Mode selectivity in ion–molecule reactions of NH_3^+

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Abstract. Ammonia ions (NH_3^+) are prepared in two internal states of nearly the same energy, a state with five quanta in the umbrella bending mode ($E_{int} = 0.60$ eV) and another state with one quantum in the all-symmetric stretch and two quanta in the umbrella bending mode ($E_{int} = 0.63$ eV). These ions are allowed to react with different neutral reagents, and the product ions are mass analyzed and detected. For each reaction, the product branching ratios are measured as a function of center-of-mass collision energy. Whereas reactions with D_2O, D_2, and CD_4 are found to be uninfluenced by the state preparation of the NH_3^+ reagent, reactions with ND_3, partially deuterated methylamine (CD_3NH_2), and tetrahydrofuran (c-$(CH_2)_4O$) show varying degrees of mode selectivity, the reaction with tetrahydrofuran to the least extent. We suggest that mode selectivity in these ion–molecule reactions should be a general feature when the charge transfer channel is energetically open, the geometry of the reagent ion differs markedly from the corresponding neutral, and different reaction pathways compete for product production.

PACS: 82.30.Fi

Professor J. Wolfrum has pioneered the use of lasers to study combustion processes and elementary reaction dynamics [1–3]. An example is his method of laser photolysis followed by laser-induced fluorescence in which he and his co-workers have been able to study, for example, the classic reactions $H + O_2 \rightarrow OH + O$ and $H + H_2O \rightarrow OH + H_2$. In a similar spirit, we use laser multiphoton ionization to prepare ions in known internal states and study their ion–molecule chemistry using a tandem quadrupole-octopole-quadrupole mass spectrometer. It is a pleasure to contribute this brief report for this special issue celebrating the achievements of Professor Wolfrum.

Since the advent of high-powered coherent light sources, chemists have sought to control the outcome of reactions at

the molecular level [4–7]. A specific goal is to excite different regions of a molecule or different internal motions to cause differing reactivities. Examples of such mode-selective behavior have been demonstrated for reactions of both neutral [8–16] and ionic species [17–26]. This behavior is rare, in general, and has been limited to small molecules. We report here that state-selected ammonia ions display vibrational mode selectivity in reactions with methylamine (CH_3NH_2) and to a lesser extent with tetrahydrofuran (c-$(CH_2)_4O$). Thus, mode selectivity has been demonstrated for reagents possessing together 17 atoms with 45 degrees of internal freedom. We suggest that mode selectivity can occur whenever a charge-transfer channel (involving a fast electron transfer) is active in ion–molecule reactions in which the geometry of the ion and the corresponding neutral differ. The degree of the mode selectivity involves a variation in product yield that is less than 30 percent in the reactions we have explored to date, but the effect is reproducible.
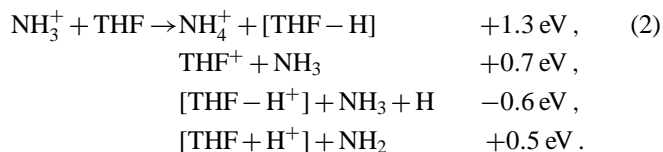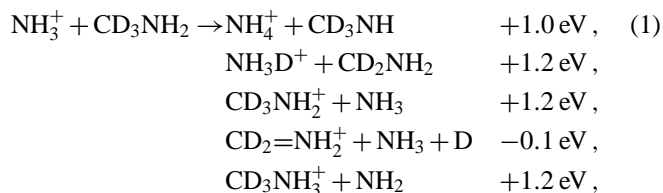
1 Mode-selective reactions of ammonia ions

An initial study of the reaction of state-selected ammonia ions, prepared with varying degrees of excitation in the symmetric, in-plane ν_1 stretch and the out-of-plane ν_2 umbrella bend, with ND_3 was found to be mode-selective [19]. For this reaction, umbrella bending enhanced the charge-transfer channel, whereas the symmetric stretch was inactive. Subsequent studies of the reactions of NH_3^+ with D_2O [24], D_2 [25], and CD_4 [26], for which charge transfer is endothermic, showed no evidence of mode selectivity. We postulated that the high degree of vibrational overlap (Franck–Condon principle) between the ammonia ion excited in the ν_2 vibrational mode and the nascent neutral ammonia resulting from charge transfer drives mode selectivity for ion–molecule reactions involving the NH_3^+ ion.

