Studying ion-molecule reactions within the orbit of a Rydberg electron - the effect of the $\Lambda-$doubling in NO on the He$^+$ + NO reaction rate coefficient in the $k_{\mathrm{B}} \cdot (0 - 10)$ K collision-energy range

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Fast, exothermic and barrierless ion-molecule reactions drive rich chemistry in the cold ($\sim 10 - 150$ K) and tenuous environment of the interstellar medium [1, 2]. These reactions proceed with high rate coefficients even at low temperatures, and are typically modelled by the classical Langevin model, which predicts a temperature- and collision-energy-independent reaction rate coefficient (k_{L}). At low temperatures and collision energies (E_{coll}), however, the rotational-state-dependent Stark shifts experienced by the molecule in the electric field of the ion can lead to a strong modification of the interaction potential and reaction rate coefficients [3, 4]. These Stark shifts arise from the presence of molecular dipole and, to a lesser extent, quadrupole moments and can lead to the reaction being suppressed in some molecular states or proceeding with enhanced rate coefficient in other states at the lowest collision energies [5, 6, 7].

We present experimental data and calculations on the reaction between He$^+$ and nitric oxide in the collision-energy range $k_{\mathrm{B}} \cdot (0 - 10)$ K. In order to suppress heating by stray electric fields, the He$^+$ ions are replaced by helium atoms in a Rydberg state [He(n)]. To reach low collision energies, we employ the merged-beam approach [6, 8]. The He(n) atoms are merged with a supersonic molecular beam containing NO molecules using a curved Rydberg-Stark surface-electrode deflector [9, 6]. The energy of the collision is varied by changing the velocity of the He(n) atoms with the deflector, while the velocity of the NO beam is kept fixed. The reaction product ions are collected in a time-of-flight mass spectrometer.

We observe a strong enhancement of the total reaction yield with decreasing collision energy, and a particularly sharp increase below $\sim k_{\mathrm{B}} \cdot 1$ K, with the total capture rate coefficient reaching values of $\sim 3\, k_{\mathrm{L}}$ at the lowest energies ($\sim k_{\mathrm{B}} \cdot 100$ mK). This increase is attributed to the dipole moment of NO ($\mu_{\mathrm{e}}^{\mathrm{NO}} = 0.159$ D), the effect of which is strongly enhanced by the presence of the $\Lambda-$doubling (NO has a $X\ ^2\Pi_{1/2,3/2}$ electronic ground state). To emphasise this effect, we also present results on the He$^+$ + CO reaction. Carbon monoxide has a similar dipole moment to nitric oxide ($\mu_{\mathrm{e}}^{\mathrm{CO}} = 0.112$ D), but it has a $X\ ^1\Sigma^+$ ground electronic state and thus no $\Lambda-$doubling. The total product ion yield of the He$^+$ + CO reaction exhibits a *decrease* with decreasing E_{coll} [7]. This effect is attributed to the negative quadrupole moment of CO ($Q_{zz} = -9.470 \times 10^{-40}$ C m^2).

References

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