indicates that only 32% of respondents correctly address the entropy change (rubric score ≥3) on the pre-quiz. After finishing the tutorial 84% of the responses reflect expert-like connections in addressing the Entropy change. This equates to an overall average gain of 1.5 (30%) on our scoring rubric. In looking at individual student shifts, only one student showed a decline (from 2 down to 1) and nine students show no shift (including the 6 who scored a 4 on the pre-quiz). These overall results show that the tutorial has helped a large fraction of the students connect the fundamental thermodynamic properties of Gibbs Energy, Enthalpy, and Entropy together for a given reaction.

Question 3 was added to the pre and post quizzes after the summer 2006 semester in order to specifically address the temperature dependence of the given reaction and its effect on spontaneity. Table 7.7 shows that only 21% of the students (rubric score ≥3) correctly identify and address that the reaction is not spontaneous at all temperatures. This number rises to 64% after completion of the tutorial with an average gain of 1 (20%) on the scoring rubric. Students with the largest gains on question 3 also showed gains of 2 or more on question 2 indicating that they initially struggled with both connecting the thermodynamic properties together and the concept of the temperature dependence of the Gibbs energy (spontaneity).

In addition to the gains reflected in table 7.7 for questions 2 and 3, student responses showed declines in the misconceptions present in those responses. On the pre-quiz responses, 5 students (16%) state that the entropy increases for the reaction because "entropy must increase for a spontaneous process". After the tutorial only one student (3%) response shows this belief. The pre-quiz also shows that 16% of the students associate the cold feeling of the ice pack as indicating thermal energy leaving the reaction mixture. This number drops to zero after the tutorial.

7.3.4.3 Reaction Kinetics

The pre-tutorial quiz in section 7.3.2.3 reflected the level of understanding of several fundamental topics connected with Reaction Kinetics. Here we will outline the effect on students' understanding, using the same topics and questions, after use of the tutorial designed to cover these topics. A copy of the post-tutorial quiz can be found in appendix B5.

The kinetics simulation utilized in this tutorial provides a molecular level picture for the students about what is needed for a product molecule to become a reactant molecule. The effect of the tutorial can be seen in the post scores represented in Table 7.8. Here we see an increase from 75% to 88% (rubric score of 2) in the correct responses to question 1 about the conditions needed to form a product molecule. Only one student's response did not show some sign of correctness after performing the tutorial. Field notes indicate that this student only answered questions during the tutorial session when directly asked by the tutorial leader and that the other three students in the group excelled at the material.

Table 7.8 Reaction Kinetics post-quiz results and pre-post gains. Data reflects percentage of students with each individual rubric score. Questions 1 and 2 are scored using Table 7.1, question 3 is scored using Table 7.2. Average gain is calculated for question 3 only.

Question N = 24		Rubric Score					
		0	1	2	3	4	Avg. Gain
1	Pre	25	0	75			
	Post	4	8	88			
2	Pre	46	8	46			
	Post	0	0	100			
3	Pre	0	42	46	12	0	36%*
	Post	0	0	21	21	58	

*Note: Each individual student gain is calculated as post score minus pre score; average gain reflects the entire sample group.

In interviewing students it became clear that many students believe that heating a reaction actually affects the potential energy profile of the reaction as indicated in Fig. 7.2 of section 7.2 above. Question 2 of the pre-quiz indicates that 46% of the student responses reflect this belief (rubric score of 0). However, after using the simulation and performing the tutorial this number drops to zero. This dramatic change speaks highly about the visual nature of the tutorial design and its specific attention to this misconception.

The last question on the pre/post quiz asks students to address the temperature dependence of a reaction. Initially only 3 students (12%) have a response which somewhat matches an expert response but lacks an important detail (rubric score of 3), no responses completely address the question. After completing the tutorial nearly 80% of the responses yield a rubric score of 3 or more and 58% match an expert response with a rubric score of 4. This means that after completing the tutorial, a majority of the students can correctly address the temperature dependence of a reaction using the same conceptual connections as an expert. This results in an overall gain of 1.8 (36%) on the rubric presented in Table 7.2.

The main misconception associated with this material is the temperature dependence of the reaction potential energy. This is nicely addressed in the results of question 2 where 100% of the students report that the reaction barrier itself is not temperature dependent.

7.3.5 Exam Questions

Based on the results presented in the previous sections there is no doubt that the tutorials have a large positive impact on student responses. However, this data may be biased by the fact that the post-testing was performed immediately after performing the tutorial. This test method does not reflect any impact on students longer term comprehension and understanding of the material contained within tutorial. In order to gauge the effectiveness of the tutorial after some period of time we set out to analyze students responses on exam questions placed on the in-class exams during the Spring 2006 semester. This testing format also allows a comparison between those students' scores who participated in the tutorials to those who did not, on average about 50% of the class did not participate in the tutorials. However, for reasons that do not need to be covered in this thesis, the exam questions submitted to the course instructor were not implemented on the exams. There was at least one semi-conceptual question on each exam which will be reviewed here. In the course implementation and evaluation section (7.4 below), common exam questions are analyzed for both a test and control group. This analysis will allow some determination of longer term effects of the tutorial use as well as providing a direct comparison with a control group that did not participate in the tutorials.

The first in-class exam covers material through the First Law of Thermodynamics. The exam contains only one conceptual question which can be loosely tied to students' fundamental understanding of the First Law concepts, this question is presented below.

Define heat and work. Why is it incorrect to speak of heat or work associated with a system? While this question will provide data about students' definition of heat and work, it will not tell us anything about their connection to changes in internal energy for a given process. For this first exam 14 of the 28 students in the class participated in the First Law (Air Can) tutorial. This exam question was scored using the rubric in Table 7.1 with a maximum score of 2. The average score for the 14 students who participated in the tutorial was 1.6, the average score for the 14 non-participants was 1.4. These numbers indicate no statistical difference between the two groups of students and provide us no gauge of the students' conceptual knowledge of the First Law of Thermodynamics.

The second class exam covered material through the Second Law of Thermodynamics. On this exam the only conceptual question involving Gibbs energy comes as the second part of a calculation. The first part of the question tells students to consider a given reaction and to calculate the change in Gibbs energy given a table of ΔH°_f and S° data for the molecules which participate in the reaction. After students perform the calculation they are asked in part B:

Will this reaction be spontaneous at all temperatures? Explain.

It is this portion of the question that we are interested in. However, a students' response will be greatly affected by their calculation from part A of the question. Therefore, we only compare student responses whose calculation in part A is correct. When scoring these questions we find that the average scores for both sets of students (9 with tutorial participation and 8 with out) are identical at a value of 1.3.

The fourth exam (the third exam contained material not covered in any of the tutorials) during the semester covered the topics of the Kinetic Molecular Theory of gasses and Reaction Kinetics. On this exam, one conceptual question appears (which is very similar to the actual submitted question) which will allow us to gauge students understanding of the temperature dependence of a reaction rate.

Explain why for thermally activated reactions, an increase in temperature results in an increase in the rate of the reaction. Provide a molecular level explanation for what is going on.

There were 10 students who participated in the kinetics tutorial and 13 students who did not. This question was scored using the five-level rubric in Table 7.2. The average score for the group who performed the tutorial was 3.5, for the other group the average was 2.6. These numbers reflect a statistically significant difference (P value = 0.005) in the responses of the two groups. Responses from students who performed the tutorial addressed most of the major components correctly, while those in the group not participating in the tutorial lacked one or more vital components.

This data from this last exam question shows us that we can indeed measure a difference in scores on a conceptual question which pertains to the concept(s) at hand. During the next section we will analyze a series of these exam questions as we compare one section of a physical chemistry course which took part in all three tutorials to a section which did not use any tutorials.

7.4 Course Implementation and Evaluation

The learning tutorials presented in this chapter have been designed to target difficult or often misunderstood concepts which are fundamental in a physical chemistry course. These tutorials are meant to enhance the lecture material for the course, not replace it. Therefore, the tutorials should be integrated into the curriculum at an appropriate time to provide the most benefits for the students. This integration can take place in two fashions. First, the tutorials can be used very early on in the introduction of these topics in order to provide a launch pad for the rest of the material. Or second, they can be place just after the normal coverage of the topics and serve as an enhancement and review of the lecture material on the topic.

The final versions of the tutorials, presented in Appendix B, were integrated into the Physical Chemistry course at CU-Boulder during the Spring 2007 semester. Each tutorial was performed in class and the tutorials were inserted after the instructor covered the lecture material on the given topics. Students were given participation points for performing the tutorial and associated quizzes.

7.4.1 Pre/Post Analysis

The pre-quiz was taken during the first 10 minutes of the class period in which the tutorial was performed. The post-quiz was taken during the first 10 minutes of the class period immediately following the tutorial class period. Data from both quizzes will be presented and discussed here; copies of the individual quizzes can be found in Appendix B.

The First Law of Thermodynamics tutorial took place during the fourth week of the semester, roughly 2 weeks prior to the first exam in the course. Table 7.9 shows the pre and post quiz scores as well as the average gain for question 2. Here we see that all 26 students correctly answer question 1a about whether work is done ON or BY as gas being compressed, the tutorial had no affect on this question. On question 1b, about the thermal energy transfer, we see an increase in the percentage of correct responses (rubric score = 2) from 69% before the tutorial to 85% after. Even after performing the tutorial we still see 15% (rubric score $\leq$ 1) of the students struggling with the correct conceptual understanding of thermal energy transfer for a given process. Question 2 asks students about the temperature and internal energy change upon an adiabatic compression. Here we see over 30% of students scoring 3 (responses essentially match an expert response) or above on the pre-quiz. After performing the tutorial 81% of the responses are scored as 3 or above. The average gain for this group of students is

Table 7.9 First Law of Thermodynamics pre/post-quiz results and pre-post gains. Data reflects percentage of students with each individual rubric score. Questions 1a and 1b are scored using Table 7.1, question 2 is scored using Table 7.2. Average gain is calculated for question 2 only.

