Intra-cluster photoelectron interactions: Scattering and dissociative attachment in halide-methyl halide cluster anions

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Abstract. Comparison of photodetachment images of I⁻·CH₃I with those of I⁻ and I⁻·CH₃Cl over a range of wavelengths reveals generally similar spectral features but a strikingly different evolution of the photoelectron angular distributions. These measurements reveal the effect of intracluster electron scattering and in particular the influence of a vibrational Feshbach resonance on the angular distributions of the I⁻·CH₃I photodetachment.

The photoelectron angular distribution (PAD) is often described as a signature of a parent molecular orbital, particularly in the case of anion photodetachment [1]. There is certainly a relationship between the free electron wave function and the parent orbital via the spectroscopic selection rules. Support for, and the limitations of, this description are both to be found in I⁻·X cluster anion detachment. In nearly every reported example (X=Ar, H₂O, CH₃CN, aniline, phenol, pyrrole) [2,3] the PAD seems consistent with detachment from an atomic p orbital, but there is a notable exception. The single PAD reported to date for I⁻·CH₃I (267 nm) is strikingly different [2].

The link between the PAD and details of an anionic detachment process is complicated by its photoelectron kinetic energy (E_K) dependence. Even in the case of atomic anions the angular distribution associated with detachment from an ℓ > 0 orbital shows significant changes within a small energy range of the detachment threshold. It is therefore desirable to study the PAD as a function of E_K, which in the past has been experimentally challenging. In this work we couple the power of charged particle imaging with a tunable dye laser to study the energy dependence of the PAD for two methyl halide based cluster anions (I⁻·CH₃Cl and I⁻·CH₃I) in comparison to free I⁻ over the range 0 < E_K < 1.2 eV. In particular we aim to better understand the relationship between the PAD and details of the detachment process such as the formation of a temporary anion state via a vibrational Feshbach resonance [4,5].

1. Experimental Details
Details of the instrumentation have been presented elsewhere and only points relevant to the current work will be given here [6]. Anions and cluster anions are produced via impact ionization using a 1 kV electron beam crossing a pulsed supersonic expansion of Ar (80 psig) seeded with the ambient vapor pressure of CH₃I (for I⁻ and I⁻·CH₃I anions) or a mixture of the ambient vapor pressures of CH₃I and CH₃Cl (for I⁻·CH₃Cl). Ion selective photodetachment is achieved by synchronizing a linearly polarized dye laser pulse (resolution 0.08 cm⁻¹ at 570 nm) to the anion time of flight in a Wiley-McLaren mass spectrometer [7]. Wavelengths accessed in this work cover the range 370 – 260 nm, achieved by
Figure 1. Selected photodetachment images. (a) 280 nm photodetachment of (L to R) \( \Gamma \), \( \Gamma \cdot \text{CH}_3\text{Cl} \), and \( \Gamma \cdot \text{CH}_3\text{I} \). (b) 350 nm photodetachment. (c) Expanded inverse Abel transform of the 350 nm \( \Gamma \cdot \text{CH}_3\text{I} \) image in inverse color scaling to highlight the weak \( \Gamma \) photofragment transition.

frequency doubling the dye laser output using a BBO crystal. The laser operates at a repetition rate of 10 Hz, which sets the duty cycle of the experiment. Photoelectrons are detected using a three electrode velocity mapped imaging arrangement, similar to that first described by Eppink and Parker \[8\]. The electron flight axis is perpendicular to the ion time of flight axis. The position sensitive electron detector consists of a pair of matched imaging quality microchannel plates, MgO coated on the input side and coupled to a P20 phosphor screen. Photoelectron impacts are recorded using a CCD camera and images are collected by accumulation, typically over 5-10 minutes.

2. Results

A small selection of the images obtained in this study (recorded under the same velocity map focusing conditions) is presented in figure 1. Electrons with higher (in plane) momentum are found further from the image center, whilst slow electrons are seen in the center of the image. Each image represents a 2D projection of the 3D momentum space photoelectron probability density onto the plane of the detector. Projection onto the detector scrambles the original 3D momentum distribution. However, the cylindrical symmetry conferred by the linear polarization of the photon (\( \varepsilon_p \), which is vertical in the plane of the images) allows mathematical reconstruction of the original distribution via an inverse Abel transform \[9\]. The momentum space distribution is easily converted to the energy domain photoelectron spectrum (figure 2) by the appropriate Jacobian transformation. Within a given energy range the angular distribution, \( I(\theta) \) conforms to

\[
I(\theta) \propto 1 + \beta P_2(\cos \theta)
\]  

(1)

where \( P_2(\cos \theta) \) is the second Legendre polynomial and the anisotropy parameter \( \beta \) completely characterizes the angular distribution. \( +2 \geq \beta > 0 \) has \( I(\theta) \) polarized parallel to \( \varepsilon_p \), whilst \( -1 \leq \beta < 0 \) corresponds to a perpendicularly polarized distribution.

