Cold Ion–Molecule Chemistry: The Very Different Reactions of He+ with CO and NO

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Abstract: The ion–molecule reactions He+ + CO → He + C+ + O and He+ + NO → He + N+ + O have been measured at collision energies between 0 and $k_B \cdot 10$ K. Strong variations of the rate coefficients are observed below $k_B \cdot 5$ K. The rate of the He + CO reaction decreases by ~30% whereas that of the He+ + NO reaction increases by a factor of ~1.5. These observations are interpreted in the realm of an adiabatic-channel capture model as arising from interactions between the ion charge and the dipole and quadrupole moments of CO and NO. We show that the different low-energy behavior of these reactions originates from the closed- vs. open-shell electronic structures of CO and NO.

Keywords: Cold ion chemistry · Dipole moment · Quadrupole moment · Rydberg atoms

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1. Introduction

Studies of ion–molecule reactions at low temperatures or low collision energies (E_{coll}) are very challenging,[1,2] primarily because even weak electric fields heat up the ions.[1,3] To overcome this challenge, we study these reactions within the large orbit of a Rydberg electron in a state of high principal quantum number n ($n \geq 30$ in the present work). The Rydberg electron compensates the positive ionic charge and shields the reaction from stray electric fields. Its distance to the ion is sufficiently large so that it does not influence the reaction taking place within its orbit.[3]

To reach low collision energies in the range between 0 and $k_B \cdot 10$ K, which were not easily accessible before, we merge a supersonic beam of Rydberg atoms or molecules with neutral molecules in their ground state using an on-chip Rydberg-Stark deflector and decelerator[4] and adjust their relative velocity.[3]

In the work summarized in this article, we employed this technique to study the reactions of He+ with CO[5,6] and NO[7] below $k_B \cdot 10$ K. NO and CO have similar masses m, polarizabilities α, and electric-dipole (μ_{el}) and -quadrupole (Q_{zz}) moments (see Table 1). Assuming that their capture rates by He+ at low energies are governed by the charge–dipole and charge–quadrupole interactions would suggest that they should display the same low-temperature behavior. However, the experiments show that this is

not the case: whereas the rate of the He+ + CO reaction decreases near $E_{coll} = 0$, the rate of the He+ + NO reaction increases sharply. We attribute this difference to the open-shell electronic structure of NO and to the fact that the rotational levels in the NO X $^2\Pi_{1/2}$ ground state occur in near-degenerate pairs of states of opposite parity that are very easily perturbed by the electric field of the colliding ion.

Table 1. Comparison of the relevant physical constants of CO and NO.

Molecule	CO	NO
Mass m (g/mol)	28.01	30.01
Electronic ground state	$^1\Sigma_{1/2}^+$	$^2\Pi_{1/2}$
Polarizability α (10^{-40} Cm^{2}V^{-1})	2.173[8]	1.889[8]
Dipole moment $|\mu_{el}|$ (D)	0.112[9]	0.157[10]
Quadrupole moment Q_{zz} (DÅ)	–2.839[11]	–2.421[12]

2. Experimental Method

Two translationally cold ($T_{transl} \ll 1$ K) supersonic beams, one of He atoms and one of either NO or CO molecules, are produced using home-built valves delivering gas pulses of short duration (~20 μs).[6,7] The adiabatic expansion of the molecular gases into vacuum also cools their rotational temperature to about 5 K so that only their lowest two rotational levels are significantly populated, *i.e.*, $J = 0,1$ in the X $^1\Sigma_{1/2}^+$ (v = 0) ground state of CO and $J = 1/2,3/2$ in the X $^2\Pi_{1/2}$ (v = 0) ground state of NO. The He atoms are excited first to the (1s)(2s) $^3S_1$ metastable state (He*) in an electric discharge, and then by a UV laser (~260 nm) to a selected Rydberg state [He(n)] with principal quantum number n (30≤n≤45). Initially, the two beams propagate along axes separated by a 5° angle. To merge them, the He(n) beam is deflected using a 50-electrode Rydberg-Stark deflector and decelerator.[3,13] This device can also be used to precisely adjust

the final velocity of the He(n) beam and set the relative velocity of the two beams and thus the collision energy of the reaction. Merged beam techniques have been previously used to study Penning-ionization reactions involving neutral species at low collision energies.[14,15]

3. Results

We observe the reaction yield as a function of the collision energy by extracting the product ions with a pulsed electric field and recording mass-resolved time-of-flight (TOF) spectra of the ions in the reaction volume. Typical TOF spectra for the reactions of interest are presented in Fig. 1.

