A pulsed, low-temperature beam of supersonically cooled free radical OH molecules

H.J. Lewandowski [*], Eric R. Hudson, J.R. Bochinski, Jun Ye

JILA, National Institute of Standards and Technology, University of Colorado, Campus Box 440, Boulder, CO 80309-0440, USA
Department of Physics, University of Colorado, Campus Box 440, Boulder, CO 80309-0440, USA

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Abstract

An improved system for creating a pulsed, low-temperature molecular beam of hydroxyl radical (OH) radicals has been developed. We use a pulsed discharge to create OH from H_2O seeded in Xe during a supersonic expansion, where the high-voltage pulse duration is significantly shorter than the width of the gas pulse. The pulsed discharge allows for control of the mean speed of the molecular packet as well as maintains a low temperature supersonic expansion. A hot filament is placed in the source chamber to initiate the discharge for shorter durations and at lower voltages, resulting in a translationally and rotationally colder packet of OH molecules.
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1. Introduction

The hydroxyl radical (OH) is important in many diverse fields of science, including ultracold collisional physics [1,2], physical chemistry [3,4], astrophysics [5,6], atmospheric physics [7], and combustion science. Laboratory studies of OH molecules require a controlled and a well-characterized source of the radicals. However, because of their highly reactive nature, a controllable source is difficult to generate in the laboratory. We present a controllable discharge-based system to create a cold pulsed beam of OH molecules.

There are several different techniques to produce a molecular beam of OH radicals. The four main methods for creating OH molecules are photolysis [8,9], radio-frequency discharge [10], DC discharge [11,12], and chemical reactions [13]. We chose DC discharge because,

of all of the methods, it is the simplest and most cost-effective technique. As presented below, the system we have developed also fulfills the goal of producing a large sample of cold molecules with a high phase-space density. We report several key improvements to the standard DC discharge system, including a pulsed high-voltage discharge to reduce heating of the molecular packet and to allow for control of the mean speed of the molecular packet. Also the introduction of a hot filament into the source chamber allows the discharge to operate more stably and at a lower voltage, thus reducing the heating of the OH molecules during their production. Through controlled application of a high voltage discharge pulse, we are able to create packets of OH molecules at reasonable densities that vary in mean speed from 265 to 470 m/s with full-width half-maximum (FWHM) velocity spread as low as 16%.

In this Letter, we describe the components of our OH source as well as the detailed characterization of the molecular beam. Our particular motivation for creating a cold beam of OH molecules is to use the beam as an input to a Stark-effect based molecular decelerator. A

* Corresponding author. Fax: +1 303 492 5235.
  E-mail address: lewandoh@jilau1.colorado.edu
(H.J. Lewandowski).

Stark decelerator is an apparatus that takes advantage of the Stark energy shift, such as in the $^2\Pi_{3/2}$ ($J = 3/2$) state in OH, to slow the mean longitudinal velocity of a molecular packet to near zero via interactions with inhomogeneous electric fields [14–17].

2. Experimental

A diagram of the experimental apparatus and discharge assembly is shown in Fig. 1. The vacuum system consists of two chambers separated by a mechanical skimmer, which maintains a differential pressure between the chambers. During operation the source (hexapole) chamber is at a pressure of 4×10^{-4} Torr (1×10^{-6} Torr) (1 Torr = 133 Pa). A current loop actuated valve, commercially available from R.M. Jordan Company Inc. [18], operates at 5 Hz to create a gas pulse ~100 μs long. Directly in front of the 0.5 mm diameter valve nozzle is a set of stainless steel disc electrodes, electrically isolated from one another as well as from the valve body by Boron nitride spacers. The relevant dimensions are shown in Fig. 1. The electrode closest to the valve has a 0.5 mm diameter hole to match the valve nozzle. The downstream electrode has an inner diameter of 4 mm to allow the gas to expand as it travels between the electrodes. The valve nozzle is placed ~8 cm away from the downstream wall of the vacuum chamber to ensure carrier gas atoms scattered from the wall do not interfere with the supersonic expansion and beam propagation.

