LASER PROBING of TRANSPORT PROPERTIES and ROTATIONAL ALIGNMENT of N_2^+ DRIFTED in He

by

Eric Baxley Anthony

B. A., Middlebury College, 1987

A thesis submitted to the

Faculty of the Graduate School of the

University of Colorado in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Department of Physics

1998

This thesis for the Doctor of Philosophy Degree by
Eric Baxley Anthony
has been approved for the
Department of Physics
by
Stephen R. Leone
Veronica M. Bierbaum
Date

Anthony, Eric Baxley (Ph. D., Physics)

Laser Probing of Transport Properties and Rotational Alignment of N₂⁺ Drifted in He

Thesis directed by Professor Adjoint Stephen R. Leone and Research Professor Veronica M. Bierbaum

Results of transport property and rotational alignment experiments of the atmospherically important molecule N₂⁺ are presented, as measured in a flow-drift apparatus using the technique of single-frequency laser-induced fluorescence (LIF). A trace amount of N₂⁺ is drifted in helium as a buffer gas; the external axial electric field of the drift tube varies the center-of-mass collision energy of the ion-neutral pair. The net effect over hundreds of buffer gas collisions is to establish a steady-state anisotropic ion velocity distribution, the precise character of which is determined by the ion-neutral interaction potential, mass ratio, and field strength. A single-frequency ring dye laser is used to probe Doppler profiles of various rotational lines of the (v',v'') = (0,0) band in the $B^2 \Sigma_u^+ - X^2 \Sigma_g^+$ system at 390 nm. The single-frequency cw laser technique allows one to measure the velocity component distribution function (VCDF) along the laser propagation direction k; the VCDF is a projection of the complete ion velocity distribution function. Additionally, the rotational alignment of the ions as a function of one component of sub-Doppler laboratory velocity is probed by polarized LIF.

Drift velocities and ion mobilities are determined from the shift of the first moments of the coaxial LIF Doppler profiles, while perpendicular and parallel translational temperatures are determined from the widths or second central moments of the profiles in the direction probed. Drift velocities measured up to a field strength of 16 Td appear to be in good agreement with data derived from earlier arrival-time measurements. A small but definite increase in mobility with increasing rotational state from J=13.5 to J=22.5 is observed. A significant difference of over 100 K between the parallel and perpendicular temperatures is measured at the highest field strength employed (16 Td). A small degree of positive skewness or third central moment is observed as well in the parallel VCDF's, which is of particular interest since a high-velocity tail has not been previously reported for any molecular ion system. Additionally, by probing with linearly polarized light and measuring the degree of polarization of the resultant LIF, the collision-induced quadrupole rotational alignment parameter $A_0^{(2)}$ is determined as a function of field strength and velocity subgroup. A strong correlation is found between the degree of rotational alignment and the velocity subgroup when probed parallel to the field direction, with the alignment parameters generally increasing monotonically across the distribution. A dramatic difference in velocity-selected alignment as a function of rotational state is observed as well, for experiments conducted on various rotational lines at a fixed field strength of 12 Td. For sufficiently low rotational state (J about 9), it appears that $A_0^{(2)}$ changes sign across the Doppler profile.

Acknowledgments

As I reach the end of the valley of sweat, blood, and tears (in approximately that order) that has been the graduate school experience for me, I become very much aware that, although it has been largely a solitary enterprise, I didn't get through it alone. There is a long list of "invisible contributors" that I need to thank somehow. Coupled with the frustration, at the end, of realizing that I seemed to have had to learn absolutely everything the hard way, is the realization that it would have been infinitely worse without the many people I've interacted with along the way.

Firstly, I need to thank my co-advisors Steve Leone and Veronica Bierbaum. Although I have certainly not been one of Steve and Ronnie's most successful (far from!) or their easiest graduate student, they have been extraordinarily patient throughout the whole process. They never completely gave up on me, even though, at times, they certainly had every right to. Particularly in this last year, I have really grown to appreciate Steve's truly encyclopedic knowledge of chemical physics and his wisdom about the "big picture" of the field. Ronnie's ever-cheerful demeanor, scientific precision, and willingness to drop everything in the middle of an otherwise hectic day to sit down and talk about a scientific or personal problem has always been appreciated.

Secondly, I would like to thank my committee members: Chris Greene, David Nesbitt, and Robert Parson. Chris is one of the best teachers I've had at CU and even though always busy, has somehow found the time and patience to talk to a dumb experimentalist such as myself. I've always respected David for his extraordinary insights, the enthusiasm he always brings to science, and for always encouraging

people to do their absolute best. Robert has been an absolutely great person to talk to and bounce ideas off through the years; I've always been astonished by his ability to both ask and field good questions on almost any topic.