The relationship between the anisotropy parameter and the parent orbital of an atomic anion is relatively easily understood. Within the central potential approximation, partial wave analysis allows quantitative prediction of \( \beta \). Here we use the simplified Bethe-Cooper-Zare \[10\] approach of Hanstorp et al. \[11\] which gives (in the case of detachment from an atomic p orbital)

\[
\beta = \frac{2(A \cdot E_K)^2 - 4A \cdot E_K \cos \delta_{A,p}}{[1 + 2(A \cdot E_K)^2]} \]

(2)
Figure 2. Photodetachment spectra corresponding to the images of figure 1. (a) 280 nm photodetachment. (b) 350 nm spectra showing vibrational structure. The fragmentation channel is indicated by the vertical arrow. The global maximum in each spectrum is arbitrarily scaled to unity.

The partial wave cross sections ($\sigma_\ell$) and their relative phases ($\delta_{d-s}$) are important in determining the PAD. In this case we need only consider the presence of $s$ and $d$ partial waves as a consequence of the $\Delta \ell = \pm 1$ selection rule. The partial wave cross sections vary at different rates with respect to $E_K$. The $A$ factor in equation (2) is defined by the partial wave cross section ratio, $\sigma_2/\sigma_0 = A \cdot E$. Both $A$ and $\delta_{d-s}$ can be obtained by fitting equation (2) to the experimentally determined $\beta(E_K)$.

2.1. Photodetachment Spectra

The images recorded in this study reveal photoelectron intensity confined to narrow rings corresponding to narrow transitions in the photoelectron spectra of figure 2. As the photon energy increases so does the image size. This is in accordance with energy conservation $E_{\text{ph}} = E_K + E_{\text{b}}$, where $E_{\text{b}}$ is the electron binding energy and $E_{\text{ph}}$ is the energy of the detachment photon. The two intense features seen in shorter wavelength measurements (figure 1a) correspond to the production of ground ($^2P_{3/2}$) and excited ($^2P_{1/2}$) state iodine atoms. The separation between these features arises due to spin-orbit interaction, is 0.94 eV and is retained in all these results. Subsequently we refer to the photodetachment transitions in terms of the final I atom electronic state.

In all spectra (cluster or free anion) the $^2P_{3/2}$ transition is broader than the $^2P_{1/2}$ transition due to the decreasing resolution of the imaging detector as $E_K$ is increased. In general, the cluster anion spectra have slightly broader transitions (e.g. 0.06 eV for $^2I\cdot CH_3Cl$ ($^2P_{3/2}$) vs. 0.04 eV for $^2I$ ($^2P_{3/2}$) at $E_K=0.30$ eV) and their electron binding energies are higher (vertical detachment energies of $^2I\cdot CH_3Cl$ ($^2P_{3/2}$, $^2P_{1/2}$) = 3.41, 4.35 eV and $^2I\cdot CH_3I = 3.43, 4.37$ eV, compared to 3.06, 4.00 eV for $^2I$). The broadening is due to the low frequency van der Waals modes. Despite this, there are significant similarities between the spectra. The spectral features are narrow and the spin-orbit splitting of I is preserved. Additionally ab initio calculations and similar findings in other iodide based cluster anions [2,3] allow us to consider these cluster anions as an atomic (iodide) anion moiety in the presence of a neutral molecule. In terms of cluster anion structure, the principal role of the neutral molecule is to stabilize $^2I$, which accounts for the shift in $E_b$ upon cluster anion formation.

The outer feature in the 280 nm images is the same as that in the 350 nm measurements (figure 1b). Closer inspection of the 350 nm spectra in figure 2b reveals structure near the $^2P_{3/2}$ threshold. The peak separation is 90 meV for $^2I\cdot CH_3Cl$ and 65 meV for $^2I\cdot CH_3I$, very similar to the excitation of 1 quantum in the $v_3$ (predominantly C-X) methyl halide stretching mode, (91 and 66 meV respectively) [12]. The
The apparent absence of these features at higher $E_K$ (e.g. figure 2a) is actually due to the reduction in resolution of the imaging detector. In the case of $\Gamma^{-}$CH$_3$I the relative intensities have been shown to display non-Franck-Condon behavior [5]. We also noted that in current experiments we observe similar structure associated with the $^2P_{3/2}$ transition in the cluster anions at wavelengths below 280 nm.

