Use of heavy-Rydberg ion-pair states to probe dissociative electron attachment

M Kelley, S Buathong and F B Dunning
Department of Physics and Astronomy, MS-61, Rice University, Houston, Texas, USA

E-mail: mjk2@rice.edu

Abstract. Electron transfer in collisions between Rydberg atoms and targets that attach free low-energy electrons can lead to the formation of heavy-Rydberg ion-pair states comprising a positive-negative ion pair that orbit each other at large separations weakly bound by their mutual electrostatic attraction. It is shown that measurements of the velocity distribution of the ion-pair states produced in such collisions provide a novel probe of the dynamics of dissociative electron attachment.

1. Introduction
Low-energy electron attachment to molecules can lead to formation of long-lived negative ions both through dissociation and through intramolecular vibrational relaxation, i.e., through the reactions

\[ A^- + BC \rightarrow ABC^- + e^- \]

where \( ABC^- \) denotes the short-lived excited intermediate formed by initial electron capture, and \( ABC^- \) a long-lived metastable parent anion [1]. Many interesting questions concerning the dynamics of such reactions center on the lifetime and decay energetics of the \( ABC^- \) intermediate. As we demonstrate here, information on both quantities can be obtained from studies of electron transfer in collisions between atoms in high-\( n \) Rydberg states and attaching targets.

Collisions between Rydberg atoms and neutral targets are frequently discussed using the essentially-free electron model. This model recognizes that, for sufficiently large values of \( n \), the ranges of the Rydberg electron-target and core ion-target interactions become less than the size of the atom whereupon the atom behaves not as a single entity but rather as a pair of independent scatterers. Thus studies of collisions dominated by the Rydberg electron-target interaction can provide information on electron-molecule scattering at thermal and sub-thermal energies characteristic of the Rydberg electron [2,3]. Indeed, Rydberg atom collisions at high \( n \) have been used to measure rate constants for electron attachment to a wide variety of targets at electron energies extending down to a few micro-electronvolts. As \( n \) decreases, however, the Rydberg electron cloud shrinks and the product positive-negative ion pairs must, on average, be formed at ever smaller separations whereupon their post-attachment electrostatic interactions become important. As a result, for thermal-energy collisions, an increasing fraction of the ion pairs possess insufficient kinetic energy of relative motion to
overcome their mutual electrostatic attraction and separate. They therefore remain bound creating an ion-pair state in which the ions orbit each other at relatively large radii [4-9]. Such states are also termed heavy-Rydberg states because many of their properties parallel those of Rydberg atoms [10,11]. While Rydberg atom collisions can be used to create a wide variety of ion-pair states and study their properties, we demonstrate here that ion-pair formation can also be used to explore the lifetimes and decay energetics of short-lived negative ion intermediates. The principal target species employed is BrCN, electron transfer to which can lead to ion-pair formation via the reaction

\[ \text{K}(np) + \text{BrCN} \rightarrow \text{K}^+ + \text{BrCN}^- \rightarrow \text{K}^+..\text{CN}^- + \text{Br} \]  

(2)

where K⁺..CN⁻ denotes an ion pair state. (The CN radical is a pseudo-halogen with an electron affinity, \( \text{EA}_{\text{CN}} = 3.862 \) eV, that exceeds those of the halogens themselves.) The experimental data are analyzed with the aid of a Monte Carlo collision code that models the detailed kinematics of electron transfer reactions. The results show that the velocity and angular distributions of the product ion pairs are sensitive to the assumed decay energetics of the BrCN⁻* intermediate.

