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REACTIONS OF IONS WITH ATOMIC AND
MOLECULAR FREE RADICALS

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W. Ronald Gentry

University of Minnesota

Minneapolis, Minnesota 55455

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Abstract

Analysis and interpretation of the data on the reactions of H_2^+ with N, C, O and F were completed, along with some supplementary investigations of collision-induced dissociation of the exotic species NH_3^{2+} and CS_2^{3+} . As the focus of this project shifts to other systems and phenomena, construction of a new crossed, pulsed molecular beam apparatus has been begun, and is now about 75% complete. The new instrument will permit state-resolved studies of energy transfer and reactive processes to be carried out with unprecedented sensitivity.

I. RESEARCH DESCRIPTION

We have completed analysis and interpretation of our merged-beam data on the reactions $\text{H}_2^+ + \text{C}, \text{N}, \text{O}, \text{F} \rightarrow \text{CH}^+, \text{NH}^+, \text{OH}^+, \text{FH}^+ + \text{H}$. The energy dependence of the absolute total reaction cross section was measured in each case from about 0.002eV to about 20eV, and product speed and angle distributions were determined over much of this energy range. The low-energy data on total cross sections can be interpreted in terms of capture processes occurring on long-range potentials consisting of charge-quadrupole and charge-induced dipole terms. We have calculated these potentials from electronic structure data on each of these atoms. Higher-energy data on both the total reaction cross sections and the product speed and angle distributions reflect the microscopic atom-transfer mechanism and energetics.

An auxiliary set of experiments were performed on collision-induced dissociation of the multiply-charged polyatomic species NH_3^{2+} and CS_2^{3+} . This data has now been fully analyzed to reveal the dissociation mechanisms which follow vibrational excitation or charge-transfer electronic excitation. The energy distributions of the products from "Coulomb explosions" can be used to infer the energetic pathways for the dissociation. Especially in the case of CS_2^{3+} , these are numerous and highly complex.

The above work is currently being prepared for publication in five articles.¹⁻⁵

We have also begun a shift of emphasis in our DOE-supported program to take advantage of the new opportunities for incisive experiments in molecular dynamics which are afforded by recent development in pulsed molecular beam and high-power pulsed dye laser technology. A new apparatus has been designed for the study of state-resolved energy transfer and

reactive phenomena in molecular collisions. The pulsed molecular beam sources developed at the University of Minnesota produce 20 μ sec pulses at 10 Hz, with intensities roughly 10^3 higher than those which could be sustained continuously without overloading most laboratory-size vacuum systems. The instantaneous collision rate in a crossed-beam experiment is therefore a factor of 10^6 larger than that which would result from steady-state molecular beams. Our apparatus will take advantage of this large instantaneous signal by detecting the scattered molecules in a pulsed mode by either laser-induced fluorescence (LIF) or multiphoton ionization (MPI) using a Nd:YAG-pumped dye laser. We expect to be able to detect selectively molecules in specific vibrational-rotational states by either method, because of the 0.04 cm^{-1} resolution of the dye laser.

The unique geometry of the apparatus will permit two types of experiment to be performed.

The pulsed molecular beam sources are independently rotatable, to make it possible to vary the kinetic energy of collision E (in the center-of-mass frame) by simply varying the intersection angle. The laser beam enters the scattering chamber between the two primary beam sources and in the plane of their rotation. If the laser pulse is timed so as to intersect the two molecular beam pulses while they are at the crossing point, then the signal (LIF or MPI) arising from this region will be proportional to the total cross section σ_i for producing a product in the internal state i . The energy dependence of $\sigma_i(E)$ can then be measured by observing the crossing-point signal as a function of intersection angle, over the range from 30° to 180° (a factor of 15 in E for primary beams of equal speed). In the second type of experiment, the dye laser

pulse is delayed by 10–100 μ sec to give the scattered molecules time to fly into a separate, differentially-pumped detector chamber, the entrance aperture of which also lies on the laser beam axis. Separate LIF and MPI detectors in this chamber see only the molecules scattered through a given angle θ . Therefore, the state-selected signal in the detector chamber as a function of scattering angle, at fixed beam intersection angle, is proportional to the differential cross section $I_i(\theta, E)$. Furthermore, this dual-mode character of the apparatus will enable us to normalize measurements of the differential cross sections $I_i(\theta)$, at various values of E , to the total cross sections $\sigma_i(E)$. This has seldom been possible with previous instruments.

The construction of the new apparatus is now about 75% complete. The vacuum system has been constructed and tested, and the molecular beam sources are being installed as this report is written. Computer control of the beam angles and the laser frequency and timing has been worked out. The work remaining to complete the apparatus consists of installing the detector optics and electronics, and the development of software for data acquisition.

II. REFERENCES

1. G.F. Schuette and W.R. Gentry, "The Dynamics of the Reaction $D_2^+ + C \rightarrow CD^+ + D$ ", to be submitted to J. Chem. Phys.
2. G.F. Schuette and W.R. Gentry, "The Dynamics of the Reaction $D_2^+ + F \rightarrow FD^+ + D$ ", to be submitted to J. Chem. Phys.
3. W.R. Gentry, "Reactions of Molecular Ions with Atomic Free Radicals", invited paper to be published in Accounts of Chemical Research.
4. G.F. Schuette, E. Borreson and W.R. Gentry, "Collision-Induced Dissociation of Multiply-Charged Polyatomic Ions: NH_3^{2+} ", to be submitted to J. Phys. Chem.
5. G.F. Schuette, E. Borreson and W.R. Gentry, "Collision-Induced Dissociation of Multiply-Charged Polyatomic Ions: CS_2^{3+} ", to be submitted to J. Phys. Chem.

III. PERSONNEL

The principal investigator, W.R. Gentry, has devoted 25% time to work on this contract and will continue to contribute this same fractional effort for the remainder of the present contract period. Other researchers on this project include Gregory Hall, Graduate Research Assistant, 50% time, Michael McAuliffe, Postdoctoral Research Specialist, 100% time since Oct. 1, 1981, and Brant Nease, Undergraduate Research Assistant, 50% time for the period July 15-Sept. 15. None of these researchers, except for the principal investigator, received support from other sources during their periods of DOE support.