At certain wavelengths (370 – 340 nm and 270 – 280 nm) our $\Gamma^{-}$CH$_3$I photodetachment spectra and images also reveal a weak feature (e.g. figure 1c in which the intensity and image scale is inverted for illustrative purposes) at an $E_B$ of 3.06 eV. This feature is only observed within a narrow energy window (approximately 300 meV) around the $^2P_{3/2}$ and $^2P_{1/2}$ channel thresholds. We see no evidence of this feature in our $\Gamma^{-}$CH$_3$Cl images. The binding energy of this feature identifies it as free $\Gamma^{-}$ and the wavelength dependence rules out thermal cluster anion decomposition as the source. We attributed this feature to electron transfer induced fragmentation and subsequent photodetachment.

2.2. Photoelectron Angular Distributions

The $E_K$ dependence of the angular distribution predicted by equation (2) is clearly seen within the $\Gamma^{-}$ and $\Gamma^{-}$CH$_3$Cl images of figure 1, where a much higher degree of anisotropy is readily apparent in the 280 nm images. The beta parameters show this behavior even more clearly (figure 3). The energy dependence is usually explained in terms of the changing partial wave cross section ratio. At or near threshold the isotropic s-wave dominates but the d-wave contribution is increasingly felt as $E_K$ increases. The continuous line in figure 3 is a fit of equation (2) to the $\Gamma^{-}$ ($^2P_{3/2}$) channel data (open circles) and serves as a comparison for the $E_K$ dependence of other datasets. Error bars associated with the data represent one standard deviation from the mean $\beta$ (typically over 12-16 measurements) at a given $E_K$.

It is clear from figure 3 that detachment of $\Gamma^{-}$ via the $^2P_{1/2}$ channel (filled circles) or $\Gamma^{-}$CH$_3$Cl via the $^2P_{1/2}$ channel (open diamonds) shows little deviation from that of $\Gamma^{-}$ ($^2P_{3/2}$). However, this is decidedly not the case in the $\Gamma^{-}$CH$_3$I ($^2P_{3/2}$) channel (triangles). The broad trend (filled triangles recorded at 10 nm intervals) in the $\Gamma^{-}$CH$_3$I data is an initially smooth rise in the anisotropy parameter followed by a steady decline. However, in measurements between 280 and 290 nm there is a more rapid change (open triangles). Crucially, the photon energies in this region correspond to the immediate vicinity of the $^2P_{1/2}$ threshold in $\Gamma^{-}$CH$_3$I.
3. Discussion
In this section we develop an understanding of the anomalous PADs observed in I·CH₃I detachment. In particular we explore the relationship between the PADs and the photoinduced fragmentation observed in I·CH₃I near the detachment channel thresholds.

We begin by considering atomic iodide photodetachment and any subsequent influence of the long range potential. Thus the photoelectron wave function is treated as a superposition of (ℓ = 0 and 2) partial waves. Strictly this approach applies only to a spherically symmetric potential and assumes no angular momentum transfer as the electron departs, but the retention of the signature features of I⁻ detachment in the spectra, the resemblance of the majority of I⁻PADS [2,3] to that of I⁻ and the structural predictions of ab initio calculations [13] suggest this approach will allow considerable physical insights into the underlying causes of the anomalous PADs of I·CH₃I.

The usual application of equation (2) takes the system specific A and δₛ−s factors to be Eₖ independent. Larger A values have the effect of shifting the minimum (βₘₐₓ) to lower Eₖ. However, for 0 ≤ δₛ−s < π/2 the curve will always possess a minimum. The effect of different relative phase shifts is a little more complicated. Small deviations of δₛ−s from 0 primarily cause a reduction in βₘₐₓ. Larger increases in δₛ−s further reduce βₘₐₓ but also shift it to lower Eₖ. After the minimum, β(Eₖ) rises to approach a value of +1 in the asymptotic limit. For π/2 < δₛ−s < π, β(Eₖ) rises from 0 at Eₖ = 0 to a maximum, the position of which again depends on A and δₛ−s. In this case βₘₐₓ > +1. At energies greater than Eₘₐₓ, β(Eₖ) falls and again approaches a value of +1 in the asymptotic limit.

In view of the long range potentials present in the I + e⁻ and [I·CH₃Cl] + e⁻ systems it may seem surprising that Eₖ independent A and δₛ−s factors yield such close agreement with experimental β(Eₖ). However, MERT [14] calculations for the iodine atom (for an r⁻¹ potential) show that δₛ−s(Eₖ) is approximately constant over the range of our experimental data (the exception being at very low Eₖ). We also note that the effect of a dipole potential on σ₂/σ₀ has previously been examined and the differences in β(Eₖ) are minor, at least over the energy range of our current measurements [2].