It has been a privilege to have served as a graduate student at JILA. It would not be possible to thank each individual that has contributed to my education at JILA by name—but that won't stop me from trying. JILA is well-renowned for having the best support staff on this planet. Without the help of the instrument shop staff of John Andru, Dave Alchenberger, Jim Csotty, Hans Green, Blaine Horner, and Seth Wieman, and electronics shop staff of James Fung-a-Fat, Paul Beckingham, Terry Brown, and Mike Whitmore, I wouldn't have graduated. The computing staff of Ralph Mitchell, Alan Dunwell, Joel Frahm, Anne Hammond, Patti Krog, and Chela Kunasz have been consistently fantastic. I always enjoyed visiting SRO, mostly because of the great staff of Marilee DeGoede, Judy McCorkel, Laurie Kovalenko, and Lorraine Volsky.

Thanks as always to the invisible hand of the administrative staff for keeping everything going. Marilyn Greves and Leslie Haas somehow insured I always got paid. I would particularly like to thank Jim Faller and Pat McInerny, who came up with capital funds for my project when they were most desperately needed, and Pat for providing me with an office in the tower for thesis-writing.

A couple of additional scientific thanks are in order. I am indebted to the intellectual godfathers of this experiment, Dr. Rainer Dressler of Philips Lab, Hanscom AFB, and Professor Henning Meyer of the University of Georgia. Henning in particular has been of extraordinary help through the years and always an

inspiration; anything in this thesis that sounds right or "profound" is almost certainly due to my interactions with him. I would especially like to thank Professor S. David Rosner of the University of Western Ontario for his invaluable help on N_2^+ hyperfine spectroscopy issues. Professor Millard Alexander of the University of Maryland encouraged me throughout much of this work, most especially when I was prepared to give up. Dr. John Bohn was invaluable in the very late stages of this work as a good person to bounce ideas off.

The Leone group is too large, and too many people have moved in and out over the years I've been here other than to thank the group en-masse. I would like to thank all of my personal friends both in and out of JILA. The JILA friends start with the basement: Kurt, Jun, Tom, Scott Diddams, Nada—and move up: Scott Davis, Nikki, Brad, Brana. Outside of JILA: Maela, Kristen, Linda, Jeanette, Will, Sue, Chris, Matt, Leif, Dave, Mark. My housemates through the years: Elizabeth, Charlie, James, Jos, Gina, Peter, and Sarah have kept me sane and going—I couldn't have done it without them. I would particularly like to thank my long-time housemate and friend Jetty, for having the knack of always being there when I needed her.

Lastly, and most importantly I need to thank both of my parents and my twin brother for the love and support they have always given me throughout my life, and for continually standing by me beyond all reason in my probably ill-advised decision to go to graduate school. Particularly in the last year, their unwavering support has been phenomenal—countless times I wanted to give up but they would not let me.

This thesis is dedicated to the memory of my late grandfather C. Herbert Baxley, who always encouraged me to pursue my highest educational goals regardless of their cost.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	
A. General motivation	1
B. Interaction potential	6
C. Ion transport properties	9
D. Collision-induced rotational alignment	10
References for Chapter I	12
II. GENERAL EXPERIMENTAL TECHNIQUES	14
A. Introduction	14
B. Ion source & flow-drift region	14
1. Ion source & production conditions	16
2. Flow tube considerations	23
3. Drift & charge separation regions	25
C. Ring dye laser system & diagnostic tools	29
1. General description	30
2. Diagnostic tools	34
3. Beam transport & polarization control	43
D. Laser-induced fluorescence detection techniques	46
1. Unpolarized detection	46
2. Polarized detection	50
E. Electronics and data acquisition programming	55
F. General data analysis considerations	59

G. Spectroscopy of the N ₂ ⁺ $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system	51
1. General spectroscopic structure	51
2. Hyperfine spectroscopy6	57
References for Chapter II6	59
III. ROTATIONALLY-RESOLVED TRANSPORT PROPERTIES OF N_2^+ IN He 7	1
A. Introduction	1
B. Descriptive theory	1
C. Measurement & analysis techniques	7
1. Measurement details	7
2. Velocity component distribution functional forms	34
3. Line shape analysis9	Ю
D. Results9)5
1. First moments: drift velocities & mobilities9	96
2. Second central moments: translational temperatures)4
3. Third central moments: direct measure of skewness)9
E. Possible systematics	. 1
1. Axial ion flow-velocity experiments	.3
2. LIF intensity vs. tube voltage experiments	22
F. Discussion & theory	25
1. First moments	27
2. Second central moments	35
G. Conclusions	36
References for Chapter III	8

