The Effect of the Molecular Dipole and Quadrupole Moments on Ion–Molecule Reaction Rates near 0 K

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Abstract: We review the results of our recent experimental and theoretical studies of gas-phase ion–molecule reactions involving the He$^+$ ion at low collision energies ($E_{\text{coll}}$), in the $k_B T = 0$–40 K range. To avoid heating of the ions by stray electric fields, the reactions are studied within the orbit of a Rydberg electron. We reach collision energies down to ~0 K by employing a merged-beam setup. In the case of a molecule with a dipole moment (e.g. ammonia), we observe a strong enhancement of the measured reaction yield with decreasing $E_{\text{coll}}$. This enhancement is attributed to rotational states which experience linear negative Stark shifts in the electric field of the ion. When the molecule has no dipole moment but a negative quadrupole moment (e.g. N$_2$), we observe a suppression of the total reaction yield at the lowest collision energy. Our results are interpreted with the aid of an adiabatic-channel model.

Keywords: Cold ion–molecule chemistry · Dipole moment · Quadrupole moment · Rydberg helium

We have developed an experimental technique to study ion–molecule reactions at very low temperatures (down to ~200 mK) by replacing the ion with an atom or molecule in a Rydberg state of high principal quantum number $n$.[8–16] The Rydberg electron moves on an orbit of large radius ($\sim r^2$, $\sim 50$ nm for $n = 30$) and does not affect the reaction of the ion core with the neutral molecules located within the electron orbit, but shields it from stray electric fields.[14,17–19] We use helium Rydberg atoms [referred to as He($n$)] which are merged with a supersonic beam of the molecule of interest using a Rydberg-Stark decelerator and deflector.[8,12,20] The collision energy can be varied by changing the velocity of the He($n$) atoms with the surface deflector while the velocity of the molecular beam (referred to as the ground-state (GS) beam) is kept constant. With this approach, one can achieve very low relative collision energies in the moving centre-of-mass reference frame of the colliding Rydberg-atom–molecule pair by exploiting the velocity dispersion taking place in the beam of neutral molecules, as was exploited recently in studies of Penning ionization reactions.[21,22]

1. Introduction

Ion–molecule reactions can be fast, barrierless and exothermic, proceeding with high rate coefficients even at low temperatures. These reactions play a key role for the synthesis of polyatomic species in dark molecular clouds (with temperatures in the 10–50 K range). The rate coefficients and product branching ratios of ion–molecule reactions are necessary as input parameters for kinetic models of the chemical reaction cycles in these clouds.

Ion–molecule reactions are challenging to study at temperatures below ~10 K because stray electric fields induce heating of the ions. A difference of only ~1 mV in the electric potential across the reactor zone is already sufficient to impart a kinetic energy of $\sim k_B T$ to a singly-charged ion. Effects of the interactions between the ion and the multipole moment of the molecule are expected to become significant at low temperatures, and have been studied theoretically.[3,4] Below 1 K, quantum phenomena may begin to emerge.[5–7]

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electric discharge.[12,23] After passing through two skimmers, the He⁺ beam is intersected at right angles by the frequency-tripled output of an Nd:YAG-pumped commercial dye laser (excitation wavelength ~260 nm, repetition rate 25 Hz), in the presence of a dc electric field. A one-photon excitation is driven to a low-field-seeking Rydberg-Stark state \((n,k,m) = (30,21,0)\) just below the Inglis-Teller field \((n = m)\) and the principal and magnetic quantum numbers, respectively, \(k = -(n-|m|-1):2:(n-|m|-1)\), and the Inglis-Teller field is the field at which the Stark manifolds of neighbouring \(n\) values start overlapping.[24]

After excitation, the He\((n)\) Rydberg atoms are captured in quadrupole traps formed above the surface of a 50-electrode Rydberg-Stark deflector and decelerator (see Fig. 1) by applying the appropriate electric potentials to several sets of its electrodes. By applying sinusoidally-varying potentials, the trapped cloud of Rydberg atoms (of radius ~ 0.5 mm and length ~ 3 mm) can be guided along the surface of the deflector, and accelerated or decelerated to a final velocity \((v_{\text{final}})\) in the 700–1200 m/s range. We estimate that ~100 Rydberg atoms reach the reaction region after deflection at each experimental cycle.