In the second chamber, a 13 cm long electric focusing hexapole is centered along the beam path. The hexapole is used as a tool to determine the transverse velocity spread of the molecular beam. The hexapole is formed by six, stainless steel, cylindrically shaped rods with rounded ends. They are 3.18 mm in diameter and set at every 60° at a center-to-center radius of 4.6 mm. Alternate rods are charged to equal magnitude but opposite polarity high voltage.

The experimental procedure begins with the pulsed valve opening for ~100 μs, thus creating a supersonically cooled pulse of Xenon (Xe) carrier gas seeded with a few percent water. The typical backing pressure of Xe is three atmospheres. Xe is used instead of a lighter noble gas because of the resulting lower mean speed of the molecular beam, which is advantageous for our Stark decelerator application. At a variable time after the valve opens, a high-voltage pulse is applied to the disc electrodes. The duration of the high-voltage pulse can be varied from 1 to 200 μs. A discharge duration greater than 150 μs is considered to be essentially DC because the discharge duration is longer than the gas pulse. The polarity of the voltage applied is such that electrons are accelerated against the molecular beam propagation direction, which results in a more stable discharge than the opposite polarity. During the discharge operation, 6 A of DC current is passed though a tungsten filament, which is located inside the source chamber. The products created by the filament help to initiate a stable discharge at lower electrode voltages and shorter discharge pulse durations, ultimately leading to a colder molecular beam.

After the OH molecules are produced in the discharge, they are allowed to fly to one of two detection regions, which are illustrated by black circles in Fig. 1. The density of OH molecules in the detection region is determined by laser-induced fluorescence (LIF). The OH molecules are excited by a frequency-doubled pulsed dye laser on the $A^2\Sigma_{1/2}$ ($v = 1$) $\leftarrow X^2\Pi_{3/2}$ ($v = 0$) transition at 282 nm. The fluorescence from the $A^2\Sigma_{1/2}$ ($v = 1$) $\rightarrow X^2\Pi_{3/2}$ ($v = 1$) transition at 313 nm (with a lifetime of 750 ns) is then imaged onto a gated photomultiplier tube (PMT). An interference filter is placed in front of the PMT to reduce the transmission of the excitation laser photons by $>10^3$, while still allowing 15% of the fluorescence photons to pass. This spectral discrimination, along with careful spatial filtering and imaging, greatly reduces the background signal from scattered laser light. The signal from the PMT is averaged 300 times and integrated over a 3 μs time window on a digital oscilloscope. The time from the discharge to the detection is varied to obtain a time-of-flight (TOF) profile of the OH molecular packet (see Fig. 2a).
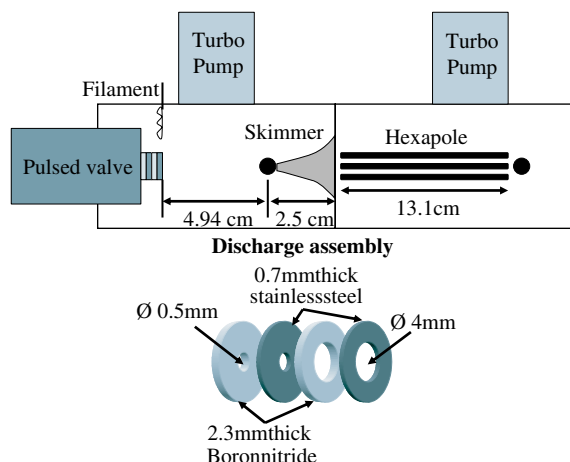