The ions detected in the blue traces correspond to the products of the Penning-ionization reactions of He* with CO (a) and NO (b), and the background gas in the vacuum chamber (H_2O, N_2 and O_2). When He* is photoexcited to He(n = 35) Rydberg states (black TOF spectra in Fig. 1), additional He^+, C^+ and N^+ ions are observed. These ions result from the field ionization of the He(n) reactant and of the C(n) and N(n) products. Because of the spectator role of the Rydberg electron, the C^+ and N^+ ion signals represent the yields of the reactions of He^+ with CO and NO, respectively. The experiments are carried out under conditions where the densities of CO and NO are much higher than that of He(n) and where less than 1% of the He(n) atoms react. Consequently, the ion signals directly reflect the reaction rate coefficients.

Figs. 2a and b depict how the C^+ and N^+ product-ion signals vary as the velocity of the He(n) Rydberg atoms is tuned while keeping the velocities of the CO and NO beams fixed. The merged-beam geometry enables us to vary the relative velocity through zero and thus to observe how the reaction rate changes as the collision energy E_{coll} is reduced to values below $E_{coll}/k_B = 1$ K. The results of such measurements for the He^+ + CO and He^+ + NO reactions are depicted in Fig. 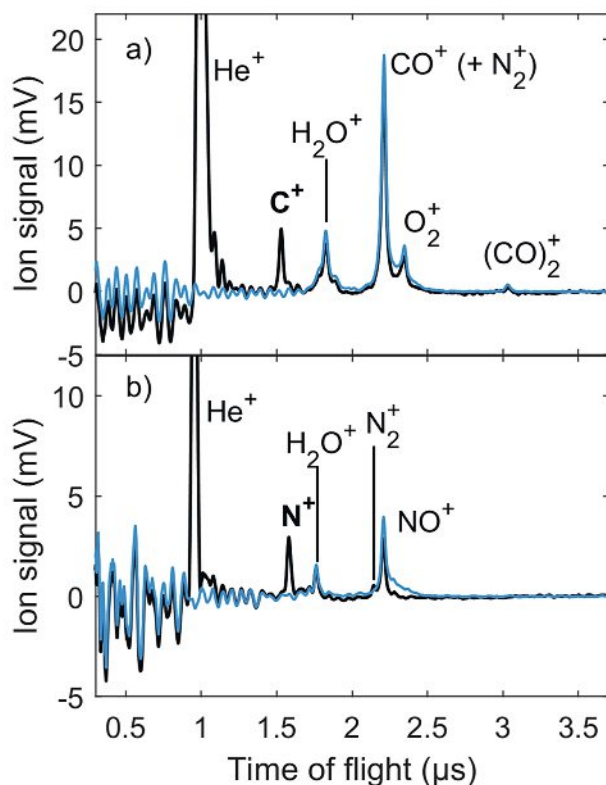2, where the black dots represent experimental data. Whereas the rate coefficient decreases with decreasing collision energy in the case of the He^+ + CO reaction, it rises sharply below 1 K in the case of the He^+ + NO reaction. To understand the origin of this difference, rotational adiabatic-channel calculations of the capture rate coefficients were carried out following the general procedure introduced by Troe[16] and Clary[17] and recently reviewed by Tsikritea et al.[18]

In such calculations, one first determines the adiabatic long-range electrostatic attraction potentials resulting from the charge–induced-dipole, the charge–dipole, and the charge–quadrupole interactions between He^+ and the CO and NO molecules in specific rotational levels. These levels are designated by their rotational quantum numbers (J, $K=\Lambda=0$, M) for CO and (J, $\Omega=\frac{1}{2}$, M) for NO. For a given rotational level of the molecule, this attraction potential is obtained as the sum of an ion–induced-dipole attraction term $V_{ind}(R)$ proportional to $-\alpha R^{-4}$, a centrifugal repulsion term $V_{cr}(R)$ proportional to R^{-2}, as well as ion–dipole (proportional to $-\mu_{el}R^{-2}$) and ion–quadrupole (proportional to $-Q_{zz}R^{-3}$) interaction terms $V_{d,q}(R)$. $V_{d,q}(R)$ corresponds to the Stark shifts of the rotational level energies in the (inhomogeneous) electric field $[e/(4\pi\varepsilon_0 R^2)]$ of the ion (see Fig. 3).