2. Methodology

The present apparatus is shown in Fig 1. Briefly, potassium atoms contained in a collimated beam are photoexcited to Rydberg states near the center of a small gas cell where they interact with the target gas. A fraction of the bound ion pairs formed traveling in the \( xy \) plane defined by the laser and atom beams exit the gas cell through a narrow slit and enter an analysis region where they are detected through dissociation induced by a pulsed electric field. The resulting positive ions are accelerated to a position sensitive detector (PSD) that records both their arrival times and positions. The ion-pair velocity distributions are determined using time-of-flight techniques. Short pulses of Rydberg atoms are formed which undergo rapid collisional destruction forming ion pairs. Position distributions for those ion pairs that enter the analysis region are recorded as a function of time following their formation. These distributions are then compared to the results of model calculations undertaken using different assumed intermediate lifetimes and decay energetics to determine the behavior of the intermediates.
The Rydberg atoms are created using UV radiation provided by an extracavity-doubled CW Rh6G laser whose output is chopped into a series of ~10 μs-duration pulses with a pulse repetition frequency of ~1 kHz using an acousto-optic modulator. To help tune the laser to the desired state, positive ions produced in the gas cell through collisions or blackbody-radiation-induced photoionization are extracted by a small (~45 Vcm⁻¹) transverse electric field and detected by a microchannel plate. (This field also prevents free ions formed in the gas cell from escaping through the slit and entering the analysis region.) A fraction of those ion pairs formed traveling within ±4° of the xy plane exit the gas cell through a slit that defines “scattering angles,” θ, defined as the angle between the initial direction of travel of the Rydberg atom and the trajectory of the ion pair, of ~22.5-67.5°. They then enter the analysis region which is bounded by two fine-mesh grids where they are dissociated by a pulsed field that rises from 0 to 5 kV cm⁻¹ in ~3μs. The resulting K⁺ ions are detected by the PSD. Since only a small fraction of the product ion pairs enter the analysis region, data must be accumulated following many laser pulses to build up the distribution of ion arrival positions and thus the initial spatial distribution of the parent ion pairs themselves.
For ion-pair states with a given binding energy, $E_B$, field-induced dissociation occurs over a broad range of fields governed by their angular momenta $L$ and the projections of $L$, $L_z$, where the $z$ axis is defined by the direction of the electric field. Thus it is not possible to assign a unique value of $E_B$ to states that dissociate in a particular field. However, as discussed elsewhere [12], a typical value for the binding energy of states that dissociate in a field $F$ is given by

$$E_B(\text{meV}) = 14[F(\text{kV cm}^{-1})]^{1/2}$$

The measured arrival position distributions are analyzed using a Monte Carlo collision code. Electron transfer is viewed as resulting from a binary interaction between the Rydberg electron and target molecule. The initial velocity of the Rydberg atom and target molecule are chosen at random from the distribution of these parameters. The probability of electron capture at some point is taken to be proportional to the local electron probability density. (To take into account the large quantum defect for $K(np)$ states, $\delta \approx 1.71$, the experimental data for a particular $K(np)$ state are compared to model predictions for the (n-2)p hydrogenic state.) Following capture, the motions of the $K^-$ ion and intermediate negative ion are computed. After some time, governed by the assumed lifetime, $\tau$, of the intermediate, the intermediate is presumed to dissociate. If its lifetime is very short, i.e., if the electron is captured directly into an anti-bonding orbital, it is reasonable to expect that the great majority of the excess energy of reaction will appear in translation resulting in a narrow translational energy release distribution peaked near the excess energy. In contrast, if the intermediate is longer lived, redistribution of the excess energy within the intermediate can occur prior to dissociation and part of the excess energy can appear as vibrational/rotational excitation of the fragments rather than in translation. In the limit of complete statistical redistribution of the excess energy within the intermediate, unimolecular decay theory predicts a Boltzmann-like translational energy release distribution of the form $e^{-\epsilon/\bar{\epsilon}}$, where $\bar{\epsilon}$ is the mean translational energy release [13,14]. Upon dissociation, the angular distribution of the fragments is taken to be isotropic in the rest frame of the intermediate. The kinetic energy of relative motion of the product positive-negative ion pair is computed to determine the final total (kinetic plus potential) energy of the ion pair and if they are bound. If bound, the final ion-pair velocity is determined. Those ion pairs that travel into the analysis region are identified and, by analyzing many collision events, their spatial (and binding energy) distribution is calculated as a function of time following the laser pulse taking into account the fact that, if the ion pairs have finite lifetimes, some will decay en route to the analysis region.

The initial position and binding energy of an ion pair governs its behavior during the ramped electric field applied in the analysis region to induce dissociation. The maximum applied field of 5 kV cm$^{-1}$ is only sufficient to dissociate states with binding energies $E_B \approx 30$ meV. Many ion pairs have larger binding energies and do not dissociate. For those that do, once dissociation occurs the trajectory of the resulting positive ion as it travels towards the PSD is computed using SIMION and its arrival position determined. Ion arrival positions at the PSD are then built up by considering many collision events, their spatial (and binding energy) distribution is calculated as a function of time following the laser pulse taking into account the fact that, if the ion pairs have finite lifetimes, some will decay en route to the analysis region.

