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13. ABSTRACT *(Maximum 200 words)*

Reactions of state-selected ammonia cation with D_2, D_2O, and CD_4 were studied using a guided-ion beam instrument. The influence of vibrational and collision energy on these reactions was investigated by measuring cross sections for reaction of NH_3^+ created with varying degrees of excitation in the umbrella bending- and symmetric stretching-modes. A comparison of the product cross sections from NH_3^+ created in two states of nearly identical internal energies, but different concerted atom motions indicated that none of these reactions is mode-selective. The state-to-state ion-molecule reaction $ND_3^+ + D_2O \rightarrow ND_4^+ + OD$ was investigated. Rotational distributions were determined for the fine-structure states of the OD product for the reaction of vibrationally excited reactant ion. We also studied the proton transfer channel for the reaction of HBr^+ with HBr. We developed two approaches exploiting optical laser sources to diagnose specific chemical species present in hostile environments In particular, cavity ring-down spectroscopy and two-photon light induced fluorescence were deployed to detect potential reactants present in a hot-filament chemical vapor deposition system used to grow diamond films. Finally, we used quadrupole mass spectrometry to detect the diatomic dications BaX^{2+} (X=F, Cl, Br, I), $SrCl^{2+}$, $CaBr^{2+}$, and $MgBr^{2+}$.

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This grant supported research on four separate projects: (1) state-selected ion-molecule reactions, (2) state-to-state ion-molecule reaction dynamics in a bulb, (3) thermodynamically stable diatomic dications, and (4) optical diagnostics for hostile environments.

A. State-Selected Ion-Molecule Reactions

Chemical problems are most commonly solved by assuming the equivalency of the available forms of energy (translational, rotational, vibrational, etc.) with respect to the reaction path. Such statistical treatments are not always valid. In some cases, the outcome of a chemical reaction may depend differently on the various forms of available energy; some having a pronounced effect and others having little or no effect. The characterization of such differences can yield much information about the mechanics of chemical reactions. With these reasons in mind, our lab began to explore the effects of collisional and vibrational energy on the outcome of chemical reactions.

The ammonia ion is particularly well suited for these studies as several of its vibrational states are readily accessed through resonance-enhanced multiphoton ionization (REMPI). These states include a progression of up to ten quanta of out-of-plane bending motion ($1^0 2^n$) and one in which a single quantum of symmetric stretch (ν_1) is combined with varying amounts of umbrella bending ($1^1 2^n$). Access to two nearly isoenergetic vibrational modes allows comparison of an ion's reactivity when its internal energy is invariant but the concerted motions of the nuclei is different. Relative cross sections for product formation can be measured at varying collision energies in the range of 0.5 - 10 eV (center-of-mass). In addition, ion time-of-flight profiles can be converted to product velocities giving information on the nature of the reactive scattering.

We previously examined the reaction of ammonia ions with neutral ammonia (ND_3) and found it to be mode-selective.[1,2] Umbrella bending was found to enhance charge-transfer and D-abstraction channels whereas it suppresses proton-transfer. The symmetric stretch was found to be essentially inactive. We have extended this study to the reactions of ammonia ion with hydrogen, water and methane.

The reaction of ammonia ion with H_2 is unusual for an exothermic ion-molecule in that it is very inefficient. The measured rate coefficient[3,4] is nearly four orders of magnitude smaller than the Langevin collision rate coefficient. We have studied the reaction of state-selected ammonia ions with D_2 and measured relative cross sections for two major products.[5] A strongly forward-scattered product with m/z 19 arising from D-abstraction is the dominant product at low collision energies. The relative cross section for its formation decreases with increasing collision energy. A second product with m/z 18 is observed with an apparent threshold for formation of ca. 5 eV. This product corresponds to formal isotope exchange (NH_2D^+) and is believed to be formed by a two-step process in which the first step is collision-induced dissociation of the NH_3^+ leaving a cold (NH_2^+ - D_2) complex which then proceeds to products. Evidence for this mechanism is given elsewhere.[6,7]

Umbrella bending is shown to inhibit the D-abstraction product at energies above 5 eV, whereas it enhances m/z 18 product formation. Examination of velocity distributions for the D-abstraction channel shows that this reaction is well described by the spectator stripping model. Comparison of cross sections for products formed from ammonia ions prepared in two isoenergetic states ($1^0 2^5$ and $1^1 2^2$) indicates that this reaction is not mode-selective.