The Stark shifts of the rotational levels of CO and NO can be calculated accurately from the known values of their dipole and quadrupole moments (see Table 1) and are depicted as a function of the ion–molecule distance R in Fig. 3. Negative (positive) Stark shifts result in attractive (repulsive) potential terms which accelerate (slow down) the reactions. Inspection of Fig. 3 reveals that the Stark shifts are larger in NO than in CO, although both molecules have dipole and quadrupole moments of similar magnitude. In the open-shell NO molecule, each rotational level consists of a near-degenerate pair of levels of opposite parity (Λ doublet).[19]
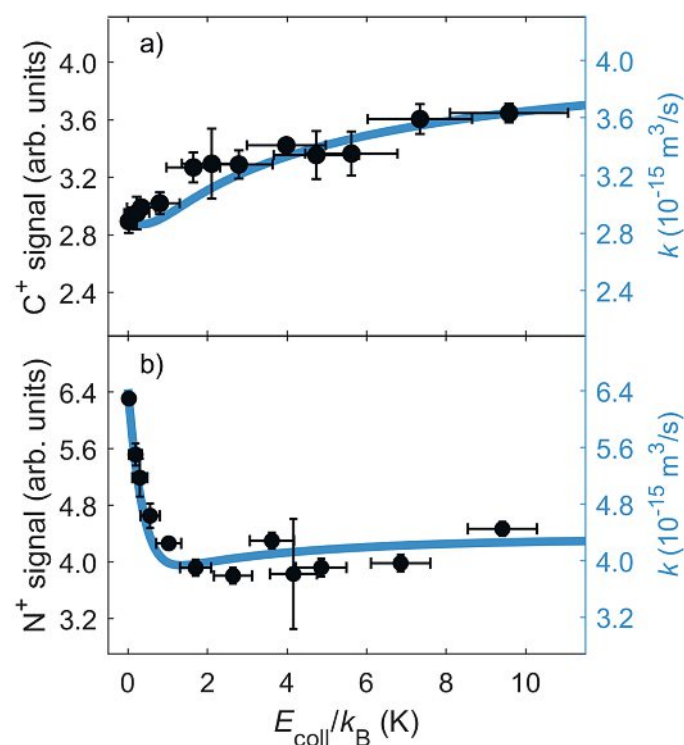

Fig. 1. Time-of-flight mass spectra of (a) the He^+ + CO → He + C^+ + O and (b) the He^+ + NO → He + N^+ + O reaction. The blue and black traces correspond to the measurement carried out after photoexcitation of He to n = 35 Rydberg states and without prior photoexcitation, respectively (data from refs. [5,7]).

Fig. 2. Collision-energy-dependent C^+ (a) and N^+ (b) yields of the He^+ + CO [NO] → He + C^+ [N^+] + O reactions in the range E_{coll}/k_B = [0,10] K. The black dots with error bars are experimental data and the blue lines are the results of capture-rate-coefficient calculations (data from refs. [6,7]).
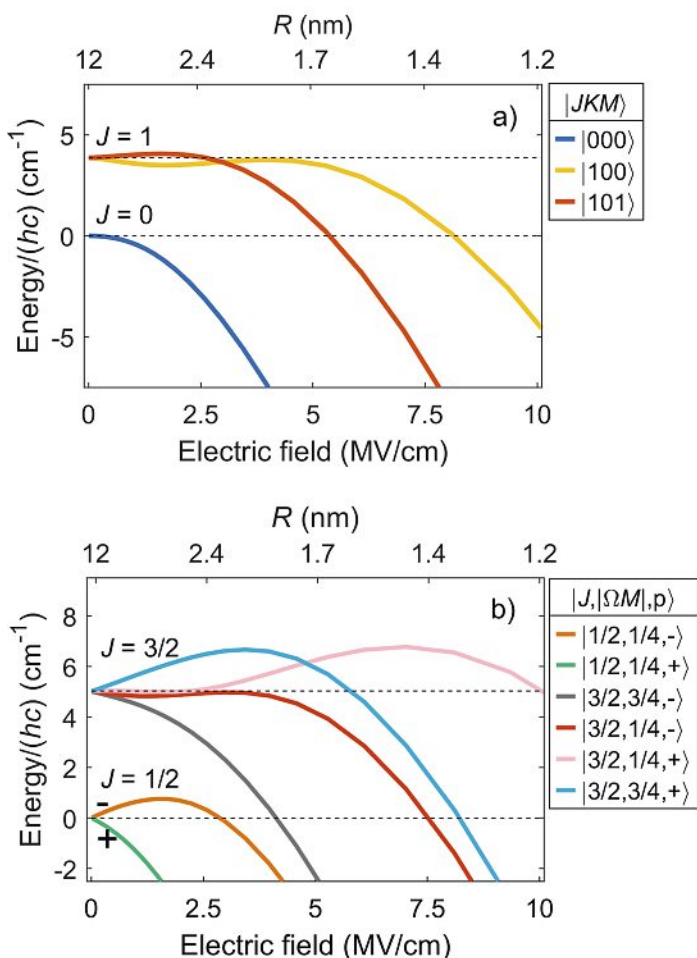
Fig. 3. Stark shifts of the lowest two rotational levels of the CO X $^1\Sigma_{1/2}^+$ (v = 0) (a) and the NO X $^2\Pi_{1/2}$ (v = 0) (b) ground vibronic states in the electric field of the He$^+$ ion as a function of the distance R (top horizontal axes) between the reactants obtained by taking into account the charge-dipole and charge-quadrupole interactions (calculated data from refs. [6,7]).

