## Influence of translational and rotational energy on the rate of ion-molecule reactions near 0 K: $D_2^+$ + NH<sub>3</sub> and $D_2^+$ + ND<sub>3</sub>

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Ion-molecule reactions are important reactions in atmospheric chemistry, astrophysics and plasma physics [1]. 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  $D_2^+ + NH_3$  as well as  $D_2^+ + ND_3$  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  $D_2$  Rydberg molecules with a supersonic beam of  $NH_3$  or  $ND_3$  and tune the collision energy  $E_{coll}$  from  $\sim k_B \cdot 150$  mK to  $\sim k_B \cdot 70$  K [2]. Short ( $\sim 20 \ \mu$ 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  $D_2^+ + ND_3$ . 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 [3-6]. We study the influence of the rotational temperature (14 K or 39 K) of  $NH_3$  and  $ND_3$  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  $Rg^+ + NH_3$  (Rg=Ar, Kr, Xe) reactions [7].

[1] B. A. McGuire, O. Asvany, S. Brünken, S. Schlemmer, Nat. Rev. Phys. 2, 402-410 (2020).

[2] P. Allmendinger, J. Deiglmayr, J. A. Agner, H. Schmutz, F. Merkt , *Phys. Rev. A* **90**, 043403 (2014).

[3] J. Troe, Chem. Phys. 87, 2773-2780 (1987).

- [4] D. C. Clary, Mol. Phys. 54, 605-618 (1985).
- [5] J. Troe, J. Chem. Phys. 105, 6249-6262 (1996).

[6] V. Zhelyazkova, F. B. V. Martins, J. A. Agner, H. Schmutz, F. Merkt, *Phys. Chem. Chem. Phys.* **23**, 21606 (2021).

[7] A. Tsikritea, K. Park, P. Bertier, J. Loreau, T. Softley, B. R. Heazlewood, *Chem. Sci.* **12**, 10005-10013 (2021).