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<p>13. ABSTRACT (Maximum 200 words) The influence of vibrational and collision energy on ion-molecule reactions was investigated by measuring the cross sections for reactions of <math>\text{NH}_3^+</math> created with varying degrees of excitation in the umbrella bending and symmetric stretching modes. Under these conditions, the three major product channels for the <math>\text{NH}_3^+/\text{CD}_3\text{NH}_2^+</math> system are <math>\text{CD}_3\text{NH}_2^+</math>, <math>\text{CD}_2=\text{NH}_2^+</math> and <math>\text{CD}_3\text{NH}_3^+</math>. Two minor product channels correspond to <math>\text{NH}_3\text{D}^+</math> and <math>\text{NH}_4^+</math>. This reaction is found to be mode selective based on the reactivity of two isoenergetic vibrational states having differing concerted atom motions. The reaction of state selected ammonia ions with <math>\text{CD}_4</math> produces two major products, deuterium abstraction (<math>\text{NH}_3\text{D}^+</math>) and collision induced dissociation (<math>\text{NH}_2\text{D}^+</math>). The reaction was found not to be mode selective. In the <math>\text{NH}_3^+/\text{THF}</math> system, four products were identified: hydrogen abstraction (<math>\text{NH}_4^+</math>), charge transfer (<math>\text{C}_4\text{H}_8\text{O}^+</math>), proton transfer (<math>\text{C}_4\text{H}_9\text{O}^+</math>) and an endothermic product corresponding to charge transfer with loss of H (<math>\text{C}_4\text{H}_7\text{O}^+</math>). The branching ratios show a dependence on ammonia ion vibrational state. In separate experiments, it was demonstrated that the new class of quantum cascade lasers that produce tunable infrared coherent radiation are well suited to cavity ring-down detection of ammonia. A detection limit of less than one part per billion was achieved.</p>					
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## Final Technical Report, F49620-98-1-0040

This grant supported research on two separate projects: (1) state-selected ion-molecule reactions and (2) detection of ammonia as a surrogate for hydrazine using cavity ring-down spectroscopy.

### 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 may have a pronounced effect while others may have little or none. The characterization of such differences can yield much information about the mechanics of chemical reactions. It was for these reasons that we sought to explore the effects of collision energy and reactant vibrational mode on the outcome of ion-molecule reactions.

The ammonia ion is particularly well suited for these studies because several of its vibrational states are readily accessible through resonance-enhanced multiphoton ionization (REMPI). These states include a progression of up to ten quanta of out-of-plane, "umbrella," bending motion ( $1^0 2^n$ ) and another in which a single quantum of symmetric stretch ( $n_1$ ) 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 motion 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 ( $\text{ND}_3$ ) and found it to be mode-selective.<sup>1,2</sup> 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. This result stands in contrast to three other systems that were found not to be mode-selective, specifically reactions of ammonia ions with  $\text{D}_2$ ,  $\text{D}_2\text{O}$ , and  $\text{CD}_4$ .<sup>3-5</sup> We have extended these studies to the reactions of ammonia ion with methylamine and tetrahydrofuran.

We completed the study of the reaction of state-selected ammonia ions with  $\text{CD}_4$  and measured relative cross sections for two major products.<sup>5</sup> 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 formation of  $\text{NH}_3\text{D}^+$  is inhibited with increasing collision energy. A second product with  $m/z = 18$ , identified as  $\text{CD}_3^+$ , is observed with an apparent threshold for formation of ca. 5 eV and a cross section which increases with increasing collision energy beyond that threshold. The mechanism for formation of  $\text{CD}_3^+$  involves collision-induced dissociation of  $\text{CD}_4$  (or  $\text{NH}_3^+$ ) which leads to the formation of a short-lived  $[\text{NH}_3\text{CD}_3]^+$  ( $[\text{NH}_2\text{CD}_4]^+$ ) complex, which then decays to products.

The cross section for the D-abstraction product is enhanced with increasing internal energy (umbrella bending) at collision energies below 6.0 eV and independent of internal energy at higher collision energies. Examination of the velocity distributions for this product shows that the enhancement is greater for forward-scattered products indicating that ammonia-ion vibrational energy enhances reactivity at large impact parameters. Also, the velocity distributions reveal that this reaction is well described by the spectator-stripping model. Collision energy and internal energy in the  $v_2$

vibrational mode of the reactant ion are equivalent in the formation of  $\text{CD}_3^+$ . Comparison of cross sections for products formed from ammonia ions prepared in the two nearly isoenergetic states discussed above indicates that this reaction is not mode-selective.