In the capture calculations, one assumes that the reaction takes place with 100% probability if the collision energy is higher than the barriers of the state-specific interaction potentials. This assumption is a good approximation for strongly exothermic barrier-free reactions. However, it disregards the possibility that some close collisions do not lead to reaction products but only to elastic or inelastic scattering, *i.e.*, that the probability of reaction upon close encounter of the reactants is not 100%. To examine this aspect in more detail, we have also carried out experiments with a CO:NO gas mixture with exactly defined concentrations and measured the ratio of the yields of the two reactions as a function of the collision energy. Comparison of this ratio with the ratio of the calculated absolute rate coefficients (see Fig. 4) reveals that the reaction of He$^+$ with CO upon close encounter is less probable than the reaction of He$^+$ with NO by about 20%. To explain this difference, calculations of the reactions that go beyond the treatment of the long-range rotational adiabatic capture and also consider the short-range interaction potentials would be required.

3. Conclusions

With this newly developed experimental method,[3] ion–molecule reactions can be investigated at very low collision energies and temperatures, as illustrated in Fig. 2 for the ion–molecule reactions between He$^+$ and CO and NO. Their rate coefficients depend on the values of the dipole and quadrupole moments and on the details of the rotational structure of the molecule. Particularly striking are (1) the strong enhancement of the rate constant of the He$^+$ + NO → He + N$^+$ + O reaction at very low collision energies, which can be unambiguously attributed to the near-degenerate nature of the rotational levels (Λ doublets), which enhance the role of the charge-dipole interaction, and (2) the reduction of the rate constant of the He$^+$ + CO → He + C$^+$ + O reaction, which results from the fact that the quadrupole moment of CO is negative. The observed rate coefficients strongly deviate from the Langevin rates, which are independent of the collision energy and the temperature.[21] The results presented in this article illustrate the richness of ion-molecule chemistry close to the absolute zero of the temperature scale.
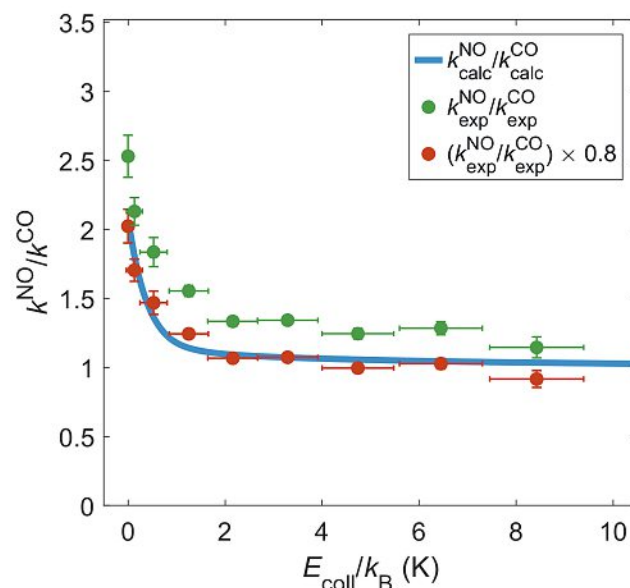
Consequently, the Stark shifts caused by the ion–dipole interaction are linear and much stronger in NO than in CO. In CO, the effects of the charge–dipole interaction turn out to be even weaker than those of the charge–quadrupole interaction.[6] These differences determine the very different low-collision-energy behavior of the two reaction systems.

The state-specific and energy-dependent capture rate coefficients are determined from the interaction potentials, and the dependence of the overall rate coefficient on the collision energy is obtained as a weighted sum of the rotational state-specific capture coefficients at the rotational temperature of the molecules in the supersonic beam ($T \approx 5$ K), as explained in detail in refs. [13,20]. The blue lines in Fig. 2 represent the calculated capture rate coefficients after convolution with the experimental distribution of collision energies (see also right-hand-side axes labels), which are in good agreement with the experimental results. The calculations reveal that the sharp enhancement observed at low collision energies for the He$^+$ + NO reaction originates primarily from the contributions of NO molecules in the lower components of the near-degenerate Λ doublets, which have negative Stark shifts.[7] In the case of CO, the decrease of the rate coefficient observed below $k_B \cdot 5$ K originates from the negative sign of the quadrupole moment of CO, which leads to a decrease of the contribution of the most populated $|JKM\rangle = |000\rangle$, $|100\rangle$ and $|101\rangle$ states.[6]

Fig. 4. Comparison of the measured ratio of the rate constants of the He$^+$ + CO (NO) reactions from measurements carried out with a CO:NO gas mixture (green dots) with ratios predicted using adiabatic capture theory (blue line). The red dots are obtained by assuming that the close collisions of the He$^+$ with NO are 0.8 times as reactive as with CO.

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