# Negative Ion Zero Electron Kinetic Energy Spectroscopy of $I^-{\cdot}CH_3I$

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The negative ion zero electron kinetic energy (ZEKE) spectrum of $I^-{\cdot}CH_3I$ is presented and discussed. In addition to the high-frequency vibrational structure previously seen in the photoelectron spectrum (PES) of $I^-{\cdot}CH_3I$, the ZEKE spectrum reveals low-frequency vibrational structure due to excitation in two van der Waals modes in the ground (X) state of the neutral $I{\cdot}CH_3I$ complex. Of the two other excited states of the neutral complex, the I state is not distinctly observed, and no vibrational structure due to van der Waals motion is observed for the II state.

## Introduction

The dynamics of the intermediates of an $X^- + CH_3Y \rightarrow CH_3X + Y^-$ gas-phase $S_N2$ reaction have recently been the focus of considerable investigation, both theoretically and experimentally.[1−9] The ion−dipole stabilized $I^-{\cdot}CH_3I$ complex, an intermediate in the $I^- + CH_3I$ identity reaction, has been of particular interest. Recently, Cyr et al. have combined photoelectron spectroscopy (PES)[1] with photofragmentation studies[2] to show that charge-transfer excited states of $I^-{\cdot}CH_3I$, which are believed to be important in the reaction,[3] lie near the detachment continuum of the anion complex. The vibrational structure observed in the PES of $I^-{\cdot}CH_3I$ suggests that the C−I bond in the methyl iodide moiety is elongated, which is likely the result of the ground ion−dipole state mixing with the charge-transfer state. This bond elongation has also been predicted in recent calculations by Truhlar.[4]

The experiments of Cyr et al. are quite striking in that photofragmentation of $I^-{\cdot}CH_3I$ into an anion and neutral fragment is observed only in the vicinity of the threshold for photodetachment. This situation represents an intracluster analogue of the phenomenon recently reported by Chupka and co-workers in which $I^-$ is observed in the multiphoton ionization of $CH_3I$ by dissociative attachment of low-energy photoelectrons onto $CH_3I$.[10] To better understand the competition between photofragmentation and photodetachment, it is useful to characterize the neutral $I{\cdot}CH_3I$ complex formed by photodetachment of the anion to a greater extent than was possible from the photoelectron spectrum alone. In this paper, we present the higher resolution negative ion zero electron kinetic energy (ZEKE) spectrum of $I^-{\cdot}CH_3I$ in which we observe that the neutral complex is bound sufficiently strongly to support several van der Waals type vibrations, at least in the ground spin−orbit state. van der Waals vibrational structure has also been observed in previously obtained negative ion ZEKE spectra of the similar but simpler ion−neutral complexes, namely, $I^-{\cdot}CO_2$[11] and several rare-gas halides.[12] The implications of our results on the $I^-{\cdot}CH_3I$ complex will be discussed in the context of the PES and photofragmentation studies.

## Experimental Section

The anion ZEKE apparatus has been described in detail previously,[13] but the basic operation is as follows. The $I^-{\cdot}CH_3I$ complexes are generated and cooled in a pulsed free jet intersected by a 1 keV electron beam per the methods of Johnson and Lineberger[14] and are mass-selected using time-of-flight. The $I^-{\cdot}CH_3I$ complex is then photodetached using a tunable dye laser, and those electrons detached with nearly zero electron kinetic energy are collected as a function of detachment wavelength. This selective detection of low-kinetic energy electrons, based on methods developed by Müller-Dethlefs et al.,[15] yields an energy resolution as good as 2-3 $cm^{-1}$. The electron signal is normalized to laser power and ion current. The dyes used in the scans on $I^-{\cdot}CH_3I$ are DMQ and coumarin 540. The latter was doubled using a BBO I doubling crystal. The spectra were signal averaged for over 3600 shots/point.

