STATE-RESOLVED DYNAMICS OF ION-MOLECULE REACTIONS IN A
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State-Resolved Dynamics of Ion-Molecule Reactions in a Flowing Afterglow

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An extensive set of studies was undertaken utilizing infrared chemiluminescence, visible chemiluminescence and laser-induced fluorescence detection to explore the dynamics of ion-molecule reactions in a flowing afterglow apparatus. Detailed product vibrational state distributions were determined for a variety of reactions including heavy atom transfer in polyatomic systems, charge transfer reactions and proton transfer reactions. Absolute branching ratios for production of electronically excited oxygen atoms were measured.
20. Abstract (cont'd.)

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A. OBJECTIVES OF THE RESEARCH

An extensive set of studies was undertaken utilizing infrared chemiluminescence, visible chemiluminescence and laser-induced fluorescence detection to explore the dynamics of ion-molecule reactions in a flowing afterglow apparatus. Detailed product vibrational state distributions were determined for a variety of reactions including heavy atom transfer in polyatomic systems, charge transfer reactions and proton transfer reactions. Absolute branching ratios for production of electronically excited oxygen atoms were measured for a reaction of atmospheric importance. The rotational state distribution of an ion in an electric drift field has been characterized and a study of the velocity distribution has been initiated.
B. STATUS OF THE RESEARCH EFFORT

1. Heavy Atom Transfer in Polyatomic Systems


Summary of Research:

Vibrational state distributions of the SF$_6^-$ + H,D + SF$_5^-$ + HF(v=0-17), DF(v=0-17) ion-molecule reactions were investigated with the flowing afterglow-infrared chemiluminescence technique. The nascent distribution for the hydrogen reaction is (0.00)$_{v=1}$:(0.17)$_{v=2}$:(0.30)$_{v=3}$:(0.24)$_{v=4}$:(0.13)$_{v=5}$:(0.11)$_{v=6}$:(0.05)$_{v=7}$ and for the deuterium reaction is (0.00)$_{v=1}$:(0.06)$_{v=2}$:(0.11)$_{v=3}$:(0.14)$_{v=4}$:(0.14)$_{v=5}$:(0.23)$_{v=6}$:(0.15)$_{v=7}$:(0.08)$_{v=8}$:(0.09)$_{v=9}$. The fractions of the available energy deposited into the HF and DF vibrations are 0.37 and 0.38, respectively. The distributions do not show the characteristics of a statistical distribution that might be expected if a long-lived complex occurs in the reaction. Instead, the distributions show a moderate amount of vibrational excitation due to an initial attractive energy release. Since the fraction of the available energy deposited into the diatomic vibration correlates well with the attractive energy release in L + HH' systems, a larger fraction of the energy is released as repulsion during S-F bond scission, favoring product translation and SF$_5^-$ vibration. The collisions are most likely direct with negligible effects due to secondary encounters.
2. **Charge Transfer**


**Summary of Research:**

The nascent vibrational state distribution of the \( \text{N}^+ + \text{CO} \rightarrow \text{CO}^+(v=0-2) + \text{N} \) charge transfer reaction was measured at thermal energy. The reaction was carried out in a flowing afterglow and the vibrational state populations were determined by laser-induced fluorescence on the \( \text{CO}^+(A^2\Pi - X^2\Sigma^+) \) system. The nascent vibrational state distribution for the \( \text{N}^+ + \text{CO} \) reaction is \( (0.71\pm0.05)_{v=0}; (0.27\pm0.04)_{v=1}; (0.02\pm0.01)_{v=2} \). The observed vibrational distribution suggests that neither a long-range Franck-Condon mechanism nor an energy resonant process adequately describes the charge transfer reaction. A dual channel mechanism of the reaction is considered, in which a fraction of the reactive collisions proceed by a long-range Franck-Condon mechanism while the remainder proceed via a long-lived NCO\(^+\) intermediate. The intermediate may lead to the observed extent of \( \text{CO}^+ \) vibrational excitation either through statistical partitioning of the energy or by dynamical changes in the \( \text{CO} \) bond length through specific molecular orbital occupancies.
Published results: "Product Vibrational State Distributions of Thermal Energy Charge Transfer Reactions Determined by Laser-Induced Fluorescence in a Flowing Afterglow: \( \text{Ar}^+ + \text{CO} \rightarrow \text{CO}^+(v=0-6) + \text{Ar} \)," C. E. Hamilton, V. M. Bierbaum and S. R. Leone, J. Chem. Phys. 83, 2284 (1985).