Question N = 26		Rubric Score					
		0	1	2	3	4	Avg. Gain
1a	Pre	0	0	100			
	Post	0	0	100			
1b	Pre	19	12	69			
	Post	3	12	85			
2	Pre	35	23	11	23	8	36%*
	Post	0	4	15	35	46	

*Note: Each individual student gain is calculated as post score minus pre score; average gain reflects the entire sample group.

1.8 (36%) , slightly lower than the previous gain of 2.0 (40%) seen in Table 7.6. Nearly 40% of the pre-tutorial responses reflect reliance on the Ideal Gas equation when trying to explain changes in gas temperature; this number drops to 4% (one student) after the tutorial. Initially, 2 students' responses (8%) equate heat (q) and temperature (T) and therefore conclude that temperature is constant for an adiabatic process. This misconception is not reflected in any of the post-tutorial responses.

The Second Law of Thermodynamics tutorial took place on the 9th week of the semester, exactly one week before the second exam. Table 7.10 shows the pre and post quiz scores as well as the average gains for questions 2 and 3. In question one on these quizzes we see that initially only 70% of the students correctly identify the direction of thermal energy transfer for the given reaction. This number rises to 100% after the tutorial. During the tutorial session this topic brought about much discussion amongst groups. At one point the entire class fell silent except for two students arguing their individual points about thermal energy transfer. A similar question was asked in the previous tutorials quizzes (Question 1b above), there we also saw a ~70% correct response rate initially with 85% post. This indicates that any gains made, concerning the transfer of thermal energy, during the first tutorial do not appear in this material 5 weeks later. This observation, combined with the quantity and depth of the conversations witnessed during the previous tutorial session on this material, indicates that students continue to struggle with this idea and may need several detailed exposures in order to connect to this concept. Question 2 asks students about the change in

Table 7.10 Second Law of Thermodynamics pre/post-quiz results and pre-post gains. Data reflects percentage of students with each individual rubric score. Questions 1 is scored using Table 7.1, questions 2 and 3 are scored using Table 7.2. Average gain is calculated for questions 2 and 3 only.

Question N= 23		Rubric Score					
		0	1	2	3	4	Avg. Gain
1	Pre	26	4	70			
	Post	0	0	100			
2	Pre	44	26	4	9	17	30%*
	Post	17	9	9	9	56	
3	Pre	22	44	17	4	13	28%*
	Post	17	9	9	9	56	

*Note: Each individual student gain is calculated as post score minus pre score; average gain reflects the entire sample group.

Entropy during the given reaction. On the pre-quiz only 26% of the student responses match that of an expert (rubric score ≥ 3). This percentage increases to 65% after performing the tutorial. The overall average gain is 1.5 (30%) on the rubric grading scale, this gain is identical to that measure previously in Table 7.7. In the last question students are asked about the temperature dependence of the reaction. In Table 7.10 we see that on the pre-quiz only 17% of the responses addressed the temperature dependence in a manner similar to an expert (rubric score ≥ 3). After completing the tutorial this percentage raises to 65%. The average overall gain is 28% with over one-fourth of the students showing individual gains of 60% or more.

In addition to the measured changes on the pre-post quiz questions, there are also some changes in the student misconceptions presented within their answers. On the pre-quiz responses, 9% of the student state that the entropy increases for the reaction because "entropy must increase for a spontaneous process". After the tutorial none of the responses show this belief. The pre-quiz also shows that 30% of the students associate the cold feeling of the ice pack as indicating thermal energy leaving the reaction mixture. This number drops to zero after the tutorial.

The reaction kinetics tutorial took place on the 13th week of the semester, exactly one week before the third exam. Table 7.11 shows the pre and post quiz scores as well as the average gain for question 3. In question 1 we see that a large percentage (83%) of the students have some idea about what a reactant molecule needs in order to become a product molecule. After the tutorial all the students' responses reflect an understanding of what is required. In question 2, greater than 50% of the responses state that the transition state barrier for the reaction is temperature dependent and lowers as the reaction temperature is raised. In addition to these responses, approximately 10% of the students state that the barrier height does not change; however, the reasoning behind their answer is lacking or flawed.

Table 7.11 Reaction kinetic pre/post-quiz results and pre-post gains. Data reflects percentage of students with each individual rubric score. Questions 1 is scored using Table 7.1, questions 2 and 3 are scored using Table 7.2. Average gain is calculated for question 3 only.

Question N= 24		Rubric Score					
		0	1	2	3	4	Avg. Gain
1	Pre	0	17	83			
	Post	0	0	100			
2	Pre	54	8	38			
	Post	0	0	100			
3	Pre	4	50	42	4	0	32%*
	Post	0	8	8	54	30	

*Note: Each individual student gain is calculated as post score minus pre score; average gain reflects the entire sample group.

After performing the tutorial, none of the students report that the barrier changes as a function of temperature. We also see this learning gain reflected in students' answers to question 3.

Before the tutorial, greater than 50% of the responses had little correlation to the important aspects needed in addressing the question. In addition, 42% of the responses had some detailed information but lacked one or more key points. After the tutorial, over 80% of the student responses match, or nearly match, the response of an expert. The average gain for question 3 is calculated to be 32%, with 41% of the students showing individual gains of 40% or more.

The main misconception addressed in the kinetics tutorial is students' belief about the temperature dependence of the reaction barrier. The results of question 2 nicely show that the tutorial effectively addresses this misconception. The visual nature of the simulation allows students to see what factors do change with temperature and how these factor influence the reaction rate. Without this information, students try to reason out answers with the parts of the problem that they understand, i.e., the change in the "energy" barrier and heat "energy" is added.

7.4.2 Comparison with Control Group

Up to this point in our testing we have only had minor comparisons (in section 7.3.5) of student responses between groups of students who have performed the tutorials and those that have not. This direct comparison on common questions will provide a more meaningful gauge of the affect of the learning tutorials on students understanding of these fundamental concepts. To do this, we have analyzed common exam questions between two different physical chemistry courses.

The test group, which utilized the learning tutorials, was taught by a faculty member at the University of Colorado in Boulder. The control group was taught by a faculty member at the University of Colorado in Denver. Both faculty members regularly teach the undergraduate physical chemistry sequence. The test group contains 32 students and the control group contains 22 students. All students in the courses are majoring in either chemistry, biochemistry, or engineering. The incoming chemistry knowledge of both groups of students was measured using a physical chemistry concept test. These scores will be used to provide some degree of normalization between the two courses. We acknowledge that sampling two different courses with two different instructors is not an ideal comparison when measuring learning aspects. However, because these tutorials focus on the fundamentals of a few important concepts, we feel that these two populations will provide some significant contrasts.

7.4.2.1 Pre-Semester Concept Exam

In order to measure students' incoming physical chemistry concept knowledge all students were given a physical chemistry concept exam on the first day of class. This exam was developed at the University of Colorado by a post-doctoral associate in the Physics Education Research group, a copy can be found in Appendix B7. The exam contains 34 questions covering concepts from the Thermodynamics and Kinetics material of an introductory physical chemistry course. The questions are either true/false or multiple choice answers, no calculations or mathematical derivations are involved.

On average, the test group scores ~7% higher on the concept exam than the control group. However, as shown in Table 7.12, this difference is not statistically significant. Therefore, because the incoming knowledge of the two groups is essentially identical the scores on the common exam questions will be evaluated in their raw form (ie: un-normalized). An additional comparison between the two groups will also be made. This comparison comes in the form of a second (calculation based) common exam question and will be addressed in the next section.

Table 7.12 Comparison of average scores on pre-semester concept exam for control and test groups. Question statements can be found in Appendix B7.

	Control Group	Test Group
Average Score (%)	49.2	56.3
Standard Deviation	19.3	21.4
Standard Error	3.31	3.67
Z	1.44	
*P-value	0.15	

*P-value for two-tailed z-test, value is not statistically significant at the $p<0.01$ level.

7.4.2.2 Common Exam Scores

In order to evaluate the learning gains associated with the tutorial use common exam questions will be evaluated comparing the test and control groups. Each of the three exams contains two common questions, one conceptual and one calculation. Each exams concept question covers student understanding of the fundamental concepts of the specific material (ie: First Law, Second Law, and Kinetics). The calculation question is used to compare the performance of the two groups on material which was not part of the learning tutorials. Both sets of questions are graded by the individual instructors using their own grade key. The conceptual questions are further evaluated using the scoring rubric presented in Table 7.2.

The first exam in both courses covers material from the First Law of Thermodynamics. The common exam questions can be found in appendix B8. Figure 7.4 shows the average scores for both the common conceptual question and the calculation. For the control group, the average score on these questions was 62% and 58%, respectively. For the test group, we see a slightly higher, but not statistically different, score on the calculation question of 60%. However, on the conceptual question the test group scores significantly higher at 90%. These test scores are the grades assigned by each instructor using their own grade key. Figure 7.4 also shows the scores on the conceptual question graded with the rubric (Table 7.2) used to evaluate the pre and post quizzes. These rubric scores are slightly lower than those assigned by the instructor but still show a statistically significant difference between the two groups. In scoring the conceptual questions with the rubric we also note differences between the content of the responses. In the control group, 32% of the responses reflect students' reliance on the Ideal Gas equation in addressing the change in the internal energy and the temperature of the air in the pump. This number drops to 6% for the test group. As noted in previous sections, students incorrectly equate thermal energy transfer (q) and temperature (T). On this exam, 6% of the responses from the control groups contain this misconception while none of the responses from the test group contain this misconception.

