# Towards detecting quantum-Langevin behavior in ion-molecule reactions

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At very low temperatures or collision energies, the rates of ion-molecule capture reactions involving polarizable, nonpolar molecules have been predicted theoretically to increase by a factor of two compared to the Langevin rate [1]-[4]. This purely quantum-mechanical effect has not been observed experimentally yet and its observation represents one of the great challenges of cold ion-molecule chemistry. The study of ion-molecule reactions at low collision energies ($E_{\rm coll}$) below $E_{\rm coll}/k_{\rm B} = 10$ K, or low temperatures, is experimentally very difficult because stray electric fields in the reaction volume heat up the ion samples. A potential difference of 1 mV across a reaction region of 1 cm accelerates the ions to 1 meV, which corresponds to heating them up to about 12 K. To overcome this problem and study ion-molecule reactions below 10 K, we have developed a new method, in which the ion-molecule reaction takes place within the orbit of a Rydberg electron at high values of the principal quantum number $n$ [5]. In high-$n$ Rydberg states, the Rydberg electron only very weakly interacts with the ion core, so that it does not significantly influence the ion-molecule reaction taking place within its orbit but shields the ion from heating by stray electric fields. Instead of studying exothermic and barrier-free ion-molecule reactions of the type

$$\mathrm{A}^+ + \mathrm{B} \rightarrow \mathrm{C}^+ + \mathrm{D}, \tag{1}$$

we study the reactions

$$\mathrm{A}^* + \mathrm{B} \rightarrow \mathrm{C}^* + \mathrm{D}, \tag{2}$$

in which $\mathrm{A}^*$ and $\mathrm{C}^*$ represent atoms or molecules in high Rydberg states with ion cores $\mathrm{C}^+$ and $\mathrm{D}^+$, respectively.

To reach very low collision energies, we use chip-based Rydberg-Stark decelerators and deflectors [6,7] to merge cold supersonic beams of $\mathrm{A}^*$ and B and to vary their relative velocities [5]. By monitoring the yield of the products ($\mathrm{C}^*$, or $\mathrm{C}^+$ after autoionization of $\mathrm{C}^*$) as a function of the relative mean velocity of the two beams, we obtain the relative reaction cross sections as a function of the collision energy. At collision energies ($E_{\rm coll}/k_{\rm B}$) below 1 K, we find that the reaction rate coefficients deviate from those estimated with Langevin-type capture models [8-12]. The deviations become particularly large when B has a permanent dipole [9,10] or a quadrupole moment [12]. To detect the factor-of-two enhancement predicted for quantum-capture reactions, it is advantageous to study reactions of ions with neutral molecules that do not have a quadrupole moment.

The talk will present recent results of studies of the reactions of ground-state $\mathrm{X}^+\ ^2\Sigma_g^+$ ($v^+ = 0, N^+ = 0$) $\mathrm{H}_2^+$ ions with ground-state $\mathrm{X}\ ^1\Sigma_g^+$ ($v = 0, N = 0$) HD and para-$\mathrm{H}_2$ molecules which reveal first signatures of quantum capture in ion-molecule reactions.

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