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LETTERS

Dynamics of the Charge-Transfer-to-Solvent States in $I^-(Xe)_n$ Clusters

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We have used femtosecond photoelectron spectroscopy to monitor the dynamics associated with the charge-transfer-to-solvent (CTTS) states in $I^-(Xe)_n$ clusters. We find that the lifetime for the $^2P_{1/2}$ CTTS state increases approximately linearly with cluster size, e.g. 550 ± 50, 700 ± 50, and 1550 ± 200 fs for clusters $n = 11$, 20, and 38, respectively. These states are determined to decay by spin−orbit autodetachment. In contrast, the $^2P_{3/2}$ CTTS state has a lifetime greater than 225 ps for even the smallest cluster studied, $n = 6$. No evidence for solvent reorganization is observed in the photoelectron spectra.

Anions solvated in polar solutions generally exhibit distinct bands in the ultraviolet known as charge-transfer-to-solvent bands (CTTS).[1,2] These states involve electron detachment from the solute anion to nearby solvent molecules and serve as precursor states to fully solvated electrons. In recent years there has been considerable experimental and theoretical interest in the complex dynamics associated with CTTS excitation, particularly for halide ions in methanol and H_2O.[3−8] To gain a complementary perspective on this problem, and as part of a broader effort to understand how effects associated with electron solvation are manifested in systems of finite size, the spectroscopy and solvation dynamics associated with the CTTS bands have been investigated in finite clusters. For example, Johnson has located the cluster analogue of the lower $^2P_{3/2}$ CTTS band in $I^-(H_2O)_n$ clusters,[9] and we have used anion femtosecond photoelectron spectroscopy (FPES)[10] to probe the dynamics associated with this band in $I^-(H_2O)_n$ clusters.[11,12] The FPE spectra showed clear evidence for nuclear rearrangement and electron solvation within the cluster for $n \geq 5$. One might expect dramatic differences in the nature of the excited state if a nonpolar solvent such as Xe is used instead of H_2O. Efforts in this direction have been initiated in experiments by Cheshnovsky and co-workers,[13,14] who located CTTS bands in $I^-(Xe)_n$. In this paper, anion FPE spectra of $I^-(Xe)_n$ clusters are reported that indeed exhibit significantly different dynamics than the spectra of $I^-(H_2O)_n$ clusters.

As shown by Cheshnovsky and co-workers,[13,14] the excitation spectra of size-selected $I^-(Xe)_n$ ($n = 1−54$) clusters exhibit two CTTS bands beginning with $n = 4$. These bands are associated with the creation of a neutral I atom core in its $^2P_{3/2}$ ground or $^2P_{1/2}$ spin−orbit excited states and a weakly bound electron that is stabilized by the cluster polarizability, e.g., $[I(^2P_{1/2})Xe_n]^-$. The bands become more prominent with increasing n, and are found to be quite narrow, e.g., 0.04 and 0.02 eV fwhm for the $^2P_{3/2}$ and $^2P_{1/2}$ CTTS states of $n = 12$. The $^2P_{3/2}$ CTTS band is broader than that of $^2P_{1/2}$ because its degeneracy is broken by the anisotropic interaction of the $I(^2P_{3/2})$ core with the surrounding solvent atoms.[15,16] A comparison of Cheshnovsky's results with the threshold photodetachment studies of Lenzer et al.,[15,16] in which the electron affinities of $I^-(Xe)_n$ clusters ($n = 1−14$) were measured, indicates that the two CTTS bands lie just below the detachment thresholds for $I(^2P_{3/2})Xe_n$ and $I(^2P_{1/2})Xe_n$.

The stability of the CTTS states is intimately related to electron solvation in bulk and clustered xenon; bulk xenon stabilizes electrons by 0.58 eV, even though a single xenon atom does not bind an electron.[17] Experimental work on Xe_n^- clusters has shown that the minimum cluster size needed to bind an electron is $n = 6$,[18,19] while diffusion Monte Carlo simulations show that electron binding in Xe_n^- clusters arises from attractive,

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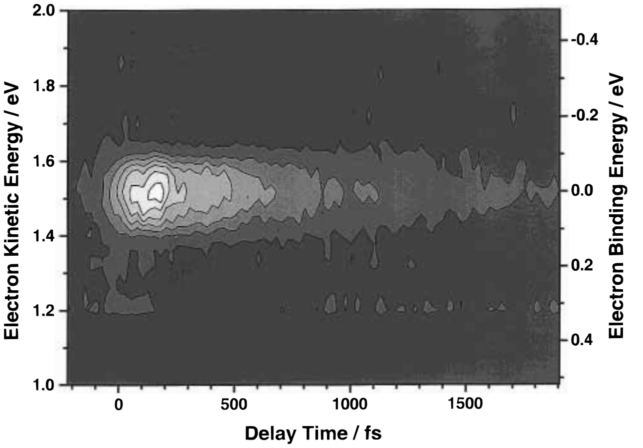

