Rydberg atom scattering in K(12p)-CH_3NO_2 collisions: role of transient ion pair formation

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Synopsis Studies of K(12p)-CH_3NO_2 collisions reveal unusually strong Rydberg atom scattering which is attributed to the formation of transient $K^+..CH_3NO_2^-$ ion-pair states.

Collisions between low-*n* Rydberg atoms and attaching targets can lead to formation of weakly-bound ion-pair states through electron transfer reactions of the type

$$X^{**} + AB \rightarrow X + AB^{-*} \rightarrow X^+..AB^- \qquad (1)$$

where AB^{-*} is a short-lived excited state populated by initial electron capture, AB^- is a long-lived metastable anion formed by intramolecular vibrational relaxation, and $X^+..AB^-$ is an ion-pair state. Ion-pair states represent a novel class of long-range molecules which, as shown by recent measurements, posses unusual physical and chemical properties [1].

Earlier studies of reaction (1) have focused on targets that form valence-bound anions. Low-*n* Rydberg collisions with polar targets can also lead to formation of dipole-bound negative ions. We explore the role of dipole binding in forming ion-pair states using CH_3NO_2 whose dipole moment is sufficient to support a dipole-bound state but that can also form long-lived valence-bound anions. As shown in Fig. 1a, pulses of K(12p) atoms are photo-excited near the center of a gas cell where they interact with the target gas. A fraction of the neutral reaction products exit through a slit and enter an analysis region where they are subject to a transverse, pulsed electric field. The resulting negative particles are detected by a position sensitive detector that records their arrival times and positions. The particles are observed to be electrons produced by field ionization of scattered Rydberg atoms. No long-lived ion-pair states are seen. The electron arrival position distributions point to strong Rydberg atom scattering with a collision cross section comparable to the geometric size of the Rydberg atom itself.

Rydberg scattering is attributed to ion-ion scattering through formation of transient ion-pair states with lifetimes ≥10 ps via transitions between the covalent K(12p)+CH_3NO_2 and ionic $K^+..CH_3NO_2^-$ terms in the quasi-molecule

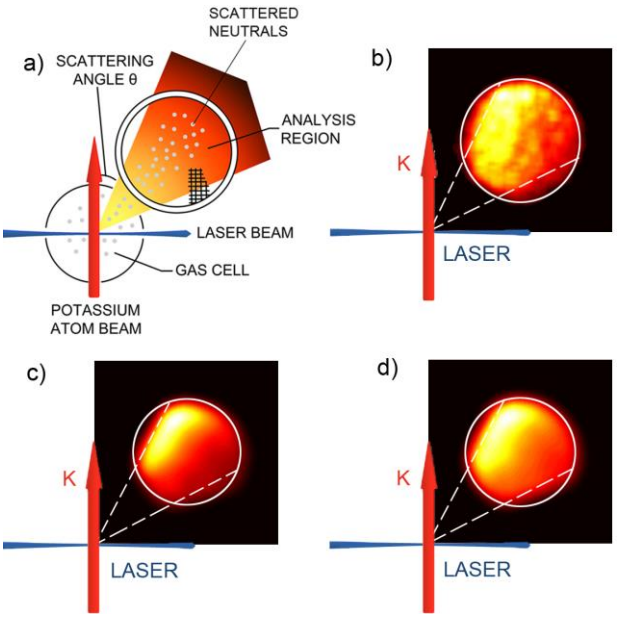

Figure 1. a) Schematic of the experimental approach. b) Measured spatial distribution of scattered Rydberg atoms following a 50 μs flight time. c), d) Results of model calculations that assume ion-pair lifetimes of 10 and 100 ps, respectively.

formed during collision. The $CH_3NO_2^-$ lifetime is limited by electron detachment induced by the field of the K^+ ion, the detached electron remaining bound to the K^+ ion in a Rydberg state. The large reaction rate observed is consistent with theoretical calculations of resonant quenching, i.e., *n*, ℓ changing, in Rydberg collisions with CH_3NO_2. [2]

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References

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