The initial position and binding energy of an ion pair governs its behavior during the ramped electric field applied in the analysis region to induce dissociation. The maximum applied field of 5 kV cm$^{-1}$ is only sufficient to dissociate states with binding energies $E_B \approx 30$ meV. Many ion pairs have larger binding energies and do not dissociate. For those that do, once dissociation occurs the trajectory of the resulting positive ion as it travels towards the PSD is computed using SIMION and its arrival position determined. Ion arrival positions at the PSD are then built up by considering many collision events, their spatial (and binding energy) distribution is calculated as a function of time following the laser pulse taking into account the fact that, if the ion pairs have finite lifetimes, some will decay en route to the analysis region.

3. Results and Discussion

In collisions with Rydberg atoms the total excess energy of reaction is given by $E_A= D_0(\text{Br-CN}) + E_{\text{int}} + E_\text{K}^-(e^-)$ where $D_0(\text{Br-CN})$ is the Br-CN bond dissociation energy, $E_{\text{int}}$ is the usable internal energy in the parent molecule (~0.02 eV) and $E_\text{K}^-(e^-)$ is the median energy of the attached electron, ~0.02 eV for $n=14$ [3]. $D_0(\text{Br-CN})$ has been measured using a variety of techniques.

Analysis of thermochemical data [15] yields the value 3.69±0.05 eV, similar to that deduced from measurements of photodissociation, 3.68±0.02 eV [16] and predicted theoretically [17]. Photodissociation studies, however, yield a somewhat higher value, 3.77±0.05 eV [18]. Taken together, these results suggest a value $D_0(\text{Br-CN}) = 3.70$ eV pointing to an excess energy of reaction, $\varepsilon$, of ~0.2 eV.
Figure 2(a) shows arrival position distributions measured at the PSD for $K^+..CN^-$ ion pairs formed in $K(14p)$–BrCN collisions. The laser pulse width is 10 $\mu$s and the delay times, $t_d$, indicated are measured from the end of the laser pulse. The color scale in each panel is normalized to the peak value in that panel. As $t_d$ increases the ion pairs move steadily away from their point of formation with a relatively broad range of speeds and an angular distribution that is peaked towards smaller scattering angles.

If the BrCN* intermediate is very short lived and undergoes immediate dissociation all the excess energy will appear in translation resulting in a narrow translational energy release distribution centered on the mean energy. Fig. 2(b) shows arrival position distributions calculated assuming a $\delta$-function translational energy release distribution centered on the expected value of 0.2 eV. Inspection of Fig. 2 shows that these distributions do not match those measured experimentally. In particular, the calculated distributions are peaked at larger scattering angles and comparison of the early-time data sets shows that the calculated ion pair velocities are greater than seen experimentally. These discrepancies cannot be removed by simply assuming that the measured values of $D_\theta$(Br-CN) are incorrect. Figure 2(c) shows calculated position distributions for a $\delta$-function translational energy release distribution centered on 0.1 eV. While this yields somewhat better agreement with experiment, sizeable differences remain. The data in Fig. 2 thus clearly demonstrate that a dissociation model in which all the excess energy of reaction appears in translation is not appropriate and that a different reaction model is required.
Earlier studies [7,8] have shown that electron transfer in K(14p)-CCl₄ collisions can lead to creation of K⁺..Cl⁻ ion pair states via the reaction

\[
K(14p) + CCl₄ \rightarrow K⁺ + CCl₄* \rightarrow K⁺..Cl⁻ + CCl₃
\]  

(2)

In this case, the bond dissociation energy \( D_0(CCl₃-Cl) \) is ~3.07 eV and the electron affinity of chlorine is \( EA_{Cl} = 3.61 \) eV pointing to an excess energy \( \epsilon \approx 0.5 \) eV. If immediate dissociation were to occur and all this energy appear in translation the majority would be acquired by the (light) Cl⁻ ion, resulting in large Cl⁻ velocities. However, earlier measurements [19] of the velocities of Cl⁻ ions produced in high-\( n \), \( n \approx 50 \), K(np)-CCl₄ collisions for which post-attachment electrostatic interactions and ion pair formation are negligible showed the product Cl⁻ ions to have much lower velocities requiring that the lifetime of the CCl₄* intermediate is sufficient to allow efficient redistribution of the excess energy of reaction among internal vibrational modes of the intermediate prior to dissociation. As noted previously, this is expected to lead to a Boltzmann-like translational energy release distribution of the form \( e^{-\epsilon/\bar{\epsilon}} \). It was shown that the observed velocity distributions could be well fit by assuming a mean translational energy release \( \bar{\epsilon} = 0.1 \) eV, the remaining energy appearing as vibrational excitation in the CCl₃ fragment.

