Cold ion chemistry within a Rydberg electron orbit: the effect of the molecular structure at the lowest collision energies

V. G. Zhelyazkova[1], F. B. V. Martins[1], S. Schilling[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]ETH Zurich, Department of Chemistry and Applied Biosciences, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

In the study of ion-molecule reactions, Rydberg atoms and molecules can be used as a proxy for the ions. The Rydberg electron shields the ion-core–molecule reaction from stray electric fields, making it possible to reach collision energies (E_{coll}) near zero Kelvin [1,2]. Rydberg atoms can possess high induced electric dipole moments which allows for the manipulation of their translational motion by modest electric-field gradients using surface-electrode devices [3]. We use such a device to merge a beam of Rydberg helium atoms [He(n)] with a molecular supersonic beam. We vary the relative velocity between the reactants by changing the velocity of the He(n) atoms, and thereby the collision energy. With this method, we can reach E_{coll}/k_B from ~40 K all the way down to ~100 mK in the moving centre-of-mass reference frame.

In this contribution, we present an overview of the results of experimental studies of reactions between the He^+ ion and several small molecules. We find that for molecules with a strong electric dipole moment (such as CH_3F [4] and NH_3 [5]) the reaction yield is strongly enhanced near 0 K, and the reaction rate coefficients reach more than ten times the typically assumed Langevin rate coefficient. For molecules with no dipole moment (e.g. N_2 [6]), the opposite effect is observed, *i.e.*, a *suppression* of the reaction yield near 0 K. We also investigate the reactions with molecules which have only a small dipole moment and find that the E_{coll}-dependence of the reaction yields in this case are determined by the character of the electronic ground state. For example, we measure strikingly different reaction yields for NO ($^2\Pi$ character [7]) and CO ($^1\Sigma^+$ character [8]). Our experimental results are interpreted with the aid of a rotationally-adiabatic-capture model [5,6] inspired by earlier theoretical treatments [9,10].

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