![Fig 1. A schematic diagram of the merged-beam setup with the 50-electrode surface Rydberg-Stark deflector and decelerator. The reaction product ions are collected in a time-of-flight mass spectrometer.](image)

The GS beam valve is operated with a pure gas containing the molecules of interest. It is temperature-stabilised to produce \(\nu = 1\) at each experimental cycle. After being merged with the molecules from the GS beam, the reaction product ions are extracted and collected on a microchannel plate (MCP) detector (schematically depicted in Fig. 1). The reaction-observation window is typically 7 μs.

The collision energy of the reaction is given by Eqn. (1):

\[
E_{\text{coll}} = \frac{1}{2} \mu v_{\text{rel}}^2 = \frac{1}{2} \mu \left(v_{\text{Ryd}} - v_{\text{GS}}\right)^2, \tag{1}
\]

where \(\mu\) is the reduced mass of the helium atom and the molecule, and \(v_{\text{GS}}\) is the velocity of the molecule. In the experiment, we change \(E_{\text{coll}}\) by varying \(v_{\text{GS}}\) with the appropriate potentials applied to the electrodes of the surface deflector, while \(v_{\text{Ryd}}\) is kept fixed.[12,13]

3. The Modified Langevin Ion–Molecule Interaction Potential

Usually, ion–molecule reactions are described by the Langevin model[26] in which the long-range interaction potential for the capture is given by Eqn. (2):

\[
V_L(R) = \frac{L^2}{2\mu R^2} - \frac{(Ze)^2\alpha^*}{8\pi\varepsilon_0 R^4}, \tag{2}
\]

where \(R\) is the separation between the ion and the molecule, \(L\) is the angular momentum of the colliding pair, \((Ze)\) is the charge of the ion, \(\alpha^* = \alpha/(4\pi\varepsilon_0)\) is the polarizability volume of the molecule and \(\alpha\) is the polarizability. The first term in Eqn. (2) is the centrifugal potential of the collision, while the second term describes the interaction between the ion and the induced dipole of the polarizable molecule. In the Langevin model, the reaction is assumed to proceed with unit probability if the collision energy is high enough to overcome the centrifugal potential energy barrier (this is known as the capture condition).

In the original Langevin model, the molecule is assumed to be a polarizable object, without any intrinsic charge distribution. Eqn. (2) leads to an expression for the Langevin capture rate coefficient, \(k_L\), which is temperature- and collision-energy-independent and given by Eqn. (3):

\[
k_L = \sigma v_{\text{rel}} = \sqrt{\frac{\pi \alpha (Ze)^2}{\epsilon_0 \mu}}, \tag{3}
\]

where \(\sigma = \pi b_{\text{max}}^2\) is the reaction cross section \((b_{\text{max}}\) is the maximum impact parameter for which the reaction still takes place).

In the presence of a molecular dipole or quadrupole moments, however, the interaction potential in Eqn. (2) must be modified in order to include the Stark shift, \(\Delta E_i\), of the molecule in rotational state \(i\) as it experiences the electric field of the ion.[13] Assuming that the molecule remains in its original quantum state as it approaches the ion, as in the adiabatic-channel model,[10,11] the total interaction potential is then given by Eqn (4):

\[
V_{\text{int, } i}(R) = V_L(R) + \Delta E_i. \tag{4}
\]

The inclusion of the Stark shift in Eqn. (4) can significantly modify the maximally-allowed angular momentum for each collision energy, \(L_{\text{max}} = \mu \nu v_{\text{rel}} b_{\text{max}}\) and lead to a reaction rate coefficient which is strongly rotational-state- and collision-energy-dependent, given by Eqn. (5):

\[
k_i(E_{\text{coll}}) = \frac{\pi L_{\text{max}, i}^2}{2\mu^3 E_{\text{coll}}}. \tag{5}
\]

