State-selected studies of the reaction of \( \text{NH}_3^+ (\nu_1, \nu_2) \) with \( \text{D}_2 \)

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Dedicated to the memory of Professor Robert R. Squires
Received 18 January 1999; in final form 1 April 1999

Abstract

The title reaction has been studied in a guided ion beam instrument at hyperthermal energies, resulting in ion products \( \text{NH}^+ \) and \( \text{NH} \). Ammonia ions were prepared with differing amounts of excitation in the in-plane symmetric stretching and the out-of-plane symmetric bending mode using resonance-enhanced multiphoton ionization. Comparison of the reactivity of two nearly isoenergetic states \((\nu_1 = 0, \nu_2 = 5)\) and \((\nu_1 = 1, \nu_2 = 2)\) with differing concerted atom motions indicates that this reaction is not mode selective. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The reaction of \( \text{NH}_3^+ \) with \( \text{H}_2 \), reaction (1), is unusual for an exothermic ion–molecule reaction in that it is very inefficient. A rate coefficient of \( 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) was established both from an ICR study by Kim et al. [1] and from a flowing afterglow study by Fehsenfeld et al. [2]. This value is nearly four orders of magnitude smaller than the Langevin collision rate coefficient \( \approx 2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

\[
\begin{align*}
\text{NH}_3^+ + \text{H}_2 & \rightarrow \text{NH}_2^+ + \text{H} \quad \Delta H = -1.04 \text{ eV} \quad (1) \\
\text{NH}_3^+ + \text{D}_2 & \rightarrow \text{NH}_2\text{D}^+ + \text{D} \quad \Delta H \approx -1 \text{ eV} \quad (2a)
\end{align*}
\]

\[
\begin{align*}
\rightarrow \text{NH}_2\text{D}^+ + \text{HD} & \quad \Delta H = 0 \text{ eV} \quad (2b) \\
\rightarrow \text{NH}_2\text{D}^+ + \text{H} + \text{D} & \quad \Delta H = 4 \text{ eV} \quad (2c)
\end{align*}
\]

In an effort to explain these results, this reaction and the isotopic variant shown in reaction (2), have been studied using a variety of techniques. The inefficiency of the reaction as well as its strong kinetic energy dependence were initially attributed to a small barrier in the entrance channel [2]. This simple picture proved inconsistent with the variable temperature work of Adams and Smith [3], Luine [4], and Barlow [5]. The exponential drop in the rate coefficient was found to level off around 100 K [3]. At very low temperatures \((< 20 \text{ K})\), the rate coefficient was found to increase with decreasing temperature. These observations suggested a mechanism involving a long-lived collision complex at low temperatures.

In addition to the D-abstraction channel, an H/D exchange channel, reaction (2b), was also observed.
in the studies mentioned above, as well as in a beam-gas study by Eisele et al. [6]. The kinetic energy dependence of both reactions (1) and (2) was studied in the range of 0.5–10 eV. No indication of isotopic scrambling was observed in this range, which suggests that the reaction does not proceed via a long-lived complex at hyperthermal energies. The formation of NH$_3$D$^+$ product was found to increase dramatically above 4 eV. This increase was attributed to the opening of a new channel, reaction (2c), in which the H–D bond is broken. Fehsenfeld et al. [2] and others [7–9] have also investigated the internal energy dependence of reactions (1) and (2). The photoionization studies of Karachevtsev et al. [7] showed an increase in the total reaction cross-section with vibrational excitation. Bowers and co-workers [8] examined both the translational (0–1 eV) and vibrational energy (1–5 eV) dependence of this reaction and found that the exchange product is enhanced primarily by vibrational energy whereas the abstraction product is enhanced by kinetic energy. In previous work from this laboratory, this reaction was studied in the range of 0.5–10 eV. (2 + 1) resonance-enhanced multiphoton ionization (REMPI) was used to prepare ammonia ions with 0–10 quanta of vibrational excitation in the $v_2$ out-of-plane bending vibration [9]. Vibrational excitation was found to affect the reaction only at collision energies above 4 eV, which was attributed to a change in the rate of reaction (2c).

Recently, our laboratory has investigated the reactions of state-selected ammonia ions with small hydrides [10,11]. Several improvements to the experiment have been made since the work of Morrison et al. [9] which allow for a more thorough investigation of these systems. First, an octopole ion guide [12] was added in the collision cell region to ensure collection of both forward- and side-scattered products [13]. Second, in addition to excitation in the $v_2$ vibrational mode, we can also access the $v_1$ in-plane symmetric stretching mode. By comparing the reactivity of ammonia ions prepared in nearly isoenergetic states with differing concerted atom motions, an indication of the vibrational mode selectivity of the reaction is obtained. Third, lab-frame velocity distributions of the reactant and product ions can be determined which provide an indication of the nature of the product scattering. This Letter describes investigations of the mode specificity of the reaction of state-selected ammonia ions with D$_2$ at hyperthermal energies.