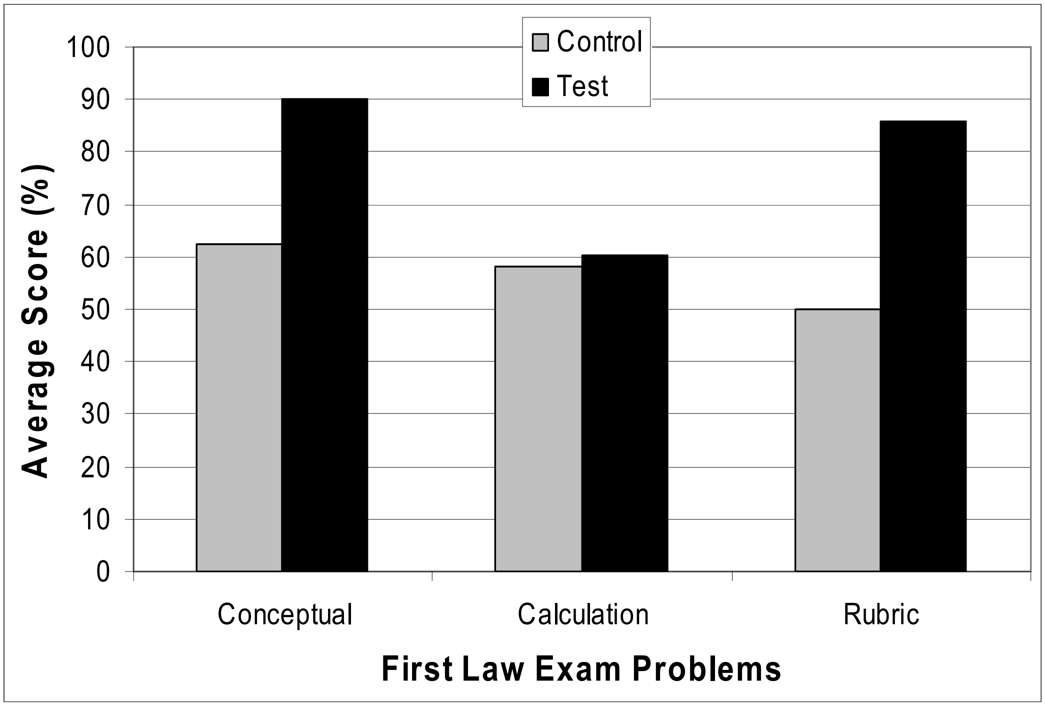

Figure 7.4 Comparison of average scores for control and test groups on common questions. Rubric score reflects average score on conceptual question using scoring rubric presented in Table 7.2. The difference in the Conceptual scores and Rubric scores are statistically significant at the $p<0.01$ level.

The second exam in both courses covers material from the Second Law of Thermodynamics. The common exam questions can be found in appendix B9. Figure 7.5

shows the average scores for both the common conceptual question and the calculation. For the control group, the average score on these questions was 37% and 79%, respectively. When we look at the scores for the test group we see that on the calculation problem the test group scores lower with an average of 67%. This 12% difference has a calculated p-value of 0.02 and indicates a statistically higher score (at the 95% level, $p<0.05$) for the control group. However, this difference is not significant at the 99% level ($p<0.01$) which is used as the criterion in the other comparisons made here. In evaluating the instructors scoring of the conceptual question we see that the test groups' average of 83% is statistically higher with a p-value < 0.00. When the conceptual question is scored with the grading rubric, the test groups' average is 80% and the control groups' average is 34%, again showing a significant difference at the 99% level.

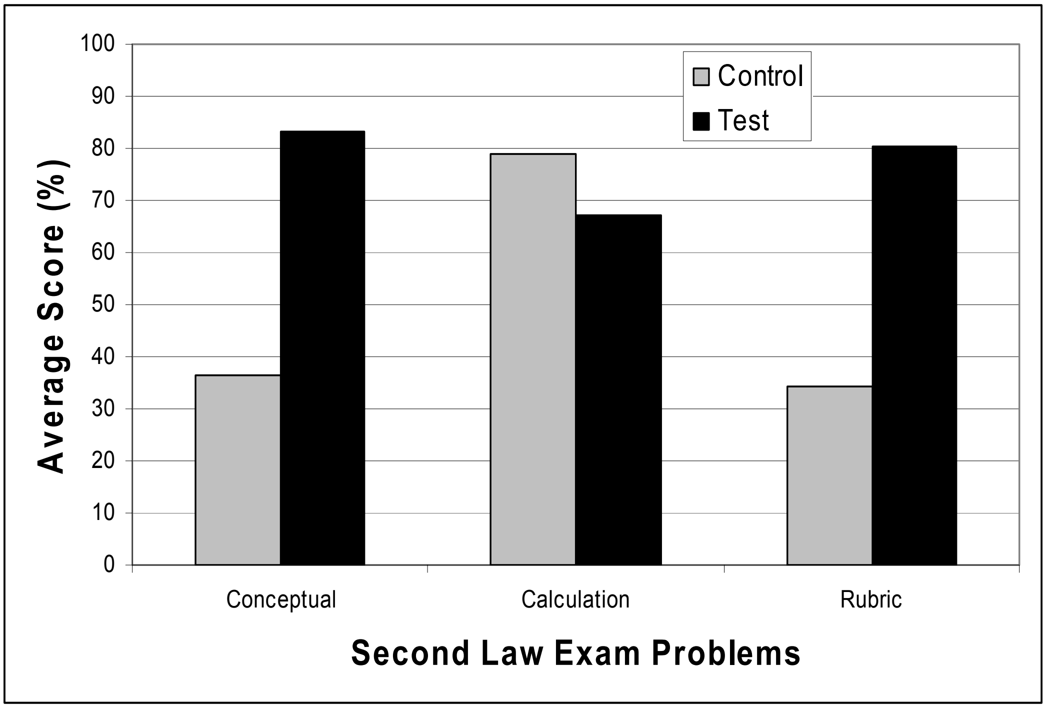

Figure 7.5 Comparison of average scores for control and test groups on common questions. Rubric score reflects average score on conceptual question using scoring rubric presented in Table 7.2. The difference in the Conceptual scores and Rubric scores are statistically significant at the $p<0.01$ level.

The conceptual question responses also show differences in the misconception that only the change in Entropy determines the spontaneity of the reaction. In the control group, 36% of the responses reflect statements stating that the reaction is spontaneous because Entropy increases, no indication is present as to the changes in either Enthalpy or Gibbs energy. In the test group, 13% of the responses fall into this category. In addition to this belief, we also note students' responses about the transfer of thermal energy during the reaction. It was previously noted that many students associate the "reaction getting cold" with thermal energy leaving the system and entering the surrounding. It is encouraging to note that only 5% of the responses from the control group and 0% from the test group reflect this belief for the conceptual question on the exam.

The results of this comparison study do show significant differences between the responses of the test and control groups. On both measures (instructor scored and rubric scored) the test group, which performed the tutorials, responses reflected and expert's response more than those of the control group. The test group responses also showed fewer indications of flawed logic or misconceptions when compared to the control. In addition, the presence of these misconceptions in the test groups' exam responses is nearly identical to what was measured directly after the tutorial use. This finding indicates that in the time between tutorial and exam the information obtained by the students remains robust and useful.

The third exam covers material from the Kinetics portion of the courses. The common exam questions can be found in appendix B10. Figure 7.6 shows the average scores for both the common conceptual question and the calculation. For the control group, the average score on these questions was 68% and 88%, respectively. When we look at the scores for the test group we see that on the calculation problem the test group scores lower with an average of 58%. This 30% difference has a calculated p-value <0.000 and indicates a statistically higher score for the control group. In evaluating the instructors scoring of the conceptual question we see that the test groups' average of 85% is higher with a p-value of 0.02. When the conceptual question is scored with the grading rubric, the test groups' average is 76% and the control groups' average is 56%, this difference in scores has a p-value of 0.03.

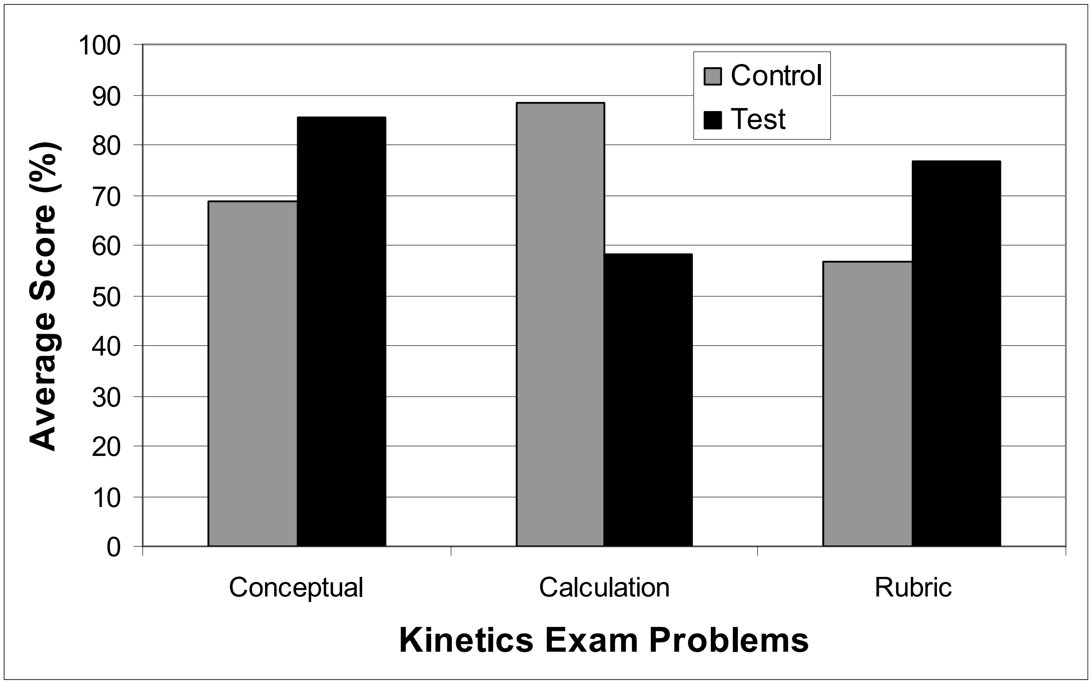

Figure 7.6 Comparison of average scores for control and test groups on common questions. Rubric score reflects average score on conceptual question using scoring rubric presented in Table 7.2. The difference in the Conceptual scores and Rubric scores are statistically significant at the $p<0.05$ level.

