INFLUENCE OF TRANSLATIONAL AND ROTATIONAL ENERGY ON THE RATE OF ION-MOLECULE REACTIONS NEAR 0 K: D_2^+ +NH₃ AND D_2^+ +ND₃

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Ion-molecule reactions are important reactions in atmospheric chemistry, astrophysics and plasma physics¹. Reliable values for the reaction rates are key to modelling the relevant reaction networks, but are difficult to study in the collision energy range relevant for astrophysics because ions are very easily heated up by stray electric or magnetic fields. To study the reactions D_2^+ +NH₃ as well as D_2^+ +ND₃ at low collision energy, we replace D_2^+ by D_2 in a Rydberg state (of high principal quantum number $n \ge 30$). The distant Rydberg electron shields the ion core from external fields without influencing the ion-molecule reaction within its orbit. We use a Rydberg-Stark deflector to merge a beam of D₂ Rydberg molecules with a supersonic beam of NH₃ or ND₃ and tune the collision energy E_{coll} from $\approx k_{\rm B} \cdot 150$ mK to $\approx k_{\rm B} \cdot$ 70 K². Short ($\approx 20 \ \mu s$) gas pulses ensure a high collision-energy resolution. We observe two reaction channels for the reaction with NH_3 : $NH_3^++D_2$ and NH_2D^++D , but these two channels are not resolvable by mass spectrometry for D_2^+ +ND₃. The rate coefficients deviate strongly from Langevin rates and increase sharply below 2 K, which is explained by rotationally adiabatic capture calculations as arising from the linear Stark effect of the two inversion tunneling components of ammonia in the electric field of the ion 3,4,5 . We study the influence of the rotational temperature (14 K or 39 K) of NH₃ and ND₃ using pure ammonia beams and beams of ammonia seeded in helium and measure the rotational states populations with (2+1) REMPI spectroscopy. We compare these results with those obtained for the $He^++NH_3^6$ and Rg^+ +NH₃ (Rg=Ar, Kr, Xe) reactions⁷.

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