Production of heavy-Rydberg ion-pair states in Rydberg atom collisions

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Synopsis The formation of bound heavy-Rydberg ion-pair states through electron transfer in collisions between K(np) Rydberg atoms and attaching targets is being examined. Measurements show that low-n collisions with a wide variety of targets can lead to formation of bound ion-pair states. Under appropriate conditions a small fraction of these can subsequently dissociate as free ions through internal-to-translational energy transfer, with typical lifetimes of ~1-5 µs.

Rydberg atom collisions with attaching targets can lead to electron transfer reactions of the type

\[ \text{K}(n\ell) + \text{ABC} \rightarrow \text{K}^+ + \text{ABC}^- \]

i.e., to creation of an excited intermediate that might dissociate, undergo rapid (τ ~ a few ps) autodetachment, or undergo intramolecular vibrational relaxation (IVR) to form a long-lived (τ ~ µs to ms) metastable parent anion. (Here ABC denotes a long-lived product, not a stable ground state negative ion.) For values of \( n < -15-20 \) product ion pairs are formed sufficiently close that their post-attachment interactions become important, especially for thermal collision energies. A sizeable number of them are electrostatically bound and orbit at relatively large separations creating so-called heavy-Rydberg ion-pair states because of their similarities to atomic Rydberg states [1]. In the present work the production and properties of such states are being examined.

Consider as an example \( \text{C}_4\text{Cl}_4^- \). Arrival-time spectra for negative particles produced in \( \text{K}(14p) - \text{C}_4\text{Cl}_4 \) collisions obtained using a time-of-flight technique are presented in Fig. 1 for initial Rydberg atom velocities of 350 and 680 m s\(^{-1}\). The data are normalized to equal initial Rydberg atom production rates. Sharp increases in signal are evident at the anticipated arrival times for Cl\(^-\) and \( \text{C}_4\text{Cl}_4^- \) ions. Following their build up the signals decay mirroring the decay of the parent Rydberg population (created using a 150 ns-wide laser pulse). A prompt electron signal is also seen that results from autodetachment of shorter-lived \( \text{C}_4\text{Cl}_4^- \) ions while en route to the detector.

As the Rydberg atom velocity is reduced the total signal decreases. This is due to the decrease in kinetic energy of relative motion of the reactants which leads to an increase in the fraction of product ion pairs that is electrostatically bound. The Cl\(^-\) signal, however, decreases more dramatically than the \( \text{C}_4\text{Cl}_4^- \) signal. This results because a small fraction of the bound \( \text{K}^+-\text{C}_4\text{Cl}_4^- \) ion pairs is able to subsequently dissociate through conversion of internal energy in the \( \text{C}_4\text{Cl}_4^- \) ion into translational energy of the product ion pair.

Detailed analysis of the data using a Monte Carlo collision model points to a mean energy conversion of ~60-90 meV, much less than the available excess energy of reaction, ~0.7 eV. (No similar internal energy conversion is possible for \( \text{K}^+-\text{Cl}^- \) ion pairs.) Additional evidence for creation of ion-pair states that later dissociate is contained in the relatively slow risetimes of the \( \text{C}_4\text{Cl}_4^- \) signal which (unlike the Cl\(^-\) signal) does not follow that of the parent Rydberg atom population. Analysis of the risetime suggests that those ion-pair states that dissociate typically have lifetimes of ~1-5 µs.

Measurements are being extended to include direct detection of ion-pair states through electric-field-induced dissociation, a process analogous to the field ionization of Rydberg atoms. Rydberg atoms provide a novel means to create heavy-Rydberg states and explore their properties.

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References

[1] E. Reinhold and W. Ubachs, Mol. Phys. 103, 1329 (2005).

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