4. Ion-dipole Enhancement of the Ion–Molecule Reaction Rate Coefficients at Low Energies

The results presented in this section are presented in more detail in ref. [13]. Shown in Fig. 2 are the reaction product-ion yields and calculated capture rate coefficients of the \(\text{He}^+ + \text{NH}_3\) and \(\text{He}^+ + \text{ND}_3\) reactions, for collision energies in the \(k_{\text{rel}}(0–40)\) K range.[13] The insets of Fig. 2 show the measured product-ion time-of-flight
mass spectra with the Rydberg excitation laser turned on (black) and off (blue). The time-of-flight mass spectra recorded with the Rydberg excitation laser turned off exhibit peaks corresponding to products of Penning-ionization processes involving He\(^+\) and ammonia and He\(^+\) and background water present in the vacuum chamber. We can assign these peaks to OH\(^+\), H\(_2\)O\(^+\), NH\(^+\), and ND\(_2\)^+. When the Rydberg excitation laser is turned on, additional peaks appear in the time-of-flight mass spectra. The first and most prominent peak corresponds to He\(^+\) ions originating from He(\(n\)) atoms which have been field-ionized during the ion-extraction pulse. A considerable amount of He(\(n\)) is present even when the GS beam is on, because only a small amount (less than ~0.4\%) of the Rydberg atoms takes part in the chemical reactions.\(^{[12]-[16]}\) In order to identify the ion–molecule reaction product ions for each reaction, the Penning-ionization contribution to the recorded time-of-flight mass spectra is subtracted.

The product ions of the He\(^+\) + NH\(_3\) (ND\(_3\)) reaction detected in our experiments are: NH\(^+\)(ND\(_3\)) and NH\(^+\)(ND\(_3\)), with a branching ratio of ~1:6 (~1:4).\(^{[13]}\) The total reaction product yield of each reaction, displayed as the green circles with error bars in Fig. 2, is obtained by summing the contributions from the two product ion signals integrated over the green windows indicated in the insets. The vertical error bars in Fig. 2 correspond to the standard deviations of five consecutive measurements, each consisting of the average of 1000 experimental cycles. The horizontal error bars indicate the spread of collision energies, \(\Delta E\)_coll\(^*\) for each value of \(E\)_coll given by Eqn. (6):\(^{[12]}\)

\[
\Delta E\text{coll} = \Delta E\text{res} + 2 \sqrt{E\text{coll}\sqrt{\Delta E\text{res}}}.
\]

The term \(\Delta E\text{res}\) in Eqn. (6) reflects the experimental resolution at zero collision energy and is determined by the velocity spread around the centre velocity (\(v\)_\(v_{\text{opt}}\)) of the Rydberg atoms released from the quadrupole traps above the surface of the deflector. Typical values of \(\Delta E\text{res}\) are in the \(150–300\) mK range. Both data sets presented in Fig. 2 show an increase of the reaction yields with decreasing values of \(E\)\(_\text{coll}\). This increase is particularly strong below ~5 K. Also shown in Fig. 2, as orange and purple circles, are the calculated collision-energy-dependent capture rate coefficients averaged over the rotational states in ammonia which are populated in the supersonic beam, assuming a rotational temperature of 6 K. The black lines represent the calculated averaged capture rate coefficients with the effect of the experimental resolution included, as described in ref. \([12]\). For both reactions, the calculation describes the experimental data very well. The total integrated product ion signals in each data set were scaled to match the value of the calculated average capture rate coefficients at the minimal experimentally resolvable collision energy. The values of \(\Delta E\text{res}\) and the rotational temperature of the molecules, \(T\)_\(\text{rot}\), were varied to obtain the best agreement with the experimental data. Following this procedure, we obtain the values \(\Delta E\text{res} = 200\) mK and \(T\)_\(\text{rot}\) = 6 K. At the lowest collision energy accessible in the experiment, the calculated capture rates of the reactions reach values of ~21 \(k\)\(_L\) in He\(^+\) + NH\(_3\) and ~21 \(k\)\(_L\) in He\(^+\) + ND\(_3\), indicating a strong deviation from Langevin behaviour.