2. Experimental section

All experiments were performed using a guided-ion-beam instrument that has been described in detail elsewhere [13]. Briefly, a molecular beam formed by expansion of a mixture of 5% NH$_3$ in He is crossed with the frequency-doubled output of a Nd:YAG-pumped dye laser operating at 20 Hz. Ionization is accomplished via a (2 + 1) REMPI scheme that has been described in detail elsewhere [14]. The nascent ions are extracted orthogonally and are focused into a quadrupole mass filter for mass selection. The mass-selected ion beam is injected into an r.f.-only octopole ion guide [12]. A constant DC offset is applied to the octopole rods which serves to define the nominal laboratory-frame collision energy. The ions pass through a collision cell that is filled with a static pressure of D$_2$ maintained at pressures (ca. 50 µTorr) corresponding to single-collision conditions. Reactant and product ions are then extracted from the octopole into a second quadrupole mass filter and detected with fast microchannel plates.

Data acquisition and analysis routines have been presented elsewhere [10,13]. Briefly, product ions are counted via a multichannel scalar with a 200 MHz discriminator. Ion time-of-flight (TOF) profiles are obtained by recording the arrival time of ions at the detector after a start pulse from a photodiode trigger off the laser pulse. Reactant ion signal is not counted because the pulse pair resolution of our discriminator is too small to insure that all reactant ions are counted. Instead the raw current off the plates is amplified, smoothed, and digitized with an 8-bit transient recorder. Relative reaction cross-sections are obtained by dividing the sum of the product counts by the integrated area of the reactant waveform. Individual product branching ratios are obtained by dividing the total counts for a single product by the sum of all product counts.

TOF profiles are recorded at collision energies in the range of 0.5–10 eV (center of mass (CM)). The CM collision energy, $E_{CM}$, is obtained from the lab-frame energy, $E_{lab}$, via $E_{CM} = E_{lab}(m/m + M)$, where
where \( M \) and \( m \) are the masses of the ion and the neutral target respectively. For this study, two excited vibrational states were investigated in addition to the vibrational ground state. One preparation has excitation in the \( \nu_2 \) bending mode only (\( \nu_2 = 0; \nu_2 = 5 \) with internal energy, \( E_{\text{int}} \), of 0.60 eV, hereafter denoted \( 1^0 2^5 \) for brevity), whereas the other has excitation in both the bend and the symmetric stretch (\( 1^0 2^7; E_{\text{int}} = 0.63 \) eV). Comparing the cross-sections obtained from the ground state and the \( 1^0 2^5 \) state gives an indication of the effect of symmetric bending on the reaction. An indication of the mode selectivity of this reaction can be obtained by comparing the reactivity of the nearly isoenergetic states \( 1^0 2^5 \) and \( 1^1 2^2 \).

3. Results and discussion

The ion–molecule reaction \( \text{NH}_3^+ + \text{D}_2 \) has been studied over a range of collision energies from 0.5 to 10 eV (CM) in which the ion reagent is prepared in selected vibrational levels of the \( \nu_1 \) in-plane symmetric stretch and the \( \nu_2 \) symmetric bending mode. Products with \( m/z = 18 \) and 19 are observed, corresponding to \( \text{NH}_2 \text{D}^+ \), from D-atom abstraction, and \( \text{NH}_3 \text{D}^+ \), from formal isotope exchange. The \( \text{NH}_2 \text{D}^+ \) product is dominant at low collision energies and has a cross-section for formation that increases slightly and then levels off with collision energy as shown in Fig. 1. The isotope-exchange product has an apparent threshold for formation of ca. 4–5 eV. Morrison et al. interpreted that \( \text{NH}_2 \text{D}^+ \) is formed from unimolecular dissociation of a vibrationally excited \( \text{NH}_3 \text{D}^+ \) molecule arising from direct D-abstraction as shown in reaction (3).

\[
\text{NH}_3^+ + \text{D}_2 \rightarrow \text{NH}_3 \text{D}^+ + \text{D} \rightarrow \text{NH}_2 \text{D}^+ + \text{D} + \text{H}
\]

(3)