We have also completed the study of the reaction of state-selected ammonia ions with  $\text{CD}_3\text{NH}_2$  and measured relative cross sections for five major products.<sup>6</sup> The most abundant product at all collision energies results from exothermic electron transfer ( $m/z = 34$ ). Additional exothermic products arise from proton transfer ( $m/z = 35$ ) and from H and D abstraction ( $m/z = 18, 19$ ). A thermoneutral product is also observed with  $m/z = 32$  that corresponds to  $\text{CD}_2=\text{NH}_2^+$ . This product likely results from dissociative charge transfer, that is, from a dissociation reaction that occurs on the charge-transfer surface. All three of the high mass ion products ( $m/z = 32, 34, 35$ ) are strongly backward-scattered in the center-of-mass frame, whereas the two low mass ion products ( $m/z = 18, 19$ ) are strongly forward-scattered. The velocity distributions of all of the products approach the spectator-stripping limit.

The relative cross section for formation of each product is a decreasing function of collision energy at all ammonia vibrational states studied. This behavior is typical for ion-molecule reactions with no threshold energy. Furthermore, the relative reaction cross section for each product, aside from  $\text{CD}_2=\text{NH}_2^+$ , decreases with increasing energy in the  $\nu_2$  mode of the ammonia ion reactant. The cross section for  $\text{CD}_2=\text{NH}_2^+$ , on the other hand, shows about a two fold enhancement at low collision energies in going from  $\nu_2 = 1$  to  $\nu_2 = 9$ , corresponding to a vibrational energy range of 0.12-1.08 eV in the ammonia ion. This trend in cross section verses vibrational energy is opposite the result seen verses collision energy, indicating that these two forms of energy are not equivalent in the formation of  $\text{CD}_2=\text{NH}_2^+$ . Comparison of the branching ratios for the products with  $m/z = 32$  and 34 obtained from ammonia ions prepared in the  $1^02^5$  and  $1^12^2$  states indicates that this reaction is vibrationally mode specific.

An abbreviated study of the reaction of state-selected ammonia ions with tetrahydrofuran has also been completed.<sup>7</sup> In this reaction, the most abundant product results from exothermic H-atom abstraction ( $m/z = 18$ ). Products arising from exothermic charge transfer ( $m/z = 72$ ) and proton transfer ( $m/z = 73$ ) are also observed. In addition, an endothermic product corresponding to charge transfer with loss of H ( $m/z = 71$ ) is observed. The branching ratios for this channel and for the charge-transfer channel show a dependence on ammonia ion vibrational state.

To date, we have examined the reactions of ammonia ions with six different neutral species that vary in size from two ( $D_2$ ) to thirteen atoms (THF). Each reaction system that has an exothermic charge-transfer channel ( $NH_3^+ + ND_3$ ,  $CD_3NH_2$ , and THF) exhibits mode selectivity, whereas those systems for which the charge-transfer channel ( $NH_3^+ + D_2$ ,  $D_2O$ , and  $CD_4$ ) is endothermic do not display mode selectivity. In addition to the results from our laboratory, Anderson, et al. have studied the reaction of state-selected ammonia ions with methanol. This reaction system also has an active charge-transfer channel, and the reaction was determined to be mode selective.<sup>8</sup>

## **B. Detection of Ammonia as a Surrogate for Hydrazine**

Cavity ring-down spectroscopy of ammonia in nitrogen using a distributed-feedback quantum cascade laser was performed at 8.5  $\mu m$ . The QC lasers demonstrated continuous temperature tuning over 15 nm with 10 nm/min scan rates. Detection limits of 250 parts per trillion (ppt) of ammonia in nitrogen were obtained with averaging, and correspond to a noise-equivalent absorbance of  $1 \times 10^{-7}$ . This detection limit sets a world record in sensitivity for any technique employing quantum cascade lasers. This work demonstrates that these new tunable sources of coherent infrared light hold much promise

for analytical applications. Based on the success of the cavity ring-down technique, we have begun making plans to use this method to examine the products of discharges and ion-molecule reactions.

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