The observed enhancement of the reaction yields with decreasing \(E\)\(_\text{coll}\) arises from the dipole moment of ammonia (1.48 D),\(^{[27]}\) and in particular from rotational states which have the largest negative Stark shifts [see Eqn. (4)]. Although NH\(_3\) and ND\(_3\) have the same dipole moment, the observed enhancement is more pronounced in ND\(_3\) compared to NH\(_3\). This is because of the smaller (by a factor of ~2) rotational constants in ND\(_3\), which induce stronger \(J\)–mixing and Stark shifts, and, to a lesser degree, smaller separation between the umbrella-motion-tunnelling doublets in ND\(_3\) \((~0.053\) cm\(^{-1}\))\(^{[28]}\) compared to NH\(_3\) \((~0.79\) cm\(^{-1}\))\(^{[29]}\). Both of these effects lead to rotational states which are shifted to lower energies in an electric field in ND\(_3\) compared to NH\(_3\).

The rotational constants of NH\(_3\) and ND\(_3\) \(A(NH_3) = B(NH_3) = 9.444\) cm\(^{-1}\) and \(C(NH_3) = 6.196\) cm\(^{-1}\))\(^{[29]}\) and \(A(ND_3) = B(ND_3) = 5.143\) cm\(^{-1}\) and \(C(ND_3) = 3.125\) cm\(^{-1}\))\(^{[28]}\) mean that only ortho and para levels with \(J\leq 1\) and \(|K|\leq 1\) are significantly populated at the rotational temperature of the supersonic source (~6 K) in both isotopologues. In addition, according to nuclear-spin statistical effects and assuming nuclear-spin-conservation in the supersonic beam, the ratio of states with \(K = 0\) to states with \(|K| = 1\) is 1:1 in NH\(_3\), and 11:16 in ND\(_3\).\(^{[13]}\) The Stark shifts experienced by rotational states with \(J\leq 1\) and \(|K|\leq 1\) are thus crucial for the observed overall collision-energy dependence of the reaction yields.

\[
\Delta E\text{coll} = \Delta E\text{res} + 2 \sqrt{E\text{coll}\sqrt{\Delta E\text{res}}}.
\]

Fig. 2. Total measured reaction product-ion yield for the He\(^+\) + NH\(_3\) (left panel, light green circles with error bars) and He\(^+\) + ND\(_3\) (right panel, dark green circles with error bars) reactions, as a function of the collision energy. The purple and orange circles are the calculated capture rate coefficients of the two reactions, averaged over the rotational state population of the ammonia molecules produced in the supersonic beam, assuming a rotational temperature of 6 K. The black lines represent the calculated averaged capture rate coefficients with the finite experimental energy resolution included. The insets show the measured product-ion time-of-flight mass spectra after a reaction time of 7 \(\mu\)s and recorded with \(v\)_\(v_{\text{opt}}\) = 1050 m/s. The figure is adapted from Figs. 3 and 4 of ref. \([13]\).
Displayed in Fig. 3 are the calculated rotational-state-dependent Stark energies, interaction potentials and reaction rate coefficients in ND$_3$ for rotational states with $J \leq 1$ and $|K| \leq 1$. The rotational states can be categorised in three groups, according to the Stark shifts they experience, as: (A) strongly high-field-seeking states which experience negative linear Stark shifts at low fields – e.g. states with $|\text{IKM}| = 1$ correlating to the lower component $(l)$ of the umbrella-motion tunnelling doublet [Fig. 3(a)]. These states are subject to strongly enhanced rate coefficients with decreasing collision energy, reaching values of $\sim 94\,k_B$ at $E_{\text{coll}} = k_B \times 100\,\text{mK}$ [Fig. 3(a)]; (B) high-field-seeking states subject to a quadratic Stark shift at low fields, e.g. some of the states with $|\text{IKM}| = 0$ [Fig. 3(a)]. These states exhibit only weak rate enhancements, reaching values of $\sim (10 – 20)\,k_B$ at the lowest collision energies [Fig. 3(c)]; and (C) low-field-seeking states at low electric fields, e.g. the states with $J = 1$ and $|K| = |L|$ in Fig. 3(a). These states exhibit rate coefficients which are completely suppressed at the lowest collision energies and only start to grow for $E_{\text{coll}} > V_{\text{int}}^{\text{max}}$ [see Fig. 3 (b) and (c)]. Displayed in Fig. 3(b) are the calculated interaction potentials $V_{\text{int}}$ (in colour), as well as the pure Langevin potential for the He$^+ +$ ND$_3$ reaction (in black) for a head-on-collision $(l = 0$, $L = \hbar v[(l + 1)]$) in solid lines and for a collision with $l = 20$ in dash-dotted lines. The height of the potential energy barrier in the Langevin potential for $l = 20$ is completely suppressed in high-field-seeking states of type (C). States of type (A), on the other hand, experience a potential-energy barrier [designated as $V_{\text{int}}^{\text{max}}$ in Fig. 3(b)] even for collisions with $l = 0$. These states are only reactive for collision energies which are sufficiently high to overcome the potential energy barrier $V_{\text{int}}^{\text{max}}$ [Fig. 3(c)]. Because the enhancement of the capture rate coefficient with decreasing energy is so striking in states of type (A), these states dictate the overall behaviour of the total rate coefficient, averaged over the population of rotational states, even though these states comprise only 19.6% (in ND$_3$) and 15.1% (in NH$_3$) of the total population at $T_{\text{rot}} = 6\,\text{K}$.