Figure 1. Contour plot of FPE spectra for the ${}^2P_{1/2}$ state of $I^-(Xe)_{11}$ excited at 272 nm. The spectra are presented as a contour plot of the photoelectron intensity versus eKE, electron binding energy (eBE), and pump−probe delay.

narrow electron "channels" that exist between the Xe atoms and a broad stabilizing potential around the cluster itself.[20,21] Although calculations have not been performed on the CTTS states in $I^-(Xe)_n$ clusters, qualitative comparisons can still be drawn between these states and Xe_n^- clusters, as will be discussed below.

The FPES experiment[10,22] involves exciting the $I^-(Xe)_n$ cluster with a femtosecond pump pulse at the resonant wavelength measured by Cheshnovsky and co-workers.[14] The photoelectron spectrum of the excess electron is then measured at a series of delay times by photodetachment with a femtosecond probe pulse. At each delay time, the photoelectron spectrum represents a complete "snapshot" of the evolving state. The time evolution of the intensity and shape of the photoelectron spectrum probe the population change of the excited state and any solvent rearrangement within this state, thereby providing a detailed picture of the excited-state dynamics.

In our experiments, $I^-(Xe)_n$ clusters are formed in a pulsed, supersonic expansion of about 5% CH_3I and 10% Xe in Ar carrier gas (2 bar total pressure) that is crossed with a 1 keV electron beam and size-selected by injection into a Wiley−McLaren time-of-flight mass spectrometer. After passing through several differentially pumped chambers, the anions are intercepted by the pump and probe pulses at the focus of a magnetic bottle photoelectron spectrometer, which provides high photoelectron collection efficiency at moderate energy resolution ($\leq$150 meV for the data presented here). The pump and probe pulses are generated with a Clark-MXR regeneratively amplified Ti:sapphire laser system that generates pulses near 800 nm (1.56 eV), 1 mJ, and 80 fs (sech^2) fwhm. About 200 μJ of this is used as the probe pulse, while the rest generates a tunable UV pump pulse by one of two methods. In the experiments pumping the ${}^2P_{1/2}$ CTTS state, the fundamental light is tuned between 825 and 790 nm, depending on the cluster size, and frequency-tripled to produce 12 μJ of UV in the range 275−263 nm (4.51−4.71 eV) with a fwhm of 110 fs. For the experiments on the ${}^2P_{3/2}$ CTTS state, the fundamental pumps a Light Conversion optical parametric amplifier (TOPAS) whose output is quadrupled, resulting in 4 μJ of UV in the range 369−344 nm (3.36−3.60 eV) with a fwhm of 110 fs. For each of the clusters studied, the pump pulse is set to within 20 meV of the vertical detachment energy measured by Cheshnovsky and co-workers.[14]

FPE spectra are shown in Figure 1 for excitation of the ${}^2P_{1/2}$ state of $I^-(Xe)_{11}$ excited at 272 nm. The spectra are presented as a contour plot of the photoelectron intensity versus electron kinetic energy (eKE), electron binding energy (eBE $= h\nu_{\mathrm{probe}} -$ eKE), and pump−probe delay. The FPE spectra of $I^-(Xe)_{11}$ in Figure 1 are typical for all clusters measured; the intensity rises to a maximum during the first 200 fs and then decays to the baseline by ~2 ps with no shift in electron kinetic energy. The peak width of ~150 meV reflects the electron energy resolution of the spectrometer and scales as $m^{-1/2}$, where m is the mass of the cluster. The vertical detachment energy (VDE), which we determine by finding the average electron binding energy at a particular delay time, is 0.007 ± 0.08 eV for this cluster and shows no time dependence.

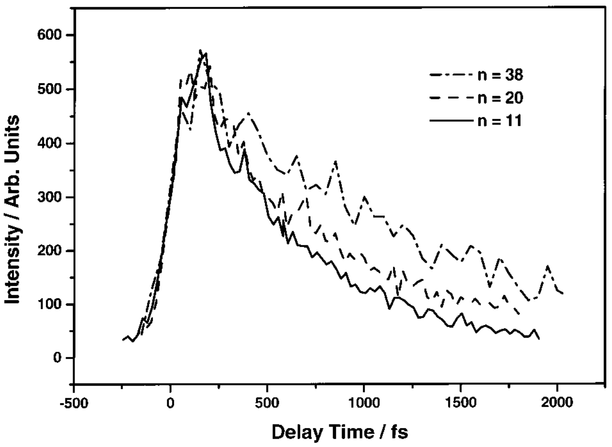

Figure 2. Integrated intensity of the ${}^2P_{1/2}$ CTTS state FPE spectra as a function of time for $I^-(Xe)_{11}$, $I^-(Xe)_{20}$, and $I^-(Xe)_{38}$.