We report here results of studies of the reactions of state-selected ammonia ions with d3-methylamine (CD_3NH_2) and tetrahydrofuran (THF), shown in reactions (1) and (2) respectively, where the approximate values of the energy released

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are indicated.

$$NH_3^+ + CD_3NH_2 \rightarrow NH_4^+ + CD_3NH \qquad +1.0\,eV, \quad (1)$$
$$NH_3D^+ + CD_2NH_2 \qquad +1.2\,eV,$$
$$CD_3NH_2^+ + NH_3 \qquad +1.2\,eV,$$
$$CD_2{=}NH_2^+ + NH_3 + D \quad -0.1\,eV,$$
$$CD_3NH_3^+ + NH_2 \qquad +1.2\,eV,$$

$$NH_3^+ + THF \rightarrow NH_4^+ + [THF-H] \qquad +1.3\,eV, \quad (2)$$
$$THF^+ + NH_3 \qquad +0.7\,eV,$$
$$[THF-H^+] + NH_3 + H \quad -0.6\,eV,$$
$$[THF+H^+] + NH_2 \qquad +0.5\,eV.$$

Both of these reactions have exothermic charge transfer channels and display mode selectivity.

2 Experimental procedure

The experimental procedure has been described in detail elsewhere [27]; consequently, only a brief description is presented. Ammonia ions are created with varying degrees of excitation in the symmetric, in-plane ν_1 stretch and the out-of-plane ν_2 umbrella bend using $2+1$ resonance-enhanced multiphoton ionization by crossing the frequency-doubled output of a Nd:YAG-pumped dye laser with a molecular beam of 5% ammonia in helium. Ions are extracted orthogonally into a quadrupole mass filter for mass selection. The ions are then focused into an octopole ion guide that is concentric with a collision cell that contains the neutral target gas. Ionic products and unreacted ammonia ions are focused into a second quadrupole for mass analysis and are detected with fast microchannel plates.

Product branching ratios are obtained by dividing the total number of counts for each product by the sum of all product counts. We measure the dependence of the product branching ratios on the collision energy and on vibrational energy. The laboratory-frame collision energy E_{lab} is varied by applying a DC offset (in the range of -0.5 to -15 V) to the octopole rods. The center-of-mass frame collision energy E_{CM} is calculated from E_{lab} according to $E_{CM} = E_{lab}[m/(m+M)]$, where m is the mass of the neutral target and M is the mass of the ammonia ion. Two excited states of ammonia ion have been studied. One of these only has excitation in the umbrella bending mode ($\nu_1 = 0$, $\nu_2 = 5$) hereafter denoted $1^0 2^5$, with internal energy, $E_{int} = 0.60$ eV. The other has excitation in both bending and stretching modes ($1^1 2^2$ with $E_{int} = 0.63$ eV). Comparison of product branching ratios from ammonia ions with the same collision energies prepared in the nearly isoenergetic $1^0 2^5$ and $1^1 2^2$ states measures the mode selectivity of the reaction.

3 Results

The reaction of ammonia ion with CD_3NH_2 at center-of-mass collision energies in the range of 0.5–10 eV produces several products. Figure 1 shows the dependence of the branching ratios on collision energy for two different ammonia ion
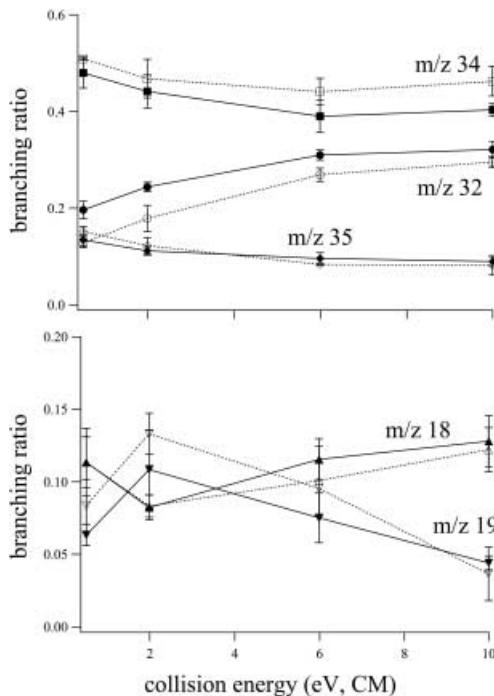
Fig. 1. Product branching ratios from the reaction of ammonia ions prepared in vibrational states $1^0 2^5$ (*solid lines* and *symbols*) and $1^1 2^2$ (*dotted lines* and *open symbols*) with CD_3NH_2. In this figure, NH_4^+ (▲), NH_3D^+ (▼), $CD_2{=}NH_2^+$ (●), $CD_3NH_2^+$ (■), and $CD_3NH_3^+$ (◆) are shown