5. Ion-quadrupole-induced Suppression of the Reactivity at Low Collision Energies

The results presented in this section were presented in more detail in ref. [15]. Shown in Fig. 4 is the total measured product ion yield (green circles with error bars) for the He$^+ +$ N$_2$ reaction, together with the calculated averaged capture rate coefficients, for a rotational temperature of 7.5 K, without (purple circles) and with (black line) the experimental resolution included, as explained above, for collision energies in the $k_B(0 – 12)\,\text{K}$ range. The ion–molecule reaction product ions detected in this reaction are N$^+$ and N$_2$$^+$ with a branching ratio of $\sim 1:1$ (see inset of Fig. 4). The experimental and calculated energy-dependent rate coefficients show a suppression of the reaction yield with decreasing energy, with the total measured product-ion signal at the lowest collision energy being $\sim 30\%$ less than that at $k_B = 10\,\text{K}$.

Since the nitrogen molecule is homonuclear, it has no dipole moment in its ground electronic state. The observed suppression of the reaction product, however, can be explained with the rotational-state-dependent Stark shifts originating from the negative value of the $Q_2$ component of the quadrupole moment tensor $(Q_2(N_2) = -1.306\,\text{DÅ}^{2})$. The negative value of $Q_2$ corresponds to an electronic configuration in which there is excess positive charge (+2$\delta$) near the N$_2$ molecule centre of mass and excess negative charges ($-\delta$) near each nitrogen atom. This charge distribution results from the one $\sigma$ and two $\pi$ bonds comprising the triple bond of N$_2$.
The ion-quadrupole interaction (\(\sim R^2\)) is much weaker than the ion-dipole interaction (\(\sim R^3\)), and thus the values of the calculated capture rate coefficients for the \(\text{He}^+ + \text{N}_2\) reaction are much closer to \(k^*\) [see Figs. 4 and 5(c)] than those for the \(\text{He}^+ + \text{N(H/D)}\) reactions.

Displayed in Fig. 5 are the Stark shifts in \(\text{N}_2\), (a), calculated as described in refs. [13] and [15], the interaction potentials for an \(l = 0\) collision with a \(\text{He}^+\) ion (b), and the calculated rotational-state- and collision-energy-dependent capture rate coefficients (c), for states with \(J \leq 2\), which are the only significantly-populated states at the rotational temperature of the supersonic source (here, 7.5 K). States with a maximal value of \(|M_\ell|\), e.g. the \((J,M) = (1,1)\) and \((2,2)\) states, result in a configuration in which the positive charge near the molecular centre is exposed to the positive charge of the ion (see Fig. 5 from ref. [15]), resulting in an overall repulsive potential. These states are thus low-field-seeking at low electric fields, are characterized by interaction potentials with potential-energy barriers even for a collision with \(l = 0\) [designated as \(V^\text{diff} \) in Fig. 5(b)], and have rate coefficients which are zero for \(E^\text{int} < V^\text{diff}\) [Fig. 5(c)]. In states with \(M = 0\), on the other hand, it is the negative partial charges located on the \(N\) atoms which are exposed to the positively charged \(\text{He}^+\) ion, resulting in an interaction potential which is more attractive than \(V^\text{diff}\). The \((0,0)\) state has no quadrupole moment to first order, but acquires one through mixing with the \((2,0)\) state. The \((0,0)\) state is thus only slightly more attractive than \(V^\text{diff}\), and exhibits a rate coefficient which starts at a value of \(k^*\) at the lowest energies and increases to \(\sim 1.5k^*\) at \(E^\text{int} = k^*_B\), 12 K. The other states with \(M = 0\), on the other hand, have rate coefficients which increase at the lowest values of \(E^\text{int}\).