The conceptual question responses do not show much difference in the misconception of the potential energy barrier variation with temperature. None of the 32 students in the test group mentioned any variation in the energy barrier with temperature; in fact, more than half of their responses contain indications of the students' knowledge about the potential energy being only a function of the molecules makeup and orientation. In the control group, only one out of the 15 responses addresses the misconception that the energy barrier itself varies as a function of temperature.

The results of this comparison study do show differences between the responses of the test and control groups. On both measures (instructor scored and rubric scored) the test group, which performed the tutorials, responses reflected more expert-like responses than those of the control group. The test groups written responses were more complete and went into more explanation than the control group's responses. In addition, the test group's responses contained more cause and effect connections which were lacking for the control students. When comparing the performance of the two groups on the calculation problem, the control group vastly outperformed the test group. In reviewing the specific material addressed by each instructor, it became clear that the control group received more instruction on reaction mechanisms and the steady-state approximation (the topic of the calculation problem). The control group also covered the Kinetic Molecular Theory of Gases in greater detail than the test group. This finding emphasizes the effectiveness of the computer simulation and tutorial in addressing this material. Despite the test groups' limited exposure to the material, their average score on the conceptual problem was ~10% higher than the control group. While this difference only has a p-value of 0.02 it does reflect the test groups higher conceptual understanding of the temperature dependence of reaction rates.

7.5 Conclusions and Future Directions

The results of this study indicate that there are several fundamental concepts within Thermodynamics and Kinetics which students commonly struggle to understand. Even after instruction in a Physical Chemistry lecture course (as well as numerous problem sets and initial instruction in a General Chemistry course) many students do not understand the building blocks of Thermodynamics. Some of these students additionally harbor misconceptions which can block their further conceptual gains.

We have developed interactive learning tutorials which are designed to target these difficult areas within Thermodynamics and Reaction Kinetics. Our tutorials are developed around a physical model or computer simulation. The physical models allow students to experience some of the thermodynamics phenomena previously only presented as pictures or word problems. The computer simulation used in the reaction kinetics tutorial provides students with an active visual medium for understanding how temperature affects reaction rate. These tools provide the students with both a "real-world" connection to and strong physical picture of the concepts themselves. The structure of the tutorial itself is designed to step students through the important building blocks which underlay the concept at hand. This guided inquiry allows students to connect with all the individual pieces needed in order to fully address the concepts covered.

During the initial testing phase (section 7.3), it was shown that the tutorials were successful in addressing student misconceptions as well as producing gains in conceptual understanding. After the First Law tutorial (Table 7.6) we saw large increases in students' understanding of thermal energy transfer and measured average gains of 40% (2 points on rubric scale) in students' responses about heat, work, and internal energy. The Second Law tutorial produced gains of 30% (1.5 points on rubric scale) for student responses about Entropy change and 20% (1 point on rubric scale) for the temperature dependence of Gibbs energy (see Table 7.7). After the Reaction Kinetics tutorial we measure large decreases in the number of students who report that the potential energy profile for a given reaction is temperature dependent (see Table 7.8). We also see a gain of 40% in the average response about the temperature dependence of a reaction rate. These findings indicate that the tutorials themselves can aid students in understanding some of the fundamental concepts addressed in a standard physical chemistry course.

When the developed tutorials were placed in a classroom setting we measure significant learning gains from the tutorial use when compared to a control course not using the tutorial materials. The students in both groups performed equally well on identical calculation problems given as part of their in class exams. However, the test group scores on the conceptual problems were significantly higher than those of the control group. While we did not control for differences such as teaching style, text book, or homework problems within the two courses, a familiarity with both instructors teaching style and course material indicates that there should be no significant differences between the courses.

In addition to this study, an important future investigation would be a comparison between the gains achieved using these “model based” tutorials and other standard “pencil and paper” tutorials. The models presented here allow students to make direct observations and predictions connected to the concepts being addressed, where the pencil and paper format does not. It is unclear whether this type of study will show a difference in gains measured immediately after the tutorial use but it may show differences in long term retention. The models give the students a “real-world” example of the material being addressed; this connection may improve retention by allowing students to relate difficult concepts to common examples.

These three tutorials are a small fraction of the possible interactive learning tutorials which can be developed to address difficulties with chemistry topics. The wealth of physical models and computer simulations available today can provide material for both General Chemistry and Physical Chemistry tutorials. The tutorials covered in this work were only used in small class settings ($N < 40$) where small group work was easily employed. These ideas can be extended to large courses by extending the tutorial sessions into the course or lab recitation sessions. This small setting will provide an ideal size to perform small group tutorials without impinging on the lecture class itself. This “tutorial session” format is being used in many different programs across the country and is currently part of the redevelopment of the Physics curriculum at CU-Boulder.

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Appendix A

CLASS-Chem Supplementary Tables

A.1 CLASS-Chem v2 Statements

All 50 statements which appear in the second version of the CLASS-Chem instrument. The letter before each statement number indicates ‘expert’ response,
where **D** = disagree, **A** = agree, and **NS** = not scored.

D	1. A significant problem in learning chemistry is being able to memorize all the information I need to know.
A	2. To understand a chemical reaction, I think about the interactions between atoms and molecules.
A	3. When I am solving a chemistry problem, I try to decide what would be a reasonable value for the answer.
A	4. I think about the chemistry I experience in everyday life.
NS	5. It is useful for me to do lots and lots of problems when learning chemistry.
D	6. After I study a topic in chemistry and feel that I understand it, I have difficulty solving problems on the same topic.
D	7. Knowledge in chemistry consists of many disconnected topics.
NS	8. As chemists learn more, most chemistry ideas we use today are likely to be proven wrong.
D	9. When I solve a chemistry problem, I locate an equation that uses the variables given in the problem and plug in the values.
NS	10. I find that reading the text in detail is a good way for me to learn chemistry.
A	11. I think about how the atoms are arranged in a molecule to help my understanding of its behavior in chemical reactions.
D	12. If I have not memorized the chemical behavior needed to answer a question on an exam, there's nothing much I can do (legally!) to figure out the behavior.
A	13. I am not satisfied until I understand why something works the way it does.
D	14. I cannot learn chemistry if the teacher does not explain things well in class.
D	15. I do not expect equations to help my understanding of the ideas in chemistry; they are just for doing calculations.
A	16. I study chemistry to learn knowledge that will be useful in my life outside of school.
A	17. I can usually make sense of how two chemicals react with one another.
A	18. If I get stuck on a chemistry problem on my first try, I usually try to figure out a different way that works.
A	19. Nearly everyone is capable of understanding chemistry if they work at it.
D	20. Understanding chemistry basically means being able to recall something you've read or been shown.
D	21. Why chemicals react the way they do does not usually make sense to me; I just memorize what happens.
A	22. To understand chemistry I discuss it with friends and other students.
D	23. I do not spend more than five minutes stuck on a chemistry problem before giving up or seeking help from someone else.
D	24. If I don't remember a particular equation needed to solve a problem on an exam, there's nothing much I can do (legally!) to come up with it.
D	25. If I want to apply a method used for solving one chemistry problem to another problem, the problems must involve very similar situations.
D	26. In doing a chemistry problem, if my calculation gives a result very different from what I'd expect, I'd trust the calculation rather than going back through the problem.

A	27. In chemistry, it is important for me to make sense out of mathematical formulas before I can use them correctly.
A	28. I enjoy solving chemistry problems.
A	29. When I see a chemical formula, I try to picture how the atoms are arranged and connected.
A	30. In chemistry, mathematical formulas express meaningful relationships among measurable quantities.
NS	31. We use this statement to discard the survey of people who are not reading the questions. Please select agree (not strongly agree) for this question.
D	32. It is important for the government to approve new scientific ideas before they can be widely accepted.
A	33. The arrangement of the atoms in a molecule determines its behavior in chemical reactions.
A	34. Learning chemistry changes my ideas about how the world works.
D	35. To learn chemistry, I only need to memorize how to solve sample problems.
A	36. Reasoning skills used to understand chemistry can be helpful to me in my everyday life.
D	37. In learning chemistry, I usually memorize reactions rather than make sense of the underlying physical concepts.
D	38. Spending a lot of time understanding where mathematical formulas come from is a waste of time.
NS	39. I find carefully analyzing only a few problems in detail is a good way for me to learn chemistry.
A	40. I can usually figure out a way to solve chemistry problems.
D	41. The subject of chemistry has little relation to what I experience in the real world.
A	42. There are times I solve a chemistry problem more than one way to help my understanding.
A	43. To understand chemistry, I sometimes think about my personal experiences and relate them to the topic being analyzed.
A	44. Thinking about a molecule's three-dimensional structure is important for learning chemistry.
A	45. It is possible to explain chemistry ideas without mathematical formulas.
A	46. When I solve a chemistry problem, I explicitly think about which chemistry ideas apply to the problem.
D	47. If I get stuck on a chemistry problem, there is no chance I'll figure it out on my own.
D	48. Spending a lot of time understanding why chemicals behave and react the way they do is a waste of time.
A	49. When studying chemistry, I relate the important information to what I already know rather than just memorizing it the way it is presented.
D	50. When I'm solving chemistry problems, I often don't really understand what I am doing.