A similar study was performed on the reaction of state-selected ammonia ions with D_2O. In this case, two products were observed, one with m/z 21, corresponding to proton transfer (D_2OH^+) and another with m/z 18 that behaves in a similar manner to the NH_2D^+ product seen in the ammonia plus hydrogen study.[6,7] As in the D_2 work, the m/z 18 product shows an apparent threshold for formation of ca. 5 eV and its cross section increases with collision energy. The proton transfer product is inhibited by increasing collision energy. Using REMPI for ion preparation, a full ν_2 (v = 0-10) progression was obtained and shows that vibrational energy enhances both products at low (0.5 eV) collision energy, whereas only the proton transfer product is enhanced at high collision energy. As with the D_2 work, comparison of product cross sections from ammonia ions prepared in two isoenergetic states ($1^0 2^5$ and $1^1 2^2$) indicates that this reaction is not mode-selective.

Preliminary results have been obtained for the reaction of state-selected ammonia ions with CD_4. The two major products that are observed are the same as those in the D_2 study, a D-abstraction product that is inhibited by increasing collision energy and an isotope exchange product that shows similar behavior to the m/z 18 product in the D_2 and D_2O studies. Small amounts of charge-transfer and proton-transfer products have been observed, but their cross sections are too small to be measured reliably. We see no evidence for formation of products corresponding to condensation reactions, e.g., CD_3NH_2.

B. State-to-State Ion-Molecule Reaction Dynamics in a Bulb

The state-to-state ion-molecule reaction $ND_3^+(\nu_2=1) + D_2O \rightarrow ND_4^+ + OD(v=0,N)$ was investigated. A slowly flowing 2:1 mixture of ND_3 and D_2O at a total pressure of 50 mTorr was irradiated with a two-color sequence of laser pulses that prepares ND_3^+ in either the $\nu_2 = 1$ umbrella bending mode or the ground vibrational state by 1 + 1' + 1 resonance-enhanced multiphoton ionization (REMPI) via the ND_3 $\tilde{A}$ and $\tilde{B}$ states. After a delay of 200 ns to allow product buildup, the rotational distribution of the OD(v=0) product was measured by recording the OD $A^2\Sigma^+$ - $X^2\Pi$ laser-induced fluorescence spectrum on the (1,1) band following excitation of the (1,0) band. Rotational distributions were determined for the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ fine-structure states of the OD product for the reaction of the vibrationally excited reactant ion: for the experimentally difficult case of the reactant ion in the ground state, a rotational distribution was determined for the $^2\Pi_{3/2}$ fine-structure state of the OD product. For the case of the reaction with excited ND_3^+, the relative rotational populations were fit to a Boltzman distribution to yield temperatures of 990±30 K and 890±70 K for the OD $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ fine-structure components, respectively. For the ground state ion, such a fit yields a temperature of 700±100 K for the OD $^2\Pi_{3/2}$ fine-structure component. The results were compared to an RRKM-type model that predicts a rotational distribution of 800 K and 940 K for the reaction of the ion with $\nu_2 = 0$ and $\nu_2 = 1$, respectively. The excellent agreement is evidence for reaction through a long-lived complex.[8]

We also investigated the proton transfer channel for the reaction of HBr^+ with HBr in a state-specific manner by preparing the reagent ion in a selected internal state by REMPI and monitoring the disappearance of this ion by laser-induced fluorescence (LIF). A rate constant for proton transfer of $(6.7\pm1.6) \times 10^{-10}$ cm^3/s was found. The reaction of HBr^+ with HBr and DBr was also studied in a selected ion flow tube. The reactions were found to be quite complex, producing charge transfer, proton transfer, and hydrogen transfer products. The rate constants were $(5.3\pm1.3) \times 10^{-10}$ cm^3/s for the removal of HBr^+ by HBr and DBr neutrals.[9]

C. Thermodynamically Stable Diatomic Dications

Quadrupole mass spectrometry has been used to detect BaX^{2+} (X = F, Cl, Br, I), $SrCl^{2+}$, $CaBr^{2+}$, and $MgBr^{2+}$. Dications were produced by electron bombardment of an effusive beam containing the stable alkaline earth monohalide radical precursor. All species but $MgBr^{2+}$ are predicted to be thermodynamically stable. $MgBr^{2+}$ is likely to be metastable but with a lifetime sufficiently long to allow its detection in the millisecond timescale. We have explained the expected trends in stability in terms of simple and highly intuitive bonding models.[10]

D. Optical Diagnostics for Hostile Environments

Two approaches exploiting optical laser sources have been developed to diagnose specific chemical species present in hostile environments. In particular, cavity ring-down spectroscopy (CRDS) and two-photon light induced fluorescence (TP-LIF) have been deployed to detect potential reactants present in a hot-filament chemical vapor deposition system used to grow diamond films, in order to study the reactions that take place and to optimize diamond growth conditions. Such hostile environments, which also encompass reactive plasmas, flames, sparks, and discharges are often complex, present highly luminous backgrounds, and preclude the use of traditional absorption techniques.

