



Postattachment interactions in K(n d)–CF3I collisions at intermediate n

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TABLE I. Geometries of the C_{2v} and D_{3h} stationary points and planar vibrational frequencies for the D_{3h} stationary point evaluated at the CASSCF $(17e^{-1/3} \text{ MO})$ level of theory with a DZ + P basis set.

	Experiment (Refs. 3 and 4)	Theory	
		D _{3h}	C 2v
N-O _{long} (one)	1.24	1.256	1.351
N-O _{short} (two)	1.24	1.256	1.224
O _{long} -N-O _{short}	120°	120°	114.7°
$v_1(e')$	1492 cm^{-1}	963 cm^{-1}	
$v_2(a'_1)$	1060 cm^{-1}	1068 cm^{-1}	
$v_3(a_2'')$	762 cm^{-1}		
$v_4(e')$	380cm^{-1}	596i cm ⁻¹	
Energy (hartrees)		- 279.094 34	- 279.096 60

 C_{2v} , or the symmetry breaking problem can be even more difficult to overcome than previously thought.^{7,9-11}

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- Post-attachment interactions in K(nd)-CF₃I collisions at intermediate *n*

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Negative ion formation in collisions between atoms in high Rydberg states and target molecules that attach free low-energy electrons is frequently treated using the so-called essentially-free electron model.¹ This model assumes that, for large values of principal quantum number n, the separation between the excited Rydberg electron and its associated core ion is so large that negative ion production can be discussed simply in terms of electron capture in the binary interaction between the Rydberg electron and target molecule. Studies with SF₆, however, show that the SF₆⁻ ion signal resulting from the electron transfer reaction

$$\mathbf{K}(nd) + \mathbf{SF}_6 \rightarrow \mathbf{K}^+ + \mathbf{SF}_6^- \tag{1}$$

decreases markedly for states with principal quantum number $n \leq 20$.^{2,3} This decrease is explained by arguing that, for such values of *n*, the ion pairs are created in sufficiently close proximity that a significant fraction of them possess insufficient kinetic energy to overcome their mutual electrostatic attraction and separate, and therefore are not observed. The K⁺ and SF₆⁻ ions initially have thermal energy distributions. The kinetic energy of relative motion required for separation is on the order of the electron binding energy, ~140 meV at n = 10 and ~35 meV at n = 20, i.e., 13.6/ n^2 eV.

Recent kinematic studies⁴ of the dissociative electron transfer reaction

undertaken at high n (n > 55) show that dissociation of the intermediate CF₃I^{-*} complex is essentially instantaneous and that the resulting I⁻ ions are formed with appreciable kinetic energy (~280 meV). This suggests that, because of the large kinetic energy of the I⁻ fragment, post-attachment electrostatic interactions should be relatively unimportant even for intermediate values of $n(9 \le n \le 20)$. Kinematic data presented here, however, provide graphic evidence that post-attachment interactions *are* important at intermediate n.

In the present work the velocities and angular distributions of I⁻ ions produced via reaction (2) at intermediate nare determined by allowing collisions to occur in a well-defined volume and measuring the displacement of the product ions a known time later. The apparatus is described in detail elsewhere.^{4,5} Briefly, potassium atoms contained in a collimated thermal-energy (320 °C) beam are excited to a selected *nd* state by two-photon excitation using the focused output of a CW Rh6G ring dye laser. The laser output is modulated by a fast Pockel's cell to provide light pulses of 1 μ s duration at a 10 kHz pulse repetition frequency. The probability that a Rydberg atom is created during any exci-

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FIG. 1. Spatial distributions of I⁻ ions detected following $K(nd)/CF_{1}I$ collisions at intermediate n. The inset indicates the directions of the laser and potassium atom beams.

tation pulse is small, < 0.05. Excitation occurs, in zero electric field and in the presence of target gas, near the center of an interaction region defined by two planar fine-mesh grids. After allowing collisions to occur for a predetermined interval (typically $\sim 1 \ \mu s$), a pulsed electric field is applied to expel any collisionally produced I⁻ ions from the interaction region and into a field-free drift region. Upon exiting the drift region the ions are detected by a 1 in. diam position sensitive detector (PSD). The PSD provides both the arrival time and position of an ion and these are recorded and stored by a microcomputer. Data are accumulated following many laser pulses to build up a two-dimensional distribution of ion arrival positions. This distribution reflects the product of the I⁻ drift times ($\sim 13 \,\mu s$) and their components of velocity in the plane of the PSD.

The arrival position distributions for I^- ions detected following $K(nd)/CF_3I$ collisions for n = 9, 15, and 26 are shown in Fig. 1. Each distribution was recorded under identical experimental conditions. The distribution for n = 26(and all higher n)⁴ is circularly symmetric indicating that the observed I⁻ ions have an isotropic velocity distribution, as would be expected if post-attachment interactions are unimportant. As n decreases, however, the observed distribution becomes increasingly asymmetric until, at n = 9, almost all the detected I⁻ ions have significant velocity components antiparallel to the initial velocities of the K(nd) Rydberg