Summary of Research:

The \( \text{Ar}^+ + \text{CO} \rightarrow \text{CO}^+(v=0-6) + \text{Ar} \) charge transfer reaction was studied at thermal energy in a flowing afterglow and the vibrational state distribution was determined by laser-induced fluorescence on the \( \text{CO}^+(A^2\Pi - X^2\Sigma^+ \text{F}^+) \) bands. The nascent vibrational state distribution is \((0.06\pm0.04)_{v=0}:(0.07\pm0.02)_{v=1}:(0.09\pm0.02)_{v=2}:(0.15\pm0.03)_{v=3}:(0.21\pm0.03)_{v=4}:(0.27\pm0.02)_{v=5}:(0.15\pm0.02)_{v=6}\). The rate constant for \( \text{CO}^+(v=4) \) deactivation by \( \text{CO} \) was measured to be \( 6.0\pm2.5 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \); the similarity of this rate constant to that for \( \text{CO}^+(v=1) \) deactivation by \( \text{CO} \) \( (5.0\pm2.0\times10^{-10} \text{ cm}^3 \text{s}^{-1}) \) suggests that vibrational deactivation proceeds by a charge transfer mechanism. The \( \text{Ar}^+ + \text{CO} \) reaction is described as proceeding via a bent \( \text{ArCO}^+ \) intermediate that forms in a side-on attack. Vibrational excitation may then result from delocalization of the bonding electron density of \( \text{CO} \) and the corresponding dynamical changes in the \( \text{CO} \) bond length in the intermediate.
3. **Proton Transfer**


**Summary of Research:**

Product vibrational state distributions for the ion-molecule reactions $F^- + \text{HBr}, \text{DBr} \rightarrow \text{HF} (v<4), \text{DF} (v<6) + \text{Br}^-$ were determined using the flowing afterglow infrared chemiluminescence technique. The nascent distributions are $(0.09 \pm 0.04)_v^1 : (0.29 \pm 0.04)_v^2 : (0.34 \pm 0.04)_v^3 : (0.28 \pm 0.04)_v^4$ for the HF product, and $(0.05 \pm 0.04)_v^1 : (0.12 \pm 0.04)_v^2 : (0.16 \pm 0.04)_v^3 : (0.25 \pm 0.04)_v^4 : (0.22 \pm 0.04)_v^5 : (0.20 \pm 0.04)_v^6$ for the DF product. The fractions of the available energy deposited in product vibration are $0.60 \pm 0.04$ and $0.63 \pm 0.05$ for the proton transfer and deuteron transfer reactions, respectively. A surprisal analysis suggests that less than 5% of the product molecules are formed in $v = 0$. The HF distribution is somewhat hotter than that reported previously, while the DF distribution was measured for the first time. Both distributions are remarkably similar to those reported for the analogous neutral processes, which suggests that direct collisions dominate the reactive encounters despite the presence of a deep attractive well in the potential surface for the ion-molecule reactions.
4. Reactions of Atmospheric Importance

Published results: "Auroral Implications of Recent Measurements on O(^1S) and O(^1D) Formation in the Reaction of N^+ with O_2," A. O. Langford, V. M. Bierbaum and S. R. Leone, Planet. Space Sci., in press.

Summary of Research:

Recent flowing afterglow measurements have shown that the reaction of N^+ with O_2 produces 70 ± 30% of the oxygen atom product as O(^1D) and <0.1% as O(^1S). These results indicate that this reaction does not contribute to the auroral green line emission (5577 Å), but can account for ~10% of the observed red line (6300 Å) auroral emission.