The nuclear-spin statistics of \(^{14}\text{N}_2\) dictate that 2/3 of the molecules are in states with \(J = 0, 2, 4, \ldots\) (ortho) and 1/3 in states with \(J = 1, 3, 5, \ldots\) (para). The behaviours of the total averaged capture rate coefficients in the \(\text{He}^+ + \text{N}_2\) reaction is thus determined by the \((0,0)\) and \((1,1)\) states, which comprise respectively \(\sim 44\%\) and \(\sim 21\%\) of the total population at a rotational temperature of 7.5 K.

6. Conclusions

We have developed an experimental technique to measure relative reaction rate coefficients of reactions between the \(\text{He}^+\) ion and several small molecules (e.g. \(\text{CH}_3\text{F}[12]\), \(\text{NH}_3[13]\), \(\text{CO}[14]\), \(\text{CH}_4[15]\)) with the orbit of a Rydberg electron. By using a merged-beam setup, we are able to access collision energies in the \(\sim k^*_B\) \((0-40)\) K range. We observe a pronounced deviation from the temperature- and collision-energy-independent Langevin capture rate coefficients \(k^*\) for molecules with a dipole or quadrupole moments. In the case in which the molecule has a significant dipole moment (e.g. \(\text{CH}_3\text{F}\) and \(\text{NH}_3\)), we observe a strong enhancement of the reaction rate coefficients at the lowest collision energies studied \((\sim k^*_B\) 200 mK), reaching values more than an order of magnitude larger than \(k^*\) \([12,13]\). This enhancement is attributed to molecular rotational states which experience strong negative and linear Stark shifts in the electric field of the ion. When the molecule has no significant dipole moment, but a negative quadrupole moment (e.g., \(\text{N}_2\) and \(\text{CO}\)), a pronounced suppression of the total product-ion yield is observed at the lowest collision energies \([14,15]\).

The adiabatic-capture theory used to aid the interpretation of the results shows excellent agreement with the experimental data, suggesting that this model is adequate to describe the collision-energy-dependence of the rate coefficients down to \(\sim k^*_B\) 200 mK. By also calculating the thermal reaction rate coefficients \([13,15,16]\) and using the measured values of the absolute thermal rate coefficients of ion–molecule reactions available in the literature for low temperatures (in the 10–50 K range), we can also determine the reaction probability (which we estimate to be \(\sim 60–70\%\) for the \(\text{He}^+ + \text{N}_2\) reaction \([15]\) and \(\sim 40\%\) for the \(\text{He}^+ + \text{NH}_3\) reaction) \([13]\). Our low-energy measurements, together with the developed model, make it possible to predict the absolute thermal rate coefficients of numerous ion–molecule reactions at low temperatures which are relevant for astrophysical kinetic models.

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Fig. 5 The calculated rotational-state dependent Stark energies, interaction potentials and capture rate coefficients for the \(\text{He}^+ + \text{N}_2\) reaction. (a) The calculated Stark shifts of the rotational levels with \(J \leq 2\) in \(\text{N}_2\). (b) Interaction potentials for the rotational states shown in (a) for \(l = 0\) (solid coloured lines) and the pure Langevin potential \(V_L\) in black. (c) The calculated rotational-state dependent capture rate coefficients. The inset shows the rotational state population in \(^{14}\text{N}_2\) at a rotational temperature of 7.5 K.

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