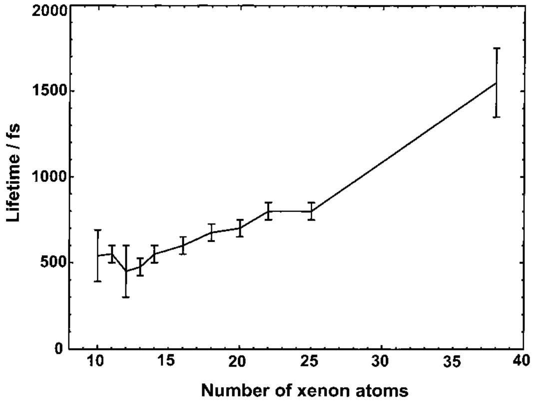

Figure 3. Lifetimes of the ${}^2P_{1/2}$ CTTS state as determined from fitting the lifetime data (Figure 2) to a single-exponential decay convoluted with an instrument response function.

Experiments on the ${}^2P_{1/2}$ CTTS states of larger clusters yield similar FPE spectra with no time dependence in the VDE. However, the VDE does increase with cluster size and is found to be 0.048 ± 0.07 and 0.096 ± 0.07 eV for $n = 20$ and 38, respectively. These spectra were taken at pump wavelengths of 269 and 265 nm. In addition, the lifetime of the CTTS state increases. Figure 2 shows integrated intensities of the FPE spectra vs time for the $n = 11$, 20, and 38 clusters. These decay with time constants of 550 ± 50, 700 ± 50, and 1550 ± 200 fs, respectively, as determined from a single-exponential fit to the data, convoluted with an instrument response function. Figure 3 plots the lifetimes of the ${}^2P_{1/2}$ CTTS states for all the clusters measured, and an approximately linear dependence on the cluster size is found. Markedly different dynamics are found for the ${}^2P_{3/2}$ CTTS states, which show no decay for even the smallest cluster studied ($n = 6$) up to the longest times measured (>225 ps), as illustrated in Figure 4.

The difference in lifetimes for the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ CTTS states

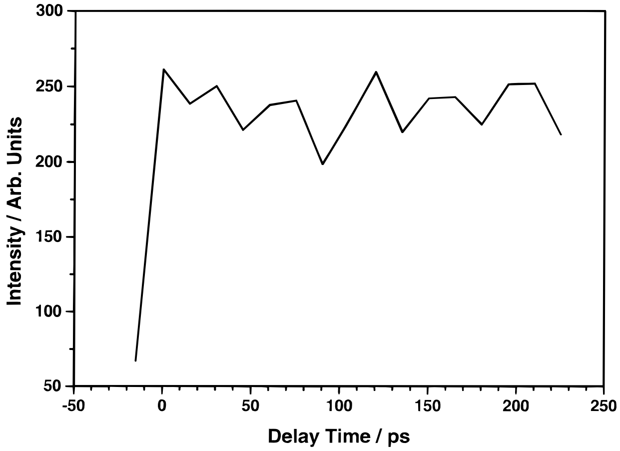

Figure 4. Integrated intensity of the $^2P_{3/2}$ CTTS state FPE spectra for $I^-(Xe)_6$.

implies that the higher energy state decays by spin−orbit induced autodetachment, i.e.

$$[I(^2P_{1/2})Xe_n]^- \rightarrow I(^2P_{3/2})Xe_n + e^- \qquad (1)$$

No such decay pathway exists for the $^2P_{3/2}$ CTTS state, consistent with its long lifetime. In fact, the experiments by Cheshnovsky and co-workers[13,14] and Lenzer et al.[15,16] suggest that the $^2P_{3/2}$ CTTS state is bound with respect to electron detachment. Vibrational-to-electronic energy transfer could also result in electron detachment if the anion cluster temperature is high or if there is a large amount of vibrational energy in the excited state. However, this energy transfer mechanism would presumably affect both clusters equally. Since we observe no such decay for the $^2P_{3/2}$ state on the time scale of our experiment, this process must be considerably slower than spin−orbit autodetachment (from the $^2P_{1/2}$ state) in these clusters.