Summary of Research:

Absolute branching ratios for production of O(^3P), O(^1D), and O(^1S) in the reaction of N^+ with O_2 were measured using the flowing afterglow/visible chemiluminescence technique. The O(^1S) product was monitored by the O(^1S)-O(^1D) emission at 557.7 nm. The O(^1D) product was monitored via sensitized fluorescence at 760 nm from O_2(b^1Π_g) formed by energy transfer from O(^1D) to O_2(X^3Σ^-). Absolute O(^1D) and O(^1S) yields of 70 ± 30% and <0.1%, respectively, of the total atomic oxygen product were inferred by comparison to the known O(^1S) and O_2(^1Σ^+_g) emission intensities from the reaction of Ar(^3P) with O_2. The low O(^1S) yield was also obtained directly from the relative O(^1S) and O_2(^1Σ^+_g) emission intensities from the N^+ + O_2 reaction.
5. Characterization of Ions in Electric Drift Fields


Summary of Research:

Results are presented for a new method of studying collisional excitation and deactivation processes of molecular ions. Translationally excited ions were prepared in the uniform electric field of a drift tube. Collisions with the inert buffer gas lead to rotational excitation (T-R). Laser-induced fluorescence (LIF) was used as a direct optical probe of the internal states of $\text{N}_2^+$ using the $B^2\Sigma_u^+-\chi^2\Sigma_g^+$ transition at 391.4 nm. In this initial experiment, rotational excitation was observed for $\text{N}_2^+$ in collisions with helium at energies up to 0.054 eV (c.m.). The rotational state distribution can be described by a Boltzmann temperature corresponding to the center-of-mass collision energy, in good agreement with theory. Approximately ten collisions or less are required to obtain full equilibration of the rotational distribution.

Current Studies:

In the last year, with AFOSR support for a cw dye laser system, we have begun a program to experimentally measure the velocity distribution of ions in well-characterized electric drift field regions. We have purchased and installed an argon ion pump laser and single mode ring dye laser manufactured by Coherent Radiation. This new laser system has been coupled to our flow-drift apparatus which has fluorescence detection capabilities. This device incorporates a highly uniform drift field region and has optical ports for axial and transverse excitation of ions by laser-induced fluorescence. In order to
preserve field uniformity, the optical access port regions are kept to a minimum and are covered with a fine wire mesh. Velocity distributions are obtained by scanning velocity profiles of the ions with the tunable single frequency laser used in the laser-induced fluorescence mode; the Doppler broadened line-shapes obtained with this 1 MHz bandwidth laser directly give the ion velocity distribution. In addition, the high average power and continuous duty cycle of the cw laser system provide the greatly improved signal-to-noise necessary to carry out these difficult studies. The cw laser also improves our detection capability by three orders of magnitude for other experiments involving species that can be excited in the visible region of the spectrum.

Figure 1 shows a narrow slice of the laser-induced fluorescence spectrum for \( \text{N}_2^+ (A^2\pi_u - X^2\Sigma_g^+) \) obtained in preliminary experiments at thermal energy with this newly coupled flowing afterglow-laser system. The (4,0) transition is pumped and the (4,1) fluorescence is monitored. The signal-to-noise is excellent even though several experimental parameters were not yet optimized; for example, an improvement of a factor of one hundred can be anticipated by employing a photomultiplier tube with higher sensitivity in this wavelength region and by aligning the phototube slit along the laser axis. The \( \text{N}_2^+ \) spectrum of Miller et al. (T. A. Miller, T. Suzuki and E. Hirota, J. Chem. Phys. 80, 4671 (1984)) in this same region is given at the top of the figure for comparison. The observed linewidth (0.0396 cm\(^{-1}\)) is in good agreement with the calculated Doppler width (0.0382 cm\(^{-1}\)). It is clear that the ultimate sensitivity and resolution of this system is superb. It will therefore also be possible to extend our previous studies of internal excitation of \( \text{N}_2^+ \) in an electric drift field to higher energies where higher rotational excitation and some vibrational excitation may be induced; the original work was limited by reduced signals at high field strengths. It will be important to
Fig. 1. Portion of laser-induced fluorescence spectrum of the $N_2^+(A^{2}u^- - X^{2}g^+)$ system near the $R_1$ bandhead. Top spectrum is from Miller et al.; middle and bottom spectra represent recent results from our laboratory.
determine whether the theory of Viehland et al. (L. A. Viehland, S. L. Lin and E. A. Mason, Chem. Phys. 54, 341 (1981)) continues to be valid at large values of E/N. This theory predicts that molecular ions drifted in an atomic buffer gas will reach an effective internal temperature corresponding to the center-of-mass collision energy.
C. PUBLICATIONS