Fig. 1. Diagram of the experimental apparatus and discharge assembly (not to scale). The system consists of chambers individually pumped by 300 1/s turbo pumps. A differential pressure is maintained between the chambers by a mechanical skimmer. A discharge assembly is mounted directly onto a pulsed current loop actuated valve in the source chamber. The discharge assembly consists of two disc electrodes separated by insulating spacers. The second chamber contains an electric hexapole. Molecule detection, by laser induced fluorescence, takes place in two regions marked by black circles.
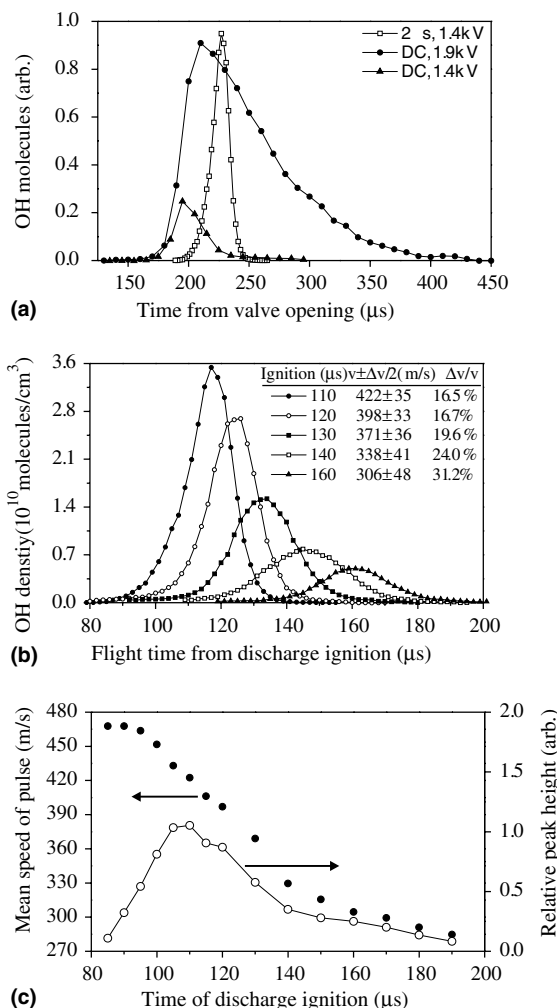
Fig. 2. (a) TOF profiles, acquired in the detection region before the skimmer, for a pulsed discharge and a DC discharge at 1.4 and 1.9 kV. (b) TOF profiles, acquired in the detection region before the skimmer, as a function of the time from the filament-assisted discharge ignition to the LIF detection. The discharge duration is 2 μs for all the data. The discharge ignition time, mean longitudinal packet speed, and velocity width are listed in the legend for each trace. The velocity width, Δ*v*, is the FWHM of the velocity distribution, which is determine from the TOF profiles taken at both detection locations. (c) Mean longitudinal speed (solid circles) and relative peak height (open circles) of the TOF profiles as a function of time from the valve trigger to the discharge ignition. For all traces, the lines serve as visual guides.

3. Results

3.1. Pulsed discharge

Creating OH using a high-voltage discharge pulse shorter than the gas pulse significantly reduces the translational and the rotational temperature, as well as permits control of the mean speed of the OH packet. We would like to point out that our pulsed system is distinctly different than the one presented in [12], where the discharge pulse duration is 2.5 ms, much longer than the actual gas pulse. In our system the applied voltage

between the discharging disc electrodes is controlled by a high-voltage MOSFET switch produced by Behlke Electronics GmbH [18]. This device can switch up to 5 kV in well under 1 μs. Using this switch to pulse the discharging voltage, the velocity spread of the OH molecular packet is greatly reduced. The TOF profiles in Fig. 2a show a dramatic narrowing of the longitudinal velocity distribution by reducing the duration of the discharge pulse from DC to 2 μs. Also the measured rotational temperature of the OH beam decreases from 195 to 28 K. The voltage on the electrodes is increased from 1.4 kV, for the short discharge duration, to 1.9 kV for the DC case. For a DC discharge, very few OH molecules are produced at 1.4 kV. To make a reasonable comparison between the two modes of operation, we increased the voltage for the DC case until the peak signal of the OH packet was approximately equal to that of the short discharge duration case. When the discharge is allowed to occur during the entire gas pulse, there is a large amount of heating from the violent discharge process. Thus shortening the discharge pulse duration greatly reduces the temperature of the OH molecular packet and significantly increases the molecular phase-space density.