IV. COLLISION-INDUCED ROTATIONAL ALIGNMENT OF N_2^+ IN He	141
A. Introduction	141
B. Descriptive theory	144
1. Qualitative & heuristic arguments	144
2. Simple classical theory	150
3. Quantum theory	157
4. Extensions to quantum theory	160
C. Experimental & analysis techniques	165
D. Results	175
1. Field dependence of alignment for single rotational line	176
2. Rotational quantum state dependence of alignment	182
E. Possible systematics	188
F. Discussion & dynamics theory	192
1. Steady-state fully-velocity averaged theory	195
2. Partial velocity selection	200
G. Conclusions	205
References for Chapter IV	206
BIBLIOGRAPHY	208
APPENDIXES	218
A. Relevant circuit diagrams	218
B. Eta-Spex program listing(on dis	skette)
C. AMCalc angular momentum calculator program(on dis	skette)

LIST OF TABLES

Ta	ble Page
2.1	Relevant transition frequencies for (0,0) band of N_2^+ $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system 66
3.1	Tabulated results of first moment experiments
3.2	Tabulated results of second central moment experiments
4.1	Example of data collection sequence for sub-Doppler alignment experiment 169
4.2	Example of program data output
4.3	Example of program data analysis output
4.4	Tabulated results of rotational state alignment experiment

LIST OF FIGURES

Figure	Page
1.1 N ₂ ⁺ -He interaction potential in Jacobi coordinates	8
2.1 Overall schematic of experimental apparatus	15
2.2 To-scale diagram of ion source region	17
2.3 Representative mass spectra for Fall '95 experiments	20
2.4 Representative mass spectra for Fall '97 & Spring '98 experiments	21
2.5 Schematic of drift tube electrical connections	26
2.6 Ring dye laser optical and electronic schematic	31
2.7 Optics table components schematic	35
2.8 Construction diagram of 20 cm long ULE Fabry-Perot cavity	38
2.9 Scope trace of Fabry-Perot transmission peaks	39
2.10 Perspective view of apparatus and PMT stack	47
2.11 To-scale plan view of stepper-motor driven PMT stack	53
2.12 Block schematic of counter portion of acquisition system	58
2.13 Typical LIF spectra of single spin-rotation line	62
2.14 Pump-fluoresce diagram for R ₁ (15) transition	64
2.15 LIF survey spectra of five rotational lines	65
3.1 Representative first-moment LIF data	78
3.2 Representative second central moment LIF data	83
3.3 Whealton-Woo functional form for various skewness parameters	88

3.4 Simulated spectra of underlying hyperfine structure
3.5 R ₁ (15) drift velocities
3.6 R ₁ (15) mobilities
3.7 Drift velocities and mobilities for various rotational lines at 12 Td 102
3.8 J-dependent mobilities at 12 Td, broken down by day of observation
3.9 Second and third central moment data on R ₁ (15), Fall '95
3.10 Translational temperatures for R ₁ (15)
3.11 Evidence of positive skewness in coaxial probe data
3.12 Field off/field on line centers as function of charge separation voltage 115
3.13 Diagnostic data on axial ion flow velocity systematic
3.14 Axial ion flow velocity experiments with different source aperture sizes 120
3.15 Results of charge-separation voltage scanning experiments
3.16 Results of drift voltage scanning experiments
3.17 Summary plot of CO ⁺ -He LIF and arrival time mobilities
3.18 Literature values of N_2^+ and CO^+ mobilities
4.1 Cartoon diagram of LIF probe-detection scheme
4.2 Cartoon m _J distribution picture
4.3 Schematic of "two-angle" LIF geometry for alignment experiment
4.4 Isotropic and aligned fluorescence intensities for the two probe directions 156
4.5a) Perpendicular probe polarization results for R ₁ (15)
4.5b) Coaxial probe polarization results for R ₁ (15)

4.6	Corresponding m _J distributions for R ₁ (15) at 16 Td	183
4.7	Raw polarization data from rotational state alignment experiment	185
4.8	Systematic plasma polarization checks	187
4.9	Polarization data of Fig. 4.7 with simple subtractive correction	189
A.1	Simple analog divider circuit	219
A.2	Simple window detector circuit	220
A.3	Stepper motor driver circuit for rotation stage	221