A.2 Robustness data for 'Personal Interest' category

Personal Interest							
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**	
	0.334	0.665	-1.775	0.917	6	7.736	
Correlation Matrix							
		S4	**S13**	**S16**	**S28**	**S34**	**S36**
	S4		0.212	0.484	0.277	0.516	0.381
	S13	0.212		0.281	0.205	0.316	0.245
	S16	0.484	0.281		0.281	0.372	0.422
	S28	0.277	0.205	0.281		0.287	0.282
	S34	0.516	0.316	0.372	0.287		0.447
	S36	0.381	0.245	0.422	0.282	0.447	
Factor Loadings							
	S34	0.754					
	S4	0.743					
	S16	0.724					
	S36	0.706					
	S28	0.545					
	S13	0.517					
Total Variance							
	slope 1-2	**slope 2-n**					
	-1.876	-0.100					

A.3 Robustness data for ‘Real World Connections’ category

Real World Connections							
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**	
	0.389	0.736	-1.373	0.999	4	9.680	
Correlation Matrix							
		S34	**S36**	**S41**	**S43**		
	S34		0.447	0.427	0.349		
	S36	0.447		0.352	0.422		
	S41	0.427	0.352		0.335		
	S43	0.349	0.422	0.335			
Factor Loadings							
	S34	0.763					
	S36	0.762					
	S41	0.711					
	S43	0.707					
Total Variance							
	slope 1-2	**slope 2-n**					
	-1.466	-0.093					

A.4 Robustness data for ‘Problem Solving: General’ category

Problem Solving: General											
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**					
	0.285	0.594	-2.565	0.977	10	7.175					
Correlation Matrix											
		S15	**S18**	**S19**	**S21**	**S28**	**S30**	**S40**	**S47**	**S49**	**S50**
	S15		0.120	0.072	0.260	0.127	0.280	0.197	0.208	0.283	0.297
	S18	0.120		0.193	0.128	0.082	0.156	0.305	0.281	0.225	0.188
	S19	0.072	0.193		0.205	0.318	0.183	0.284	0.252	0.336	0.246
	S21	0.260	0.128	0.205		0.289	0.240	0.346	0.373	0.434	0.461
	S28	0.127	0.082	0.318	0.289		0.248	0.316	0.364	0.298	0.474
	S30	0.280	0.156	0.183	0.240	0.248		0.225	0.210	0.294	0.244
	S40	0.197	0.305	0.284	0.346	0.316	0.225		0.482	0.403	0.465
	S47	0.208	0.281	0.252	0.373	0.364	0.210	0.482		0.427	0.532
	S49	0.283	0.225	0.336	0.434	0.298	0.294	0.403	0.427		0.482
	S50	0.297	0.188	0.246	0.461	0.474	0.244	0.465	0.532	0.482	
Factor Loadings											
	S50	0.770									
	S47	0.719									
	S49	0.718									
	S40	0.691									
	S21	0.641									
	S28	0.597									
	S19	0.492									
	S30	0.477									
	S18	0.399									
	S15	0.438									
Total Variance											
	slope 1-2	**slope 2-n**									
	-2.647	-0.082									

A.5 Robustness data for ‘Problem Solving: Confidence’ category

Problem Solving: Confidence							
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**	
	0.300	0.687	-0.959	0.885	4	6.599	
Correlation Matrix							
		S18	**S19**	**S40**	**S47**		
	S18		0.193	0.305	0.281		
	S19	0.193		0.284	0.252		
	S40	0.305	0.284		0.482		
	S47	0.281	0.252	0.482			
Factor Loadings							
	S40	0.785					
	S47	0.762					
	S18	0.617					
	S19	0.583					
Total Variance							
	slope 1-2	**slope 2-n**					
	-1.107	-0.148					

A.6 Robustness data for ‘Problem Solving: Sophistication’ category

Problem Solving: Sophistication								
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**		
	0.348	0.662	-2.123	0.983	7	8.479		
Correlation Matrix								
		S6	**S24**	**S25**	**S28**	**S40**	**S47**	**S50**
	S6		0.298	0.259	0.275	0.462	0.364	0.377
	S24	0.298		0.315	0.275	0.423	0.412	0.344
	S25	0.259	0.315		0.164	0.190	0.258	0.254
	S28	0.275	0.275	0.164		0.316	0.364	0.474
	S40	0.462	0.423	0.190	0.316		0.482	0.465
	S47	0.364	0.412	0.258	0.364	0.482		0.532
	S50	0.377	0.344	0.254	0.474	0.465	0.532	
Factor Loadings								
	S50	0.761						
	S47	0.754						
	S40	0.738						
	S24	0.653						
	S6	0.650						
	S28	0.611						
	S25	0.470						
Total Variance								
	slope 1-2	**slope 2-n**						
	-2.222	-0.099						

A.7 Robustness data for ‘Sense Making/Effort’ category

Sense Making/Effort										
	average CC	average fl	delta E	R^2	N	ROBUSTNESS				
	0.235	0.564	-1.941	0.973	9	6.167				
Correlation Matrix										
		S13	S21	S26	S27	S38	S42	S46	S48	S49
	S13		0.335	0.267	0.313	0.152	0.133	0.207	0.318	0.260
	S21	0.335		0.352	0.223	0.269	0.163	0.232	0.327	0.434
	S26	0.267	0.352		0.152	0.194	0.130	0.187	0.349	0.309
	S27	0.313	0.223	0.152		0.176	0.171	0.161	0.274	0.200
	S38	0.152	0.269	0.194	0.176		0.123	0.163	0.268	0.182
	S42	0.133	0.163	0.130	0.171	0.123		0.152	0.167	0.237
	S46	0.207	0.232	0.187	0.161	0.163	0.152		0.309	0.275
	S48	0.318	0.327	0.349	0.274	0.268	0.167	0.309		0.310
	S49	0.260	0.434	0.309	0.200	0.182	0.237	0.275	0.310	
Factor Loadings										
	S21	0.686								
	S48	0.674								
	S49	0.651								
	S13	0.596								
	S26	0.592								
	S46	0.514								
	S27	0.503								
	S38	0.468								
	S42	0.389								
Total Variance										
	slope 1-2	slope 2-n								
	-2.004	-0.063								

A.8 Robustness data for 'Conceptual Connections' category

Conceptual Connections								
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**		
	0.260	0.603	-1.455	0.926	7	6.007		
Correlation Matrix								
		S6	**S7**	**S15**	**S24**	**S37**	**S38**	**S50**
	S6		0.222	0.221	0.298	0.225	0.153	0.377
	S7	0.222		0.161	0.228	0.294	0.173	0.353
	S15	0.221	0.161		0.301	0.200	0.334	0.297
	S24	0.298	0.228	0.301		0.295	0.238	0.344
	S37	0.225	0.294	0.200	0.295		0.144	0.435
	S38	0.153	0.173	0.334	0.238	0.144		0.167
	S50	0.377	0.353	0.297	0.344	0.435	0.167	
Factor Loadings								
	S50	0.737						
	S24	0.650						
	S37	0.627						
	S6	0.591						
	S15	0.579						
	S7	0.566						
	S38	0.473						
Total Variance								
	slope 1-2	**slope 2-n**						
	-1.549	-0.094						

A.9 Robustness data for ‘Conceptual Learning’ category

Conceptual Learning								
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**		
	0.283	0.618	-1.758	0.918	7	6.714		
Correlation Matrix								
		S1	**S6**	**S7**	**S12**	**S24**	**S25**	**S47**
	S1		0.234	0.181	0.298	0.219	0.185	0.182
	S6	0.234		0.222	0.253	0.298	0.259	0.364
	S7	0.181	0.222		0.251	0.228	0.189	0.368
	S12	0.298	0.253	0.251		0.536	0.290	0.390
	S24	0.219	0.298	0.228	0.536		0.315	0.412
	S25	0.185	0.259	0.189	0.290	0.315		0.258
	S47	0.182	0.364	0.368	0.390	0.412	0.258	
Factor Loadings								
	S24	0.726						
	S12	0.723						
	S47	0.707						
	S6	0.595						
	S25	0.556						
	S7	0.537						
	S1	0.485						
Total Variance								
	slope 1-2	**slope 2-n**						
	-1.849	-0.092						

A.10 Robustness data for 'Atomic-Molecular Perspective of Chemistry' category

Atomic-Molecular Perspective of Chemistry							
	average CC	**average fl**	**delta E**	**R^2**	**N**	**ROBUSTNESS**	
	0.299	0.641	-1.461	0.967	6	7.128	
Correlation Matrix							
		S2	**S11**	**S17**	**S29**	**S33**	**S44**
	S2		0.448	0.376	0.415	0.265	0.346
	S11	0.448		0.341	0.530	0.163	0.293
	S17	0.376	0.341		0.352	0.146	0.130
	S29	0.415	0.530	0.352		0.125	0.339
	S33	0.265	0.163	0.146	0.125		0.217
	S44	0.346	0.293	0.130	0.339	0.217	
Factor Loadings							
	S2	0.757					
	S11	0.754					
	S29	0.750					
	S17	0.602					
	S44	0.578					
	S33	0.403					
Total Variance							
	slope 1-2	**slope 2-n**					
	-1.593	-0.132					

Appendix B

Physical Chemistry Tutorial Sheets and Concept Test

B.1 First Law Pre/Post Quiz

B.2 First Law Tutorial Worksheet (Air Can)

B.3 Second Law Pre/Post Quiz

B.4 Second Law Tutorial Worksheet (Rubber Band)

B.5 Kinetics Pre/Post Quiz

B.6 Kinetics Tutorial Worksheet (PhET Sim)

B.7 Chem 4511 Concept Test

B.8 First Law Exam Questions

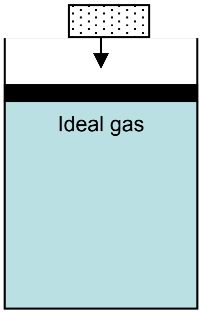
B.9 Second Law Exam Questions

B.10 Reaction Kinetics Exam Questions

B.1 First Law Pre/Post Quiz

Name: First Law Pre/Post Questions

1. The figure below shows an ideal gas contained in a non-insulated cylinder. A piston is tightly fit so that no gas escapes; friction is negligible between the piston and the cylinder walls.