An alternative mechanism for \( \text{NH}_3 \text{D}^+ \) formation exists, however, that can be proposed based on other work from our laboratory. A product of the same mass with similar threshold energy for formation was observed in the reaction of \( \text{NH}_3^+ \) with \( \text{D}_2 \text{O} \) and was identified as \( \text{NH}_3 \text{D}^+ \) [15]. In that system, little or no D-abstraction product (\( \text{NH}_2 \text{D}^+ \)) was observed at the collision energies studied (0.5–10 eV CM), arguing against unimolecular dissociation of \( \text{NH}_3 \text{D}^+ \) as the source of \( \text{NH}_3 \text{D}^+ \) in that study. A multi-step mechanism for \( \text{NH}_3 \text{D}^+ \) formation was proposed in which the first step is collision-induced dissociation of the \( \text{NH}_3^+ \) species resulting in a complex with composition \( [\text{NH}_3 \text{D}_2 \text{O}]^+ \) that then proceeds to products. The CID-mediated complex formation mechanism was supported by the nature of the \( \text{NH}_3 \text{D}^+ \) velocity profiles which are symmetric about the center of mass and very narrow (ca. 0.6 eV HWHM) at all collision energies, consistent with a long-lived complex.

A similar mechanism for \( \text{NH}_3 \text{D}^+ \) formation is proposed here for the present system as shown in reaction (4).

\[
\text{NH}_3^+ + \text{D}_2 \rightarrow \text{NH}_3 \text{D}_2^{+*} + \text{H} \rightarrow \text{NH}_2 \text{D}^+ + \text{H} + \text{D}
\]

(4)

Velocity profiles for \( \text{NH}_3 \text{D}^+ \) and \( \text{NH}_3 \text{D}^+ \) were determined according to a procedure outline in detail in the study described above [15]. Unfortunately, owing to the kinematics of this system (the center-of-mass of the system is located always nearly on the nitrogen atom of ammonia), we were unable to extract meaningful information from the velocity experiments. The spread in the velocity distributions resulting from the kinetic energy spread of the ammonia ion beam and the thermal motion of the target is on the same order as the energetic limits (all available energy into forward or back scattering) for the reaction. We can, therefore, not use product
scattering information to rule out either mechanism for NH$_2$D$^+$ formation.

The effect of symmetric bending on the present reaction was obtained by comparing reaction cross-sections for NH$_2$ formed in the 1$^6$2$^0$, 1$^6$2$^2$ and the 1$^6$2$^5$ vibrational states. Bending vibration enhances the exchange channel at high collision energies while inhibiting the abstraction channel as shown in Fig. 2. We find that vibrational energy has little or no effect on either channel at energies below 4 eV in agreement with earlier results [9]. These results are consistent with formation of NH$_2$D$^+$ from vibrationally excited NH$_3$D$^+$. However, enhancement of the NH$_2$D$^+$ cross-section at high energies could also be the result of increased NH$_2$ CID arising from internal excitation above the threshold for N–H bond dissociation. We are presently unable to distinguish between the two different possible mechanisms for NH$_2$D$^+$ formations; in fact, both mechanisms may be operable.

Fig. 3 shows the product branching ratios for NH$_2$ created in two isoenergetic states (1$^6$2$^5$ and 1$^6$2$^3$) with differing concerted atom motions. The branching ratios for both products are identical at all energies indicating that this reaction is not vibrationally mode specific. In a recent study from this laboratory, it was found that the reaction of state-selected ammonia ions with ND$_3$ was mode selective [11]. In this system, the $v_3$ bend was found to enhance both the charge transfer (CT) and D-abstraction channels while depressing the proton transfer channel. The effect of bending vibration on the different channels was rationalized in terms of motion along (charge transfer and D-abstraction) or perpendicular to (proton transfer) the reaction coordinate for product formation [10]. In a subsequent study, the reaction of NH$_2$ with D$_2$O was found not to be mode selective [15]. It was suggested that the mode selectivity observed in the ND$_3$ system was a manifestation of the large vibrational overlap between the wave functions of the vibrationally excited NH$_2$ ion reactant and the neutral NH$_3$ product during charge transfer. There is a precedent for the use of Franck–Condon factors to predict chemical reaction dynamics. Berry used a ‘Golden Rule’ analysis to calculate HF product vibrational distributions from the reaction of F + H$_2$ [16]. In addition, Schatz and Ross outlined a procedure for predicting vibration–rotation distributions in atom–diatom reactions through the use of a generalized Franck–Condon overlap theory [17,18]. Our model suggests that systems without an active CT channel should display little or no mode selectivity. None of the systems lacking a CT channel that we have studied, including the present system, NH$_2$ + D$_2$O [15], and NH$_2$ + CD$_3$ [19], show mode selectivity. Additional studies of ammonia ion reactions with active CT channels are underway.

**Acknowledgements**

The authors thank R.D. Levine for helpful comments on vibrational overlap as a reaction control mechanism. The authors gratefully acknowledge the financial support of the Air Force Office of Scientific Research (Grant F49620-92-J-0074).
References