Consider now applying the same model to BrCN. Figure 3 shows representative arrival position distributions calculated assuming a Boltzmann-like translational energy release distribution with \( \bar{\epsilon} = 0.05 \) and 0.1 eV. In deriving these results a mean lifetime of 20 ps was assumed for the BrCN* intermediate [20]. Inspection of Fig 3 reveals that, although the agreement with experiment is better than seen when using a \( \delta \)-function distribution, it is still not good. This is not unexpected as there are significant differences between electron attachment to BrCN and CCl₄. In the case of CCl₄, the CCl₃ fragment has a broad range of vibrational modes into which the sizeable (~0.5 eV) excess energy can be deposited and transported away. Assuming that the electron binding energy for BrCN is similar to that for many other attaching targets, i.e., ~1 eV, then electron capture can, if the BrCN* intermediate lifetime is sufficiently long, again lead to population of a range of vibrational states in the intermediate through intramolecular vibrational relaxation. The intermediate has sufficient energy to dissociate but the energy has to be localized in the Br-CN⁻ coordinate for dissociation to proceed, which takes time. However, the available excess energy is less than the calculated vibrational spacing in CN⁻, ~0.25 eV [21]. Energy considerations therefore require that capture lead to creation of CN⁻ ions in the vibrational ground state. (Because the vibrational spacing for the C–N stretch in BrCN is sizable, ~0.27 eV, this mode is not significantly excited in a room-temperature target gas.) In consequence, in contrast to CCl₄, excess energy can only be transported away in the form of CN⁻ rotational energy. The rotational constant for CN⁻ is small, \( B(CN⁻) = 0.23 \) meV [21]. The available excess energy is therefore sufficient to populate a broad range of rotational states. However, a Boltzmann-like translational energy release distribution, which peaks at \( \epsilon = 0 \), is unlikely as it would require that dissociation preferentially populate highly-rotationally-excited states rather than a broad, more thermal-like distribution of such states. One consequence of rotational excitation is that, as shown in earlier measurements [7], weakly-bound K⁺..CN⁻ ion pairs have finite lifetimes due to dissociation induced by conversion of rotational energy in the CN⁻ ion into translational energy of the ion pair. In the earlier measurements no significant decay of ion pair states with binding energies greater than ~30 meV was observed. States with binding energies of ~20 meV were seen to decay with a mean lifetime of ~25 \( \mu \)s, this being reduced to ~7 \( \mu \)s for binding energies of ~9 meV. Such decay during passage to the analysis region is taken into account in calculating the results presented in Fig. 3 (and in Fig. 4).
Information on the CN⁻ rotational distribution can be extracted from the measured arrival position distributions. In particular, the rotational energy distribution must be relatively broad because, as seen in Fig. 2, calculations using near δ-function translational energy release distributions, which would correspond to population of a narrow distribution of rotational states, do not provide a good fit to the experimental data. However, as shown in Fig. 4(b), excellent fits can be achieved using “triangular” translational energy distributions such as shown in the inset which models the population of a range of rotational states peaked near J=12, i.e., peaked at energies BJ(J+1) ~ 35 meV corresponding to a suprathermal distribution. Figure 4(c) includes calculations undertaken using a translational energy release distribution chosen to mirror that expected if collisions predominantly lead to the population of low-lying rotational states. However, the agreement with experiment is not as good as in Fig. 4(b). The present results therefore demonstrate that electron attachment to BrCN leads to creation of CN⁻ ions in a broad range of rotationally-excited states. This finding is consistent with the results of threshold ion pair production spectroscopy of HCN which also showed the CN⁻ fragments to be rotationally hot [22]. However, the calculated arrival position distributions are not very sensitive to the exact choice of the translational energy release distribution (provided it is broad and peaked at energies of ~150 meV) and the product CN⁻ rotational distribution cannot be precisely determined. The calculations in Fig. 4 again assume a BrCN⁻* intermediate lifetime of 20 ps [20]. The calculated arrival position distributions, however, are insensitive to assumed lifetime for values less than ~30 ps,