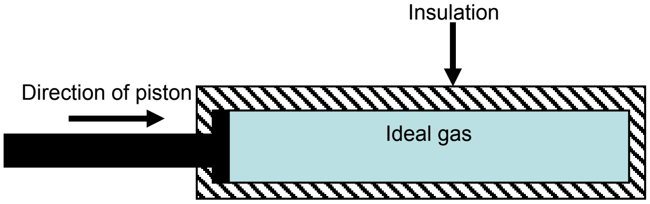


A block is dropped onto the piston compressing the gas.

a. **Is work done ON the gas or BY the gas in this example?** Explain your reasoning.

b. **After the block is dropped, is there a transfer of thermal energy as heat?** If so, in what direction is the transfer? If not, why not?

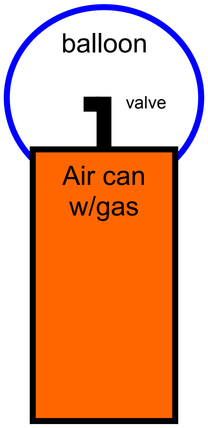
2. The figure below shows an ideal gas contained in a cylinder. A piston is tightly fit so that no gas escapes; friction is negligible between the piston and the cylinder walls. The cylinder walls are insulated.



The piston is pushed into the cylinder. **Explain how this impacts the internal energy and temperature of the gas.** Please be as thorough as possible in your answer.

B.2 First Law Tutorial Worksheet (Air Can)

Name: First Law Worksheet



Can filled with high pressure gas and sealed with a balloon.

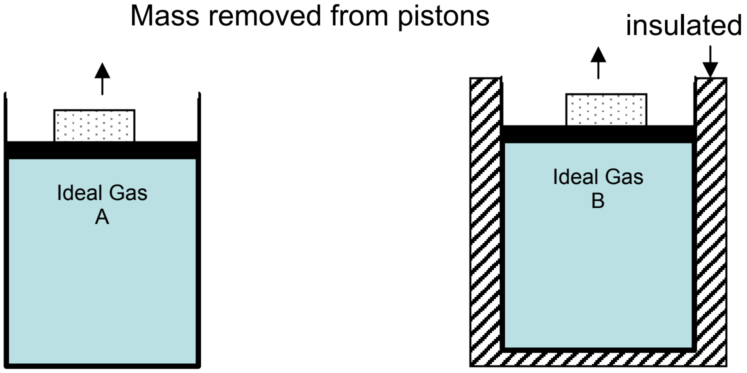
Use the figure above to make a prediction.

What happens to the temperature of the gas inside the can as you allow the gas to expand into the balloon?

Why does this temperature change occur? Explain the reasoning for your answer in a few sentences.
Note: Consider the system to be the balloon, the can, and the gas, everything outside of the can and balloon is considered the surroundings. There is NO loss of gas molecules during this expansion.

Now test your prediction with one of the air cans at the front of the room.

We will now investigate two thermodynamic systems.



Ideal gas A is isothermally expanded. Ideal gas B is adiabatically expanded.

In the figure above, two cylinders are filled with the same ideal gas. A piston is fit so that no gas escapes; friction is negligible between the piston and the cylinder walls. The block is removed from each piston, the piston moves upward.

(1) **In each case, does the gas do work or is work done on the gas?** Explain your reasoning in a few sentences.

(2) **Is there a larger transfer of thermal energy as heat between Gas A and the surrounding or between Gas B and the surroundings?** Explain your reasoning in a few sentences. **Draw an arrow on each figure indicating the direction of thermal energy flow.**

(3) **For the expansion of Gas A, how do the work and heat involved in this process affect the internal energy of the gas?** Explain your reasoning in a few sentences.

(4) **For the expansion of Gas B, how do the work and heat involved in this process affect the internal energy of the gas?** Explain your reasoning in a few sentences.

B.3 Second Law Pre/Post Quiz

Name: Second Law Pre/Post Activity Questions

The instant cold packs that you purchase for First Aid kits contain two solid chemicals initially separated from each other; the reaction upon mixing is shown below.

$$Ba(OH)_2{\cdot}8H_2O\ (s) + 2\ NH_4Cl\ (s) \rightarrow BaCl_2\ (aq) + 2\ NH_3\ (aq) + 10\ H_2O\ (l)$$

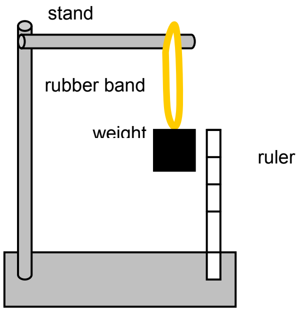
1. The chemical reaction shown above takes place at room temperature when the chemicals are mixed together. As products form, you touch the pack and notice that the pack feels cold. Is thermal energy (heat) going in or out of the reaction mixture as the reaction progresses? Explain your answer in a few words.

2. Use the Gibbs equation ($\Delta G=\Delta H-T\Delta S$) along with the changes in Gibbs energy (ΔG) and enthalpy (ΔH) to determine the change in entropy ($\Delta S = S_{(f)}-S_{(i)}$) as the reaction proceeds? Explain the reasoning you used to get your answer.

3. Is this reaction spontaneous at all temperatures? Please explain why or why not.

B.4 Second Law Tutorial Worksheet (Rubber Band)

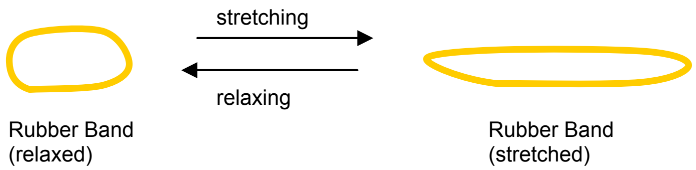
Name: Second Law Prediction



The figure above shows a rubber band stretched by a heavy weight; the ruler indicates the height of the weight.

Predict what will happen to the length of the rubber band if the temperature of the rubber band is increased. In your answer express the reasoning behind your prediction.

Once you and your group have come to a conclusion, test your prediction using the apparatus set-up at the front of the room.



1. The figure above shows the stretching and relaxing of a rubber band.

a, Does the stretched rubber band spontaneously relax? Explain your answer in a few words.

b, Based on your answer for spontaneity, does the Gibbs energy (G) increase or decrease as the band goes from the stretched to the relaxed position?

We can determine the enthalpy change (ΔH) for the rubber band by the following procedure:
-Place the relaxed rubber band in contact with your lip and note temperature
-Quickly stretch the band while still in contact with your lip
-Quickly allow the band to relax while still in contact with your lip
-REPEAT several times and note the temperature change for stretching/relaxing

2. Upon relaxing does thermal energy enter or leave the rubber band?

3. What is the sign of thermal energy transfer (q) for the rubber band? Does enthalpy increase ($\Delta H > 0$) or decrease ($\Delta H < 0$) upon relaxing? Please explain your answer in a few sentences.

Use the table below to record the sign (+ or −) of the change in Gibbs energy and Enthalpy from the previous questions.

	ΔG	ΔH
stretching		
relaxing		

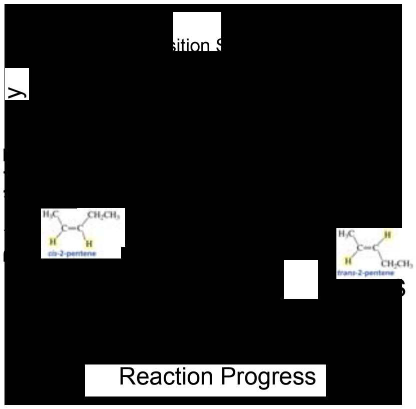
4. Use the data from the table above along with the equation for Gibbs Energy ($\Delta G = \Delta H - T\Delta S$), to reason out what the change in entropy (ΔS) is for stretching and relaxing. Explain your reasoning below.

5. Consider the values of ΔH and ΔS you observed at room temperature to be independent of T. Could you create conditions under which the rubber band will spontaneously get longer? Please explain your answer in a few sentences.

B.5 Kinetics Pre/Post Quiz

Name: Pre/Post Questions

The figure below shows the minimum potential energy profile for the conversion of cis-2-pentene to trans-2-pentene.



1. What conditions are required for a reactant molecule (cis-2-pentene) to become a product molecule (trans-2-pentene)?

2. **Does the height of the energy barrier, <u>the value shown on the figure as E_a</u>, change as the temperature increases?** In other words, does the difference in energy between the potential energy of CIS and the transition state change with temperature? Please explain your answer in a few sentences.

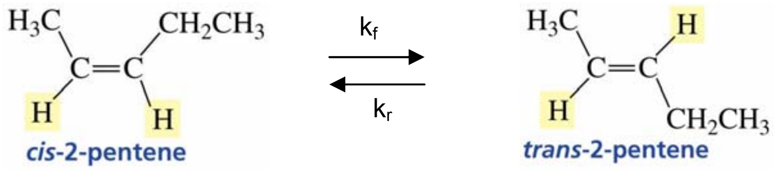
3. Experimentally, it has been determined that the rate of conversion from cis to trans increases as the temperature increases. **Why does the rate of the reaction increase with increasing temperature?** Please explain your answer in a few sentences and refer to the energy diagram if possible.

B.6 Kinetics Tutorial Worksheet (PhET Sim)

Name: Worksheet A

Model vs Physical Reality:
This simulation is a model of a chemical reaction. It indicates that reactants and products have different potential energies by physically separating them. However, in many experiments the reactant and product molecules are not physically separated but instead collide and interact with one another. The simulation represents the reactant and product species as simple spheres. In reality most molecules are not spheres.

This simulation shows a reversible reaction of one molecule (A) turning into another molecule (B) along a reaction pathway. This is analogous to what happens in a *cis*-*trans* isomerization:



Molecule A **Molecule B**

1. Using the simulation, describe your observations of how an A molecule becomes a B molecule. Be sure to note molecular motions and collisions.