A short discharge pulse duration also gives the freedom to produce OH molecules at different stages during the supersonic expansion. OH molecular packets created at different times in the expansion process are shown to have differing mean speeds and velocity widths. Fig. 2b is a plot of several example TOF profiles taken just before the skimmer where the discharge durations is 2 μs for all the data. The time between the signal triggering the valve to open and the discharge pulse, defined as 'ignition time', for each trace is listed in the legend. There is an ∼50 μs time delay between the valve trigger and the valve opening. By timing the discharge correctly, OH molecular packets can be created with a mean speed up to 465 m/s with the discharge ignition at 80 μs or down to 275 m/s with the discharge ignition at 190 μs. The mean speed of the packet as a function of the discharge ignition time is summarized in Fig. 2c.

A likely explanation for this discharge ignition-time dependent beam velocity is that our current loop actuated valve does not operate instantaneously or symmetrically. We see evidence of the asymmetric operation of the valve using our pulsed discharge to sample different parts of the expanding gas pulse. As seen in Fig. 2c, the gas speed is large and constant over the first 15 μs of the pulse when the supersonic expansion has reached a steady-state beam velocity while the number of molecules in the beam is still steadily increasing. The speed of the gas gradually decreases as the valve begins to close and the expansion is suboptimal. We note the peak signal size is reached (at ∼110 μs) only after the mean speed of the supersonic expansion beam has already decreased. However, the FWHM longitudinal velocity spread is still a mere 16.6%.

We confirm the asymmetric valve operation by measuring the Xe gas pulse with a fast ion gauge (FIG). The FIG trace shows a pulse with a fast leading edge and much longer trailing edge.

For the application of a cooled molecular beam as an input to a Stark decelerator, we require a packet of OH molecules with a high phase-space density propagating at a low mean speed. Choosing to create the OH molecules towards the end of the gas pulse, for example at an ignition time of 160 µs, produces a packet moving at an attractive mean speed of only 306 m/s. However, the amplitude of the packet is significantly smaller and the velocity width is significantly larger than a packet created at 110 µs. The variation of OH packet amplitudes for different ignition times can be seen in Fig. 2c. The optimum discharge ignition time for our application is around 110 µs. For different applications (e.g. reactive collision dynamics), the tunability of the mean speed of the molecular packet could be advantageous.

3.2. Filament-assisted discharge

The other important component in the improved discharge-based system is a hot filament in the source chamber. The hot filament has two major effects on the discharge. First, it allows the discharge to occur reliably and reproducibly even at the shortest discharge pulse duration of 1 µs. The improvements from a short discharge pulse duration are demonstrated in the previous section. Second, the hot filament allows a stable discharge to occur at lower voltages on the disc electrodes. Without the hot filament, the discharge is either not stable or does not even occur at an electrode voltage less than 3 kV; using the hot filament, the discharge is stable down to 0.7 kV, which results in a significantly colder molecular packet.