Fig. 3 As in Fig. 2, arrival position distributions for K⁺ CN⁻ ion pairs formed in K(14p)-BrCN collisions. (a) Experimental data. (b) and (c) Results of simulations assuming Boltzmann-like translational energy release distributions with mean energies $\bar{\epsilon}=0.1$ and 0.05 eV, respectively. The delay times $t_d$ are as indicated.
i.e., for values substantially less than the typical $K^+..BrCN^-*$ orbital periods. Significant changes are only apparent for assumed lifetimes greater than ~50-100 ps.

Fig. 4 As in Fig. 2, arrival position distributions for $K^+..CN^-*$ ion pairs formed in $K(14p)$-BrCN collisions. (a) Experimental data. (b) and (c) Results of simulations using the translational energy release distributions shown in the insets. The delay times are as indicated.

4. Conclusions
Measurements of the velocity distributions of heavy-Rydberg ion-pair states formed through electron transfer in collisions with Rydberg atoms provide a novel approach to probing the lifetimes and decay energetics of excited negative ion intermediates. In the future measurement precision might be improved by better controlling the collision conditions, for example by using velocity-selected Rydberg atoms created by using an off-normal laser beam and tuning to the appropriate part in the Doppler profile, and through studies using different values of $n$ to vary the binding-energy distributions of the product ion pairs.
References
[1] see, for example, Electron-Molecule Interactions and their Applications, edited by Christophorou, L. G. (Academic, New York, 1984)
[2] Dunning, F. B. in Photonic, Electronic and Atomic Collisions, edited by Fainstein, P.D., Lima, M. A., Miraglia, J. E., Montenegro, E. C., and Rivarola, R. D. (World Scientific, Singapore, 2006) p. 64
[3] Dunning, F. B. 1995 J. Phys. B.: At. Mol. Opt. Phys. 28 1645
[4] Cannon, M., Dunning, F. B. 2009 Chem. Phys. Lett. 479 30
[5] Cannon, M., Wang, C. H., Dunning, F. B. 2009 Chem Phys. Lett. 479 30
[6] Cannon, M., Liu, Y., Dunning, F. B. 2008 Chem Phys. Lett. 458 35
[7] Cannon, M., Wang, C. H., Dunning, F. B., Reinhold, C. O. 2010 J. Chem. Phys. 133 064301
[8] Wang, C. H., Kelley, M., Buathong, S., Dunning, F. B. 2014 J. Chem. Phys. 140 234306
[9] Buathong, S., Kelley, M., Wang, C. H., Dunning, F. B. 2015 Chem. Phys. Lett. 618 153
[10] Reinhold, E., Ubachs, W. 2005 Mol. Phys. 103 1329
[11] Vieitex, M. O., Ivanov, T. I., Reinhold, E., de Lange, C. A., Ubachs, W. 2008 Phys. Rev. Lett. 101 163001
[12] Reinhold, C. O., Yoshida, S., Dunning, F. B. J. Chem. Phys. 134 174305
[13] Klots, C. E. 1964 J. Chem. Phys. 41 117
[14] Klots, C. E. 1971 J. Chem. Phys. 75 1526
[15] Brüning, F., Hohndorf, I., Stamatovic, A., Illenberger, E. 1996 J. Chem. Phys. 100 19740
[16] Berkowitz, J. 1962 J. Chem. Phys. 36 2533
[17] Royal, J., Orel, A. E. 2006 J. Chem. Phys. 125 214307
[18] Davis, D. D., Okabe, H. 1968 J. Chem. Phys. 49 5526
[19] Pople, R. A., Finch, C. D., Smith, K. A., Dunning, F. B. 1996 J. Chem. Phys. 104 8485
[20] Parthasarathy, R., Suess, L., Hill, S. B., Dunning F. B. 2001 J. Chem. Phys. 114 7962
[21] Bauschlicher, Jr., C. W. 1997 Int. J. Quantum Chem. 61 859
[22] Hu, Q. J., Zhang, Q., Hepburn, J. W. 2006 J. Chem. Phys. 124 074310