To observe molecules with the simulation:
Type "20" in box next to "Molecules in Chamber" for molecule A
Hit "Enter" key on keyboard
You can click [Pause] at any time to stop all motion

Note your observations below.

Now we will observe how temperature changes impact molecular motion.

Use mouse to slide bar on "HEAT CONTROL" to "ADD"
Note your observations below.

2. What happens to molecular motion as you raise the temperature?

3. Did increasing the temperature affect the height of the energy barrier? In other words, did the shape of the potential energy curve change? Explain in a few sentences.

4. Here you'll determine how long it takes for the first B molecule to form from A.

Procedure:
Click [RESET], to erase parameters
Click [PAUSE], to stop motion while you make changes
Click "energy histograms", this will open a window with two plots
Change "temperature of new particles" to 350 K
Click [START] on stop watch in lower left corner
Type [50] in box next to A, hit ENTER key on keyboard, this will add A molecules
Click [PLAY] to start motion

Click [PAUSE] as soon as the first B molecule is formed

Time to form the first B molecule?______________________

5. Sketch the plot of Number of Particles versus Kinetic Energy. What does this plot indicate about the kinetic energy of the molecules? Note on your sketch which molecules you think have more energy than the barrier.

6. How long would it take to form the first B molecule if the temperature were 750 K? Please explain your reasoning in a sentence or two.

7. Before checking with the simulation, sketch what you think the plot of Number of Molecules verses Kinetic Energy will look like for the reaction at 750 K.

Now let's record how long it takes to form the first B molecule at 750 K.

Click [RESET]
Change "temperature of new particles" to 750 K
Click [START] on stop watch
Type [50] in box next to A, hit ENTER key on keyboard
Click [PLAY]

Click [PAUSE] as soon as the first B molecule is formed.

8. At 750 K how long does it take to form the first B molecule? How does this compare to the time needed at 350 K?

9. How does the collision rate (Z) of molecule A change as temperature is increased from 350 K to 750 K? Explain your answer in a few sentences.

The rate of formation of molecule B, d[B]/dt, for the forward reaction (A→B) is written as: $d[B]/dt = k_f[A]$.

10. How does the rate coefficient (k_f) at 350 K compare to the rate coefficient (k_f) at 750 K? Based on molecular motions, why are the two values for k different?

11. Sketch the plot of Number of Particles versus Kinetic Energy at 750 K. Compare this plot to your predicted plot in question 7.

12. How do the Number of Molecules verses Kinetic Energy plots at 350 K and 750 K differ? What does this indicate about the TOTAL energy of the molecules at the different temperatures?

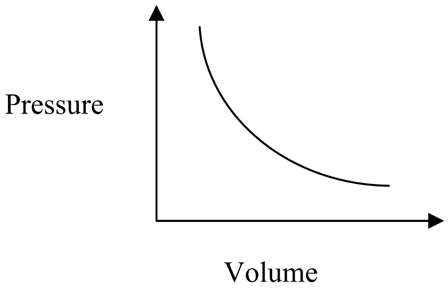
B.7 Chem 4511 Concept Test

1. In lab, a student is considering two options for increasing the internal energy of a gas. Assume the gas behaves ideally. He or she can compress the gas into a smaller volume, or let it expand against atmospheric pressure so that it takes up a larger volume. Of these two options:

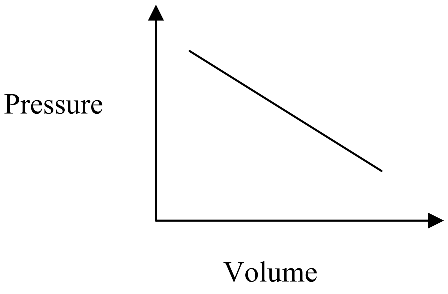
a. Either compressing the gas or letting the gas expand will increase the internal energy of the gas
b. Neither compressing the gas nor letting the gas expand will increase the internal energy of the gas.
c. Only compressing the gas will increase the internal energy of the gas
d. Only letting the gas expand will increase the internal energy of the gas

2. Which graph best represents the relationship between Pressure and Volume for an ideal gas? Volume increases to the right along the x-axis. Pressure increases as you move up along the y-axis. Assume the temperature and number of moles of gas remain constant.

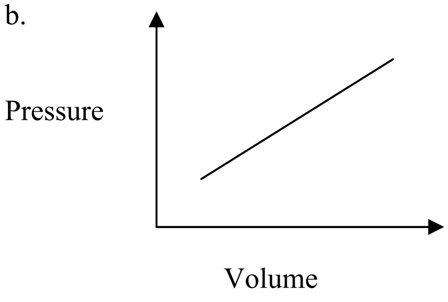
a.



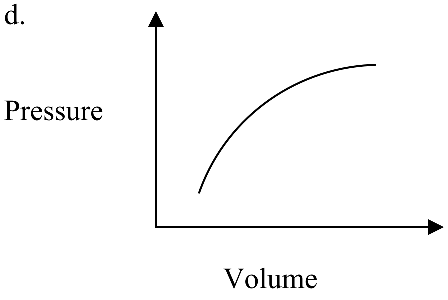
c.



b.



d.



3. A chemical reaction has a negative value for $\Delta_r S$ and negative value for $\Delta_r H$. The entropy of the products is less than the entropy of the reactants and the enthalpy of the products is less than the enthalpy of the reactants. Assume that pressure is constant, and that $\Delta_r S$ and $\Delta_r H$ do not change with temperature. This reaction:

a. will be spontaneous at all temperatures
b. cannot be spontaneous at any temperature
c. can be spontaneous at high temperatures but not low temperatures
d. can be spontaneous at low temperatures but not high temperatures
e. None of the above

4. A student is given two samples of He gas. There is one mole of He gas in each sample. The pressures and temperatures of the two samples are not the same. The student reversibly heats the first sample until it has a pressure of 2 atm and a temperature of 300 K. The student irreversibly cools and compresses the second sample until it has a pressure of 2 atm and a temperature of 300 K. In the end, which sample has greater internal energy?

a. The sample that was heated
b. The sample that was cooled.
c. It cannot be determined here, because we don’t know the initial conditions.
d. They have the same energy.

5. A cylinder of He gas is used to fill balloons. The valve on the He gas cylinder is opened, allowing some He gas to escape into a balloon attached to the valve. Assume the He behaves like an ideal gas. Immediately afterwards, which of the following is true for the He that remains in the cylinder?

a. The temperature of He in the cylinder does not change.
b. The temperature of He in the cylinder is higher than before the valve was opened.
c. The temperature of He in the cylinder is lower than before the valve was opened.
d. The direction of temperature change cannot be determined.

6. Is the following chemical reaction likely to be an elementary reaction?

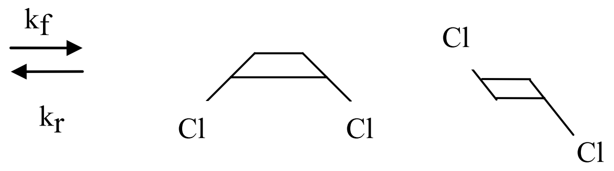
$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$

a. Yes
b. No
c. It is not possible to determine if a reaction is elementary by looking at the chemical equation.

7-10. In studying the elementary chemical reaction, $O_3 + CO \rightarrow O_2 + CO_2$, the concentration of CO is in excess of the concentration of O_3. The initial concentration of CO is 100 times the initial concentration of O_3, $[CO]_0 = 100\ [O_3]_0$. Assume there are no competing chemical reactions, but there is a non-reactive "bath" gas of He or N_2. Assume the system does not go to equilibrium. Determine if the following are true or false. Choose True(a) or False(b).

7. True(a) or False(b) Doubling the concentration of O_3 will double the initial rate of CO_2 production.
8. True(a) or False (b) Increasing the concentration of O_3 will increase the amount of CO_2 produced.
9. True(a) or False(b) Increasing the concentration of CO will increase the amount of CO_2 produced.
10. True(a) or False(b) Doubling the concentration of CO will double the initial rate of CO_2 production.

11-16. ***cis***-1,2-dichloroethylene can convert to ***trans***-1,2-dichloroethylene. Here, we will abbreviate these ***cis*** and ***trans***. The ***cis*** reacts to form ***trans*** with a rate coefficient k_f, and ***trans*** reacts to form ***cis*** with the rate coefficient k_r. Here, $\mathbf{k_f \neq k_r}$



cis ***trans***

Initially,only ***cis*** is present. Determine if the following are true or false. Choose True(a) or False(b).

11. T(a) or F(b) At equilibrium, [***cis***] = [***trans***]

12. T(a) or F(b) At all times, $\frac{[\textbf{\textit{trans}}]}{[\textbf{\textit{cis}}]}$ = A constant value (the equilibrium constant)

13. T(a) or F(b) At all times, d[***cis***] / dt = - k_f [***cis***]

14. T(a) or F(b) At early times, when the reaction begins, k_f [***cis***] > k_r [***trans***]

15. T(a) or F(b) At equilibrium, k_f [***cis***] = k_r [***trans***]

16. T(a) or F(b) After the system has reached equilibrium, k_f [***cis***] < k_r [***trans***]

17. The elementary chemical reaction, $NO_3 + NO \rightarrow 2\ NO_2$, has a rate coefficient k. Initially only NO and NO_3 are present. Assume there are no competing reactions, and that no other reactions happen at the same time. At any time during this reaction the rate of change of NO_3 can be written as:

a. $\frac{d[NO_3]}{dt} = -k[NO]$

d. $\frac{d[NO_3]}{dt} = -k[NO][NO_3]$

b. $\frac{d[NO_3]}{dt} = -k[NO_3]$

e. $\frac{d[NO_3]}{dt} = -k$

c. $\frac{d[NO_3]}{dt} = k[NO][NO_3]$

18. A student has two identical samples of N_2 gas. He or she heats one under constant volume conditions, until the temperature doubles. The other one is heated under constant pressure conditions until the temperature doubles. After heating, which is true:

a. The same amount of thermal energy or heat was added to both systems.
b. More thermal energy or heat was added to the system at constant volume.
c. More thermal energy or heat was added to the system at constant pressure.
d. Not enough information was given to determine which system required more thermal energy or heat.