The longitudinal TOF profile and rotational temperature of the OH molecular packet are measured for different discharge voltages (Fig. 3). For discharge voltages below 1.9 kV, a single peak is observed in the TOF profile. However, for voltages at or above 1.9 kV, the TOF profile starts to develop two distinct maxima and indicates a considerably larger velocity spread. We expect this heating arises from the higher energy electrons created by a larger potential difference between the electrodes. As the voltage is lowered from 1.6 to 1.2 kV, the velocity spread remains nearly constant, but the peak number of molecules decreases as the electrons' energy decreases and thus creates OH molecules less efficiently. The rotational temperature also elucidates the heating effect from the higher discharge voltages. The rotational temperature is determined by measuring the ratio of OH molecules produced in the $J = 3/2$ and $5/2$ states. The introduction of the hot filament permits the reduction of the discharge voltage from 3 kV to an optimized voltage of 1.4 kV, leading to almost a factor of four reduction in rotational temperature (Fig. 3b).
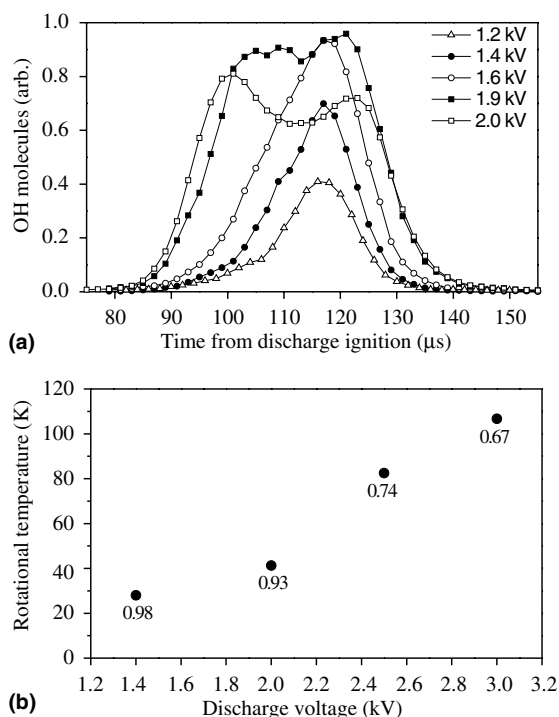

Fig. 3. (a) TOF profiles, acquired in the detection region before the skimmer, for several discharge voltages. The discharge pulse duration is 2 µs. The solid lines are visual guides. (b) Rotational temperatures for different discharge voltages. The number associated with each point is the fraction of the molecules in the lowest rotational state ($J = 3/2$).

3.3. Optimized conditions

A Stark decelerator benefits from a molecular beam that has both a high phase-space density and a low mean longitudinal speed. The optimum configuration of the source for this application uses a 2 µs discharge duration that is ignited 110 µs after the valve is triggered to open. The filament-assisted discharge is created using a potential difference between the electrodes of 1.4 kV. A molecular packet created under these conditions has a mean velocity of 422 m/s and a longitudinal velocity spread of 16.6%, which corresponds to a translational temperature of 5 K. This is a significantly colder translational temperature than was reported by [11] of 26 K and [12] of 29 K.

The transverse velocity spread is determined through the use of the hexapole focusing effect (Annual Review of Physical Chemistry, 40 (1989) 561), and detailed numerical simulations. The density of OH is measured 2 mm downstream of the hexapole for different hexapole voltages, thus producing a focusing curve. From the comparison of the numerical simulations to the hexapole focusing data the full-width transverse velocity spread is estimated to be 35 m/s, which corresponds to a transverse temperature of ~1.3 K.

The density of OH molecules just before the skimmer tip is determined from the calibrated LIF signal. The

peak density of molecules in the $\Omega = 3/2$, $J = 3/2$, f-component state created under these conditions is 3.5×10^{10} cm^{-3} measured at a distance of 5 cm from the valve nozzle. To compare with the density quoted in [11], we assume $1/r^2$ position dependence, where r is the distance from the nozzle, and an equal population in e and f parity states. Our calculated density at $r = 2.3$ cm in both parity states is $\sim 3 \times 10^{11}$ cm^{-3}, which is a factor of 2 less than [11]. This lower molecular density can be attributed to a longer flight time using Xenon versus Argon. The longer flight time allows the molecular packet to spread in both the longitudinal and transverse directions reducing the density detected at a specific location. To accurately compare our results with the work of [11] and [12], we also performed the same experiments using Argon as a carrier gas and measured a factor of five improvements in the number of OH molecules produced.

4. Conclusion

In conclusion, we have developed and characterized a controllable discharge-based source of cooled OH free radicals. Through the use of a pulsed discharge we can tune the mean velocity of the OH beam from 465 m/s down to 275 m/s, with a FWHM longitudinal velocity spread as small as 16.6%. Also the implementation of a hot filament in the source chamber allows a stable discharge to occur for short discharge pulse durations and at low discharge voltages. We have shown that decreasing the discharge pulse duration and voltage creates a colder packet of OH molecules.

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