These considerations lead us to conclude that the striking differences seen in the I·CH₃I angular data cannot be explained solely by the effect of the long range tail of the potential. There are two features which need attention. These are the very rapid change in β(Eₖ) seen over the wavelength interval 280 – 290 nm, and the more gradual trend upon which it is superimposed. It should be obvious that an Eₖ independent relative phase shift is inadequate to address these trends. However, considerable insight is gained into the nature of the gradual trend by applying equation (2) in the following manner. We assume that the A value obtained for I⁻ as a reasonable estimate for I·CH₃I detachment. An energy dependent relative phase shift can then be obtained by fitting equation (2) to the experimental data using δₛ−s(Eₖ) as the only fitting parameter (this fit is the dashed line in figure 3). This treatment yields δₛ−s(Eₖ) close to −π/2 at Eₖ near 0. Over the range of our data (0 - 1.2 eV) this value rises gradually (although not linearly) to approximately −1 radian. δₛ−s = δₛ − δₛ so the s wave phase shift (δₛ) is close to π/2 near threshold, assuming δₛ (the phase shift of the ℓ = 2 wave) is relatively small. This is indicative of a loosely bound or “almost bound” s state close to threshold [15].

The above treatment relies on the linear Eₖ dependence of σ₂/σ₀ being maintained. It should be pointed out that this Eₖ dependence might become much more complicated in cases of resonant excitation. Thus the actual trend in β(Eₖ) may be a rather complex relationship determined by non-linearly Eₖ dependent partial wave cross sections and relative phase shifts. Nevertheless, the presence of an electron molecule resonance represents a plausible explanation for the profound deviation in the angular distribution of the cluster anion compared to the free anion. In fact (as will be discussed in a forthcoming publication) the potential associated with a σ* state of CH₃I along the C-I coordinate lies within the vertical attachment region at energies relevant to this work. [16]

The σ* state is further implicated by the presence of the free I⁻ photodetachment signal near the direct detachment threshold of I·CH₃I. This signal arises as a result of a sequential two photon absorption within the width of the ns laser pulse. The first photon excites a temporary anion state (TAS) analogous to electron capture in the dissociative electron attachment channel of neutral CH₃I. The TAS decays by electron ejection or fragmentation but the fragmentation process is rapid.
compared to the width of our ns laser pulse. This allows the possibility of subsequent detachment from the I$^-$ product. The mechanism of electron capture is mediated via a vibrational Feshbach resonance which arises due to the proximity of the CH$_3$I$^-$ $^2$A dissociative state diabat (the $\sigma^*$ state) to the neutral ground state $v_3 = 1$ level [4,16]. Dissociation occurs via rapid tunneling through the barrier to form I($^2P_{3/2}$) + CH$_3$ + I. In passing we note that competition between fragmentation and electron loss from this state also accounts for the non-Franck-Condon behavior seen in near threshold photoelectron spectrum [5,13]. The timescale between excitation and electron emission is sufficient to allow relaxation of the C-I bond.

The rapid change in $\beta(E_K)$ over the wavelength interval 280 – 290 nm is particularly interesting. When the solvent shift imparted by the CH$_3$I molecule is considered, this wavelength window encompasses the threshold for the $^2P_{1/2}$ channel in I$^-$·CH$_3$I. Initially this is confusing since the $^2P_{1/2}$ channel will be associated with low energy electrons at these detachment wavelengths, whereas the rapidly changing anisotropy parameter is associated with the higher energy $^2P_{3/2}$ channel angular distribution. However, the temporary excited cluster anion formed at these wavelengths corresponds to I($^2P_{3/2}$)·CH$_3$I. Relaxation of the electronically excited I atom can result in the production of I($^2P_{3/2}$) + CH$_3$I + e$^-$, i.e. autodetachment. The electron ejected via this mechanism would be energetically indistinguishable from direct detachment to I($^2P_{3/2}$) + CH$_3$I + e$^-$ at the same wavelength. Therefore one would expect interference between these outcomes and a consequent alteration in the PAD. The narrowness of the window in which this feature occurs reflects the narrow E$_K$ window within which the dissociative attachment resonances can be accessed.

4. Summary

Photodetachment from the I$^-$·CH$_3$I cluster anion leads to photoelectron angular distributions that display markedly different energy dependence than those of other I$^-$ based cluster anions and free I$. To gain insight into this behaviour we have treated the detachment in terms of electron ejection from an atomic anion, modified by electron-molecule interactions as the electron departs the cluster. We find that consideration of the effect of the long range tail of the potential is insufficient to explain the I$^-$·CH$_3$I angular distribution. The energy dependent variation in the relative phase shift is particularly telling in this regard, highlighting the role of an “almost bound” state and the importance of the dissociative attachment process on the observed PAD.

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