19. An NO molecule collides with an O_3 molecule. The NO molecule removes an O atom from O_3 to create NO_2 and O_2. Assume there are no competing reactions.

a. The rate for this reaction can be written as $k[NO][O_3]$, where k represents the rate coefficient for the reaction.
b. The rate for this reaction can be written as $k[NO][O_3]^2$, where k represents the rate coefficient for the reaction.
c. The reaction is first order overall, and second order with respect to NO.
d. It is not possible to write the rate for this reaction, or determine its order unless given information that the reaction is elementary.

20– 22. The First Law of Thermodynamics may be stated as: Energy can be converted from one form to another, but cannot be created or destroyed. For the following 3 mathematical statements, choose True (a) if the expression is a restatement of the first law. Choose False (b) if the expression does not restate the first law.

20. T(a) or F(b) $w = -\int P\,dV$, work is the integral of the pressure multiplied by the change in volume

21. T(a) or F(b) $q = \int C_v\,dT$, heat is the integral of the Heat capacity multiplied by the change in temperature.

22. T(a) or F(b) $\Delta U = q + w$, A change in internal energy for a system can be the result of changes in heat and work.

23. You are given two cylinders of O_2 gas. The pressure and volume of the two cylinders may be different. In the first cylinder, the collision frequency of the O_2 molecules is 100 collisions per second. In the second cylinder the collision frequency of the O_2 molecules is 500 collisions per second. Which statement is true?

a. The gas molecules colliding at a higher frequency are colliding more often because they are at a higher temperature.
b. The gas molecules colliding at a higher frequency are at a higher temperature because the collisions release energy as heat.
c. The gas molecules colliding at a higher frequency are at a lower temperature because the collisions release energy as heat.
d. Not enough information is given to determine which of the two gas samples is at a higher temperature.

24. A sample of He gas is compressed adiabatically. The sample of He gas is the system. Assume ideal gas behavior for the He. In this case,

a. The system absorbs heat.
b. The surroundings absorb heat.
c. The temperature of the system goes down.
d. Work is done on the surroundings.
e. The surroundings do work.

25. An ideal gas occupies a container at pressure P_1, temperature T_1, and volume V_1. The same amount and type of gas exists in a second container with pressure P_2, volume V_2, and temperature T_2. If the second container is twice the size of the first, ($V_2 = 2 \times V_1$), and the temperature in the second container is half the temperature of the first, ($T_2 = \frac{1}{2} T_1$), which best describes the pressure in the second container?

a. The pressure is the same in both containers $P_1 = P_2$
b. The pressure in the second container is half the pressure in the first, $P_2 = (\frac{1}{2})\ P_1$
c. The pressure in the second container is $\frac{1}{4}$ the pressure in the first, $P_2 = (\frac{1}{4})$
P_1
d. The pressure in the second container is $\frac{1}{8}$ the pressure in the first, $P_2 = (\frac{1}{8})\ P_1$
e. None of the above

26. You add a large amount of table salt (NaCl) to a glass of water and thoroughly stir the solution. Some NaCl precipitates out as a solid on the bottom of the glass. You add more NaCl to the solution. The result of adding more NaCl is:

a. There will be more Na^+ and Cl^- ions in the solution
b. There will be more solid NaCl on the bottom of the glass
c. Both a and b

27-28. Choose True(a) or False(b). Under certain experimental conditions the chemical reaction:

$NO\ (g) + O_3\ (g) \rightarrow NO_2\ (g) + O_2\ (g)$

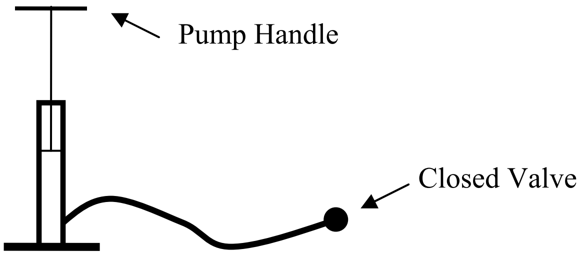
proceeds spontaneously. Under those same experimental conditions, it **must** be true that for this reaction:

27. T(a) or F(b) Gibbs energy goes down, $\Delta_r G^o < 0$

28. T(a) or F(b) Entropy increases, $\Delta_r S^o > 0$

29. In an endothermic chemical reaction, the reactants must absorb energy in order to form products. Can an endothermic reaction occur spontaneously at room temperature?
a. Yes
b. No

30. Imagine you are compressing the air in a bicycle pump by quickly pushing down on the pump handle. Assume there is no friction in the pump. The valve on the pump is closed so that air cannot escape.



In each statement, 'air' refers to air inside the pump that is being compressed. Which statement is true?

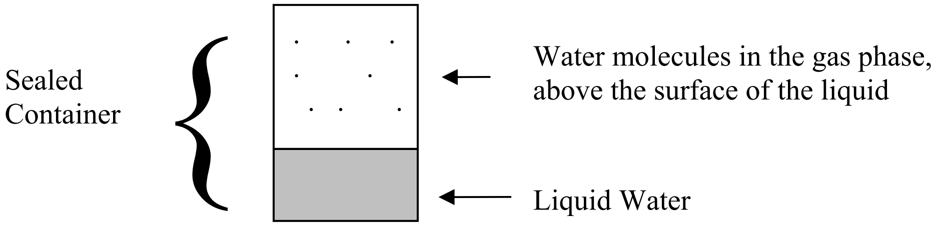
a. The temperature of the air goes up because thermal energy or heat goes into the air during compression.
b. The temperature of the air doesn't change because thermal energy or heat does not go into the air during compression.
c. The temperature of the air goes up because of work done on the air in compression, not because of thermal energy or heat going into the air.
d. The temperature of the air goes up because of work done on the gas in compression, and because thermal energy goes into the air.

31. You are given a cylinder containing a mixture of Oxygen gas and Helium gas. The mixture is in equilibrium. Which atoms or molecules are moving with greater speed?

a. The O_2 molecules
b. The He atoms
c. Neither, they are the same.
d. The one that has a higher partial pressure.
e. The one that has a lower partial pressure.

32. Which statement is true for a chemical reaction at equilibrium?
a. The Gibbs energy is zero.
b. As time passes, there is no change in the Gibbs energy. In other words, the change in Gibbs energy with time is zero.
c. Both the Gibbs energy and the change in Gibbs energy with time are zero.

33. Choose T(a) or F(b). Pure liquid water and air are in a sealed container. Some water has evaporated, so there is water in the gas phase above the liquid. If salt is added to the liquid water, equilibrium will shift so that there are fewer water molecules in the gas phase.

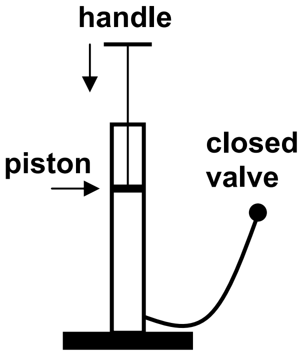


34. Work is done on a system. Based on the conventions we have used in this class,
a. For the system, $dw > 0$, (the change in work for the system is positive)
b. For the system, $dw < 0$, (the change in work for the system is negative)
c. The change in work for the system is zero if the process is done reversibly
d. The change in work for the system is zero if the process is done adiabatically

B.8 First Law Exam Questions

10 point concept question

The figure below shows a bicycle tire pump with the valve closed so that no air can escape. Imagine that you quickly push the handle down, compressing the air inside. You can assume that there is no friction in the pump and that the air behaves like an ideal gas.



During this adiabatic compression, what happens to the temperature of the air inside the pump? **Explain, in a few sentences, the reasoning behind your answer. In your answer be sure to address heat, work, and internal energy.**

10 point calculation question

A 2-liter bulb contains n moles of nitrogen gas at 0.5 atm pressure and temperature T. On addition of 0.01 mole of oxygen, it is necessary to cool the bulb to a temperature of 10°C in order to maintain the same pressure. **Calculate the number of moles n and the temperature T of nitrogen present originally. Assume that the gases behave as perfect gases.**

B.9 Second Law Exam Questions

10 point concept question

The “instant ice packs” you can buy commercially contain two liquid chemicals. When these two chemicals are mixed together, a spontaneous reaction takes place and the ice pack feels cold to your hand.

a. (5 pts.) What is the sign of ΔS (entropy) for the reaction? Please explain your reasoning in a few words.

b. (5 pts.) Is this reaction spontaneous at all temperatures? If so, WHY? If not, WHY NOT? Please explain your reasoning in a few words, be sure to address both enthalpy and entropy in your answer.

15 point calculation question

One mole of an ideal, monatomic gas initially at 1 atm and 273 K expands isothermally and irreversibly to 44.8 litre, under conditions such that $w = 420$ J.
Calculate q, ΔU, ΔH, and ΔS for the process.

B.10 Reaction Kinetics Exam Questions

10 point concept question

Experimentally, it has been determined that the rate of decomposition of nitrogen dioxide, shown below, increases with increasing temperature. **Why does the rate of decomposition increase with increasing temperature?** Explain your answer in terms of the molecular motion of nitrogen dioxide.

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

15 point calculation question

Consider the reaction: $H + O_3 \rightarrow OH + O_2$

Calculate the Arrhenius A factor at 300 K. Assume that the collision diameter $d_H = 100$ pm and $d_{O3} = 300$ pm. Compare this result with the experimental value of 1.7×10^{10} $dm^3\ mol^{-1}\ s^{-1}$ for this reaction.