atoms. This striking asymmetry is a direct consequence of post-attachment interactions and may be explained qualitatively as follows. Although the Rydberg atoms have a thermal distribution of speeds, their mean velocity of $\sim 5.7 \times 10^4$ cm s⁻¹ is close to the mean velocity of I⁻ ions created by dissociative electron capture, $\sim 6.5 \times 10^4$ cm s^{-1.4} Thus, if an I^- ion is initially formed traveling in the same general direction as the K⁺ core ion, the relative kinetic energy of the ion pair in the center-of-mass frame will be very small. In contrast, if the ions are initially traveling in opposite directions, their relative kinetic energy will be large. As n decreases, an increasing amount of relative kinetic energy is, on average, required to permit the ions to overcome their mutual electrostatic attraction. In consequence, at lower n, a substantial fraction of those ion pairs for which the I^- ion is initially travelling in the same direction as the K⁺ ion possess insufficient relative kinetic energy to separate and are therefore not detected, resulting in an I⁻ angular distribution that is peaked in the opposite direction. We have observed a similar effect in studies of Br^- formation in K(nd)/ CF_3Br collisions at intermediate n.

The present data show that even in cases where the product negative ions are formed with sizeable kinetic energies, post-attachment interactions must be considered. Similar kinematic effects may also be important in interpreting data obtained in other electron transfer studies.⁶

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¹For a discussion of this model see, for example, the articles by M. Matsuzawa and by A. P. Hickman, R. E. Olson, and J. Pascale, in *Rydberg States of Atoms and Molecules*, edited by R. F. Stebbings and F. B. Dunning (Cambridge University, New York, 1983).

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Femtosecond studies of electron photodetachment of simple ions in liquid water: Solvation and geminate recombination dynamics

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Aqueous solutions of simple ions such as OH^- and $Cl^$ have fascinated many scientists. In this communication we present the first femtosecond time-resolved studies of electron photodetachment in aqueous solution. The solvation of the ejected electron in the aqueous media and the subsequent recombination dynamics of the neutral atom with the electron have been measured. Relevant to this are several recent experimental studies of electrons in neat liquids using femtosecond lasers.¹⁻⁴

The experiments discussed here were performed with a Nd:YAG amplified CPM laser; the operational details can be found elsewhere.^{2,3}

Work done over 30 years ago showed that solvated electrons were produced when UV light irradiated simple ions in solution.⁵ These transitions are called CTTS, charge transfer to solvent spectra.⁶ The production of electrons in this case is not due to photoionization, in the normal sense, since an intermediate excited state of the parent species is involved. The existence of an excited state from which the electron originates was inferred from several studies in which the effect of quenchers and temperature on the quantum yield of solvated electrons was measured.^{7,8}

Reflecting the widespread interest in the dynamics of electron solvation in water, are the many theoretical⁹⁻²⁸ and experimental studies ^{1,3,4,29,30} of electron and ion solvation. Using femtosecond pump/probe spectroscopy at 312.5 nm/ 625 nm, we find that the solvation dynamics of the electron ejected from a chloride ion Cl-, in aqueous solution are slower than that for an electron originating from a water molecule, Fig. 1(a). Using the signal from n-octane as an instrumental response, a rise time of 500 fs is found for the Cl⁻, compared with 350 fs for water. The solvation time for the electron originating from the OH⁻ was also found to differ from neat water. These results are inconsistent with continuum theories of electron solvation, which predict that there be almost no change in the observed solvation dynamics.^{31,32} We thus conclude that molecular effects are playing a large role in the electron solvation dynamics. It should be noted that the rise time in the infrared, i.e., the region where the presolvated electron absorbs, is as fast as the n-octane signal. We therefore conclude that the lifetime of the CTTS state is much shorter than the solvation times that we are observing, but it is our view that improved time resolution is needed to confirm fully this point. If the electron ejected from the CTTS state thermalizes very near the atom, then the solvent structure around the previously solvated species can greatly influence the solvation dynamics. In our previous multiphotonionization experiments we estimated the electron thermalization distance to be about 13 Å.^{3,4} At these larger electron–atom separations, much smaller local solvent effects would be expected.

At longer times, decays are seen in the solvated electron absorption signal, Fig. 1(b). The decays seen in NaCl, NaOH and neat water are all different from each other.^{3,4} It is known that solvated electrons do not react with Na⁺, Cl⁻, OH⁻ ions on the time scale of these experiments.³³ With the additional fact that there was no concentration dependence seen in the decay, the possibility of the solvated electron reaction with the Na + or the Cl⁻ ions is discounted; concentrations of up to 1M were studied. Therefore we conclude that the observed decays are due to geminate recombination of the electron with the chlorine atom or OH radical formed upon photodetachment of the electron by the UV pulse. The marked differences we have observed between the neat water and the ionic solution experiments are thus expected, since in the former the electron recombines with an ion, whereas in the latter the electron recombines with a neutral.

In this initial report we have compared our data to a continuum diffusion model.³⁴ Using a survival probability for the geminate recombination of hard spheres, i.e., the solvated electron and the chlorine atom, we see from Fig. 1(b) that the best fit we can obtain is poor. The fit was not significantly improved by using a distribution. Although we have not completed a quantitative comparison, we find that the molecular theory of Northrup and Hynes yields a trend consistent with our results.³⁵

In conclusion, we have performed femtosecond electron photodetatchment studies of simple ions in aqueous solutions. On the femtosecond time scale, the solvation dynamics of the electron originating from Cl^- and OH^- are slower