The time-independent vertical detachment energies are in sharp contrast to the FPE spectra of $I^-(H_2O)_n$ ($n \geq 5$) clusters.[12] For those species, the electron kinetic energy drops by ∼0.3 eV within the first picosecond. This shift was attributed to stabilization of the excess electron via solvent reorganization, i.e., electron solvation. Reorganization occurs because the geometry of the H_2O molecules in the ground state of $I^-(H_2O)_n$ clusters is not the most favorable for minimizing the energy of the excess electron in the excited state. Similar but less pronounced solvation dynamics were seen in $I^-(NH_3)_n$ clusters.[23] Although the peak width is 150 meV for $I^-(Xe)_{11}$, we have shown in previous studies that we are sensitive to *changes* in electron affinity on the order of 10 meV.[24] The absence of any shifts indicates that only minimal solvent reorganization takes place after excitation of the CTTS bands.

The absence of solvent reorganization is consistent with the frequency domain spectroscopy of these clusters. Our ZEKE/threshold photodetachment spectra of $I^-(Xe)_n$ clusters and the accompanying molecular dynamics calculations show that in the lowest energy geometry, Xe atoms surround the I^- to the greatest extent possible and that I^- clearly lies inside a cluster of Xe atoms for $n \geq 11$.[16] The narrow CTTS bands seen by Cheshnovsky and co-workers indicate that similar structures hold for the excited states.[14] Excitation of these states will therefore access at least a local minimum on the excited-state surface, in which case no solvent reorganization should occur.

The lack of cluster rearrangement can be understood in the context of calculations on Xe_n^- clusters. The work by Martyna and Berne shows that Xe_n^- clusters are essentially neutral Xe_n clusters surrounded by a very diffuse electron cloud that is considerably larger than the nuclear core of the cluster.[20,21] For Xe_{13}^-, the electron probability distribution peaks ∼2 Å outside and extends ∼36 Å beyond the nuclear core. Because the excess electron is bound solely by the polarizability of the cluster atoms, and the polarizability of iodine and xenon are very similar ($\alpha_I = 30.05a_0^3$; $\alpha_{Xe} = 27.16a_0^3$), the wave function for the excess electron should resemble that of the CTTS states in $[I(Xe)_n]^-$ clusters. The essential feature in both cases is that the excess electron does not perturb the nuclear cluster geometry, because the binding energy of the electron per atom is small and the electron is spatially diffuse. Under such circumstances, it is unlikely that nuclear rearrangement could produce an overall lower energy structure in which the excess electron is more solvated (and more localized). This situation differs markedly from $I^-(H_2O)_n$ clusters, in which stronger interactions between the excess electron and solvent molecules drive the solvation dynamics in the excited state.[12]

Finally, we consider the size dependence of the autodetachment rate from the $^2P_{1/2}$ excited states. As shown in Figure 3, the upper state lifetime increases with the number of Xe atoms. The mechanism given by eq 1 requires an interaction between the excess electron and the $I(^2P_{1/2})$ core in order to induce a spin-flip of the unpaired electron on the I atom. Thus, the increase in lifetime of the $^2P_{1/2}$ CTTS state with cluster size presumably reflects a reduction in this interaction. A simple explanation of this trend would be that the I atom, which sits at the center of the cluster, is more effectively shielded from the diffuse electron cloud by Xe atoms in the larger clusters, resulting in a lower excess electron probability density at the I atom.

The calculations by Martyna and Berne[20,21] on Xe_n^- suggest the situation is more complex. They find that as n increases, the electron cloud becomes less diffuse and the probability of finding the excess electron close to a Xe atom increases, as reflected in their calculated electron−Xe pair correlation function. However, the pair correlation function is averaged over all Xe atoms. The electron density may actually decrease around the innermost Xe atom because the interior electron−Xe channels narrow with cluster size. Since the I atom in $I^-(Xe)_n$ clusters is structurally analogous to the innermost Xe atom in Xe_n^- clusters, it is possible that the electron probability density around the I atom decreases with increasing cluster size, even though the excess electron cloud is less diffuse in the upper state for the larger clusters. In any case, it appears that the degree of electron−iodine interaction is a subtle effect, and calculations specifically on $I^-(Xe)_n$ CTTS states are needed.

In conclusion, we have measured the dynamics and lifetimes associated with the $^2P_{1/2}$ and $^2P_{3/2}$ CTTS states in size-selected $I^-(Xe)_n$ clusters. We suggest that the increasing lifetime of the $^2P_{1/2}$ CTTS state with cluster size is due to the electron−iodine interaction decreasing, resulting in less probable spin−orbit autoionization. Solvent rearrangement is not observed, probably because excitation of the $I^-(Xe)_n$ cluster directly accesses the origin of the CTTS state. In this case, the iodine remains at the center of the cluster and the electron does not access states exclusively solvated by xenon atoms. Higher resolution experiments and theoretical calculations are needed to test these hypotheses.

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