19. "Auroral Implications of Recent Measurements on O(\textsuperscript{1}S) and O(\textsuperscript{1}D) Formation in the Reaction of N\textsuperscript{+} with O\textsubscript{2}," A. O. Langford, V. M. Bierbaum and S. R. Leone, Planet. Space Sci., in press.

D. PROFESSIONAL PERSONNEL ASSOCIATED WITH THE RESEARCH

Stephen R. Leone: Co-principal Investigator. Adjoint Professor, Department of Chemistry, University of Colorado. Staff Physicist, Quantum Physics Division, National Bureau of Standards.

Veronica M. Bierbaum: Co-principal Investigator. Senior Research Associate, Special Member of the Graduate Faculty, Department of Chemistry, University of Colorado.

G. Barney Ellison: Co-principal Investigator. Associate Professor, Department of Chemistry, University of Colorado.

Michael A. Duncan: NRC Postdoctoral Research Associate. Presently Assistant Professor, Department of Chemistry, University of Georgia.


Andrew O. Langford: Postdoctoral Research Associate. Presently Visiting Fellow, CIRES, University of Colorado.

Rainer Dressler: Postdoctoral Research Associate.

Henning Meyer: Postdoctoral Research Associate.
E. PROFESSIONAL INTERACTIONS

S. R. Leone - Seminars and Conferences

"State-detected molecular reaction dynamics: Establishing the relationship between reactivity and energy transfer," Dept. of Chemistry Seminar, University of Southern California, Los Angeles, California, April 1983.
"State-selected reaction dynamics," Chemistry Department Colloquium, Wayne State University, Detroit, Michigan, October 1983.
"State-selected reaction dynamics," Chemistry Department Colloquium, Iowa State University, Ames, Iowa, October 1983.
"State-selected reaction dynamics," Physical Chemistry Seminar, University of California, Irvine, California, November 1983.
"State-selected reaction dynamics," Chemistry Department Colloquium, University of Cincinnati, Cincinnati, Ohio, March 1984.
"State-selected chemical dynamics," Physical Chemistry Seminar, University of Utah, Salt Lake City, Utah, October 1984.
"Spectroscopic investigations of molecular reaction dynamics," Coblentz Prize Award Symposium, The 39th Annual Symposium on Molecular Spectroscopy, The Ohio State University, Columbus, Ohio, June 1984.
"Lasers and chemical dynamics," University of Georgia, Athens, Georgia, April 1985.
"Laser probing of energy transfer and chemical reaction dynamics," Texas A&M, College Station, Texas, October 1985.
"Laser probing of energy transfer and chemical reaction dynamics," University of Texas at Austin, Austin, Texas, October 1985.
"Laser probing of energy transfer and chemical reaction dynamics," University of Michigan, Ann Arbor, Michigan, October 1985.

V. M. Bierbaum - Seminars and Conferences

"Gas phase ion chemistry: Reactive intermediates," National Science Foundation Physical Organic Meeting, Workshop on Reactive Intermediates, Santa Catalina Island, California, June 1983.
"The chemistry of ions -- from interstellar space to biomedical applications," Natural Science Colloquium, Tougaloo College, Tougaloo, Mississippi, March 1984.
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