preparations. 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 $CD_2{=}NH_2^+$. This product likely results from dissociative charge transfer, that is, from a dissociation reaction that occurs on the charge-transfer surface. Product as-
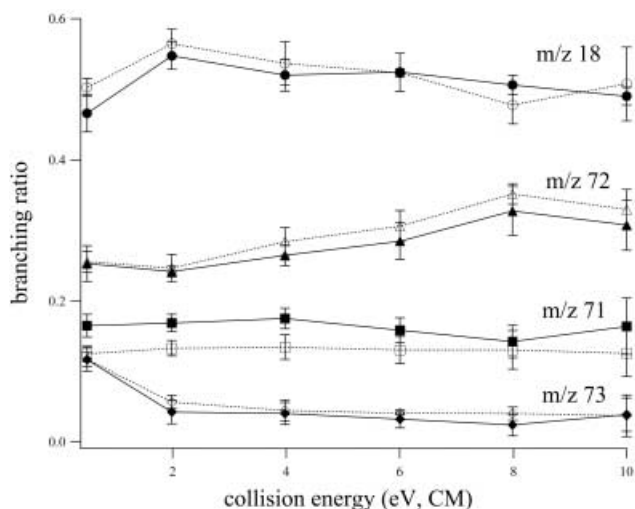
Fig. 2. Product branching ratios from the reaction of ammonia ions prepared in vibrational states $1^0 2^5$ (*solid lines* and *symbols*) and $1^1 2^2$ (*dotted lines* and *open symbols*) with c-$(CH_2)_4O$. In this figure, products arising from H atom abstraction (m/z 18, ●), charge transfer (m/z 72, ▲), charge transfer with loss of hydrogen (m/z 71, ■), and proton transfer (m/z 73, ◆) are shown

signments are based, in part, on results of isotopic substitution experiments using ND_3^+ as the reactant ion and CD_3ND_2 as the reactive neutral. Comparison of the branching ratios for the products with $m/z = 32$ and 34 obtained from ammonia ions prepared in the $1^0 2^5$ and $1^1 2^2$ states indicates that this reaction is vibrationally mode specific. The error bars represent one standard deviation from the mean.

Figure 2 shows the collision energy dependence of the product branching ratios from the reaction of NH_3^+ with THF. 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. Although the error bars overlap in some cases, the Student's t-test indicates that the two product distributions ($1^0 2^5$ and $1^1 2^2$ data sets) are distinct to within 95% confidence.

4 Conclusions

To date, we have examined the reactions of ammonia ions with six different neutral species that vary in size from 2 (D_2) to 13 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. [22] 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.

The charge-transfer reactions investigated in this work can be described by direct electron-transfer mechanisms, i.e., they do not proceed via long-lived complexes. This mechanism is supported by the facts that (a) we do not observe forward–backward symmetry in the center-of-mass product velocity distributions, and (b) we do not observe products arising from isotope scrambling, such as NH_2D^+ from the reaction of $NH_3^+ + CD_3ND_2$. Further, the electron-transfer reaction is fast as compared to the time scale for nuclear motion. The fact that we see reproducible differences in product branching from ions prepared in different vibrational modes indicates that the internal energy of the ammonia ion is not randomized through intramolecular vibrational relaxation during the reactive encounter. The difference in reaction product yield is therefore a direct result of the concerted atom motions of the state-selected ion.

Charge-transfer reactions between ions and molecules have been studied in detail [28–30]. For small systems such as $Ar^+ + HD$, it has been shown that energy resonance is an important consideration [31]. Charge-transfer reactions necessarily involve a nonadiabatic curve crossing. For such a crossing to occur, coupling between the diabatic states corresponding to products and reactants must be large. In the reactions of ammonia ions with methylamine or THF, the large number of degrees of freedom readily cause the energy-resonance condition to be met.

We ascribe the mode selectivity in these reactions to result from increased Franck–Condon vibrational overlap between the ammonia ion excited in the ν_2-vibrational mode and the nascent neutral ammonia molecule resulting from charge transfer. Thus, in systems with many degrees of freedom, the identity of the neutral reactant molecule is unimportant so long as it can donate an electron to the ammonia ion. We predict that this mode-selective behavior, although often small, is a general result. Potentially, such effects might be observed with very large neutral targets, even including surfaces.

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