CRDS is a novel diagnostic tool based on enclosing the sample of interest in an optical resonator, and probing the absorption losses inside the resonator by measuring its finesse. This is accomplished by injecting light into the resonator over a finite amount of time, and then monitoring the rate of decay of light trapped inside the resonator with a photodetector as a function of time. CRDS has two significant advantages as a diagnostic in hostile environments. It is many orders of magnitude more sensitive than traditional absorption spectroscopy, and it is insensitive to collisional quenching processes or bright background light. By implementing CRDS with a 216 nm laser system, the absolute concentration of methyl radicals present in the hot-filament reactor were measured as a function of distance from the hot-filament. These radicals are generated with a 2400 K filament from a 20 Torr mixture of 0.5% methane in hydrogen gas. The sensitivity to methyl radicals achieved was comparable to column densities of 3 x 10^{12} radicals/cm^2 . The spatial profiles revealed a cylindrical symmetry about the filament axis, with a peak in the methyl concentration at 4 mm from the filament (1.04 x 10^{14} molecules/cm^3). Preliminary work was also performed to explore the 3 μm fingerprint region for other potentially interesting hydrocarbon free radicals (CH_2, CH, C_2H, etc.) that exist under diamond deposition conditions. Sensitive detection of water vapor by its overtones in the near-infrared spectral region suggests that CRDS is well-suited for further spectroscopic studies of radicals in the mid-infrared.

TP-LIF was used to investigate the effects of atomic hydrogen (H) on diamond synthesis, in order to determine the actual mechanisms involved, such as preferential etching of graphite rather than diamond, clearing of growth sites by recombination of two H atoms on the diamond surface, or generation of carbon-containing free radicals, like methyl. The large energy spacing between the H ground state, 1s, and its first excited state, 2p (10.2 eV), means that single-photon optical techniques would require regeneration of 121.5 nm in the vacuum ultraviolet. A two-photon LIF setup to determine both the temperature and absolute concentration of H in the hot-filament reactor was constructed as follows. A ground-state hydrogen atom was excited from 1s to 2s by absorbing two 243 nm photons, then was collisionally mixed with 2p. Subsequently, it fluoresced to the 1s level. Lyman-a emission at 121.5 nm was detected by a solar-blind photomultiplier tube (PMT) detector that efficiently rejects any incandescent background. In this experiment, the background noise was so low that a statistical error bar was 50 K or less in the temperature measurements from the Doppler line width, which is superior to current temperature measurements in similar conditions. Generally, the LIF signal was linearly proportional to the concentration of the fluorescence species and gave the relative concentration or even absolute concentration after additional calibration with a sample of known concentration. For the relatively thin optical medium, Lyman-a radiation was not completely trapped by the surrounding hydrogen. Therefore, once the detected signal was normalized to the laser pulse energy, it was experimentally possible to obtain a square law energy dependence, expected from the theory of two-photon absorption, and to obtain a reasonable temperature and concentration for the H atoms present.

Overall, in terms of the diamond synthesis reactions, it was found that with no molybdenum deposition substrate present, a large temperature slip occurred at the filament owing to the small surface area of the filament. This phenomenon is called "weak filament control" on the gas-phase temperature, so that a reversed hydrogen temperature appears in the absence of a substrate. Higher filament temperatures produced higher spatial profiles of H temperatures, because the filament remains the only heating source in the reactor. It was also found that the gas temperatures reach a stable value of 400 K away from the filament, as thermal conditions stabilized close to room temperature. It was found that power increases of the substrate directly translates into higher gas phase temperatures, more or less independent of the filament temperature, because the filament power supply provides only 10 to 30% of the power input to the substrate. It was therefore impossible to separate the substrate influence on the phase temperature of the filament, and in future studies, both must be considered simultaneously. Thus, the TP-LIF method allowed measurements of both H temperature and absolute concentration on an absolute basis. The concentration is of particular value because most other methods yield only the relative concentration without additional calibration. Presently, H temperatures have been confirmed with further methyl radical measurements inside the reactor.

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PERSONNEL SUPPORTED

GRADUATE STUDENTS

Glenn C. Jones, Jr., Ph. D. 08/95, "Reactions of Mode-Selected Ammonia Ions with ND_3 and D_2".

Robert D. Guettler, Ph. D. 02/95, "State-Selected Studies of the $NH_3^+ + ND_3$ Ion-Molecule Reaction".

Skip Williams, Ph. D. 01/94, "Degenerate Four-Wave Mixing Spectroscopy in Collisionally Dominated Environments: Theory and Application".

Richard J. Green, Ph. D. 04/97, "State-to-State Ion-Molecule Chemistry in a Thermal Gas Cell: The Reaction of the Ammonia-D_3 Ion with Deuterium Oxide".

Yeming Ma, Ph. D. 08/97, "Measurements of Atomic Hydrogen Temperature and Methyl Radical Concentration in a Diamond Chemical Vapor Deposition Reactor".

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