## Results and Discussion

The ZEKE spectrum and the previously obtained PES[2] of $I^-{\cdot}CH_3I$ are shown in Figure 1, where the top panel shows the PES obtained using a detachment wavelength of 4.66 eV, the center panel shows the ZEKE spectrum of band X in the PES, and the lower panel shows the ZEKE spectrum of band II in the PES. Band X in both the ZEKE spectrum and the PES corresponds to the transition to I ($^2P_{3/2}$)$\cdot CH_3I$ complex from the anion, and band II is the transition to the spin−orbit excited I ($^2P_{1/2}$)$\cdot CH_3I$ complex. The two bands are separated by 0.955 ± 0.020 eV in the ZEKE spectrum, which is very close to the spin−orbit splitting in the bare neutral iodine atom, 0.943 eV. Also, compared to the spectrum of bare $I^-$, these features are shifted to higher photon energy by 0.365 ± 0.020 eV, which is fairly close to the enthalpy of formation for the ion dipole complex, $\Delta H_a = -0.39 \pm 0.01$ eV.[16]

Both the photoelectron and ZEKE spectra exhibit high-frequency vibrational structure associated with excitation of vibrations in the neutral methyl iodide moiety: nominally the $\nu_3$ C-I stretch in $CH_3I$. The $\nu_3$ frequency extracted from the position of this $3_0^1$ transition in the ZEKE spectrum is approximately 550 ± 20 $cm^{-1}$, which is very close to the $\nu_3$ frequency of bare $CH_3I$ (533 $cm^{-1}$).[17] However, band X in the ZEKE spectrum exhibits further (partially) resolved low-

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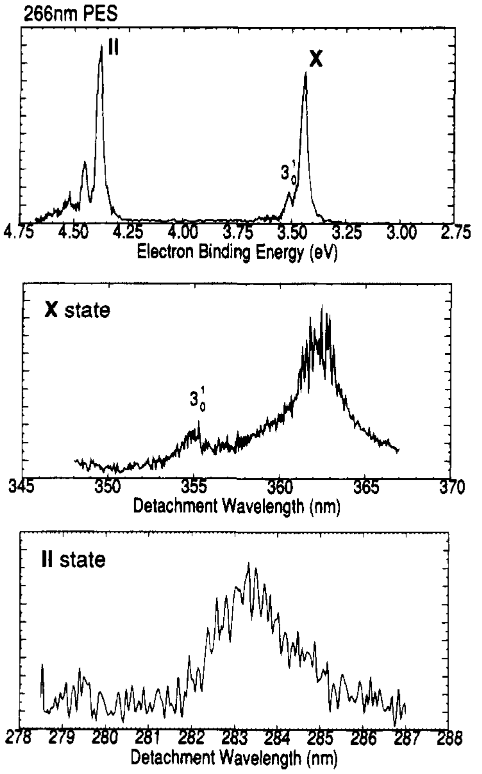

**Figure 1.** Previously obtained PES[2] and ZEKE spectrum of $\mathrm{I^-\cdot CH_3I}$. The PES shown in the upper panel was obtained using 4.66 eV detachment energy. The center and lower panels show the ZEKE spectrum in the energy region of the transition to the ground and excited spin–orbit states, respectively, of the neutral complex.

frequency vibrational structure with spacings on the order of tens of wavenumbers. This structure, the spacing of which is consistent with motion along a van der Waals bond, shows that this particular state of the neutral–dipole $\mathrm{I\cdot CH_3I}$ complex is bound. The noise level in the ZEKE spectrum of band **II** is such that no definite structure could be unambiguously discerned. Since the van der Waals well for the excited spin–orbit state is almost certainly shallower than that for the ground state,[11,12] the resulting lower frequency vibrational structure may be too congested to be resolved.

While the quality of the spectrum does not warrant the extensive analysis that we have previously applied to other weakly bound systems,[11] there is a definite pattern to the positions of most of the peaks in the origin band. To find the simplest possible picture of the vibrational structure, we have performed a simulation within the Franck–Condon approximation, in which transitions between vibrational levels of the anion ($\nu_n''$) and the neutral ($\nu_n'$) are assumed proportional to their Franck–Condon factors, $|\langle \nu_n''|\nu_n'\rangle|^2$. Figure 2 shows a simulation (solid trace) superimposed onto the ZEKE data (dotted trace). The simulation includes two low-frequency modes of the neutral, where the neutral vibrational wavefunction was taken to be the product of a Morse oscillator wave function with $\omega_e = 54.9$ cm$^{-1}$, $\omega_e\chi_e = 0.4$ cm$^{-1}$ (mode A), and a harmonic oscillator with $\omega_e = 33$ cm$^{-1}$ (mode B). For a reasonable fit, the anion geometry had to be displaced along both vibrational coordinates of the neutral. Therefore, the majority of the structure in the simulation is the result of combination bands (e.g., $A^x_0B^y_0$, $x$, $y$ = 1, 2, ...) in these two modes. The $A^v_0B^1_0$ progression in the simulation is indicated on the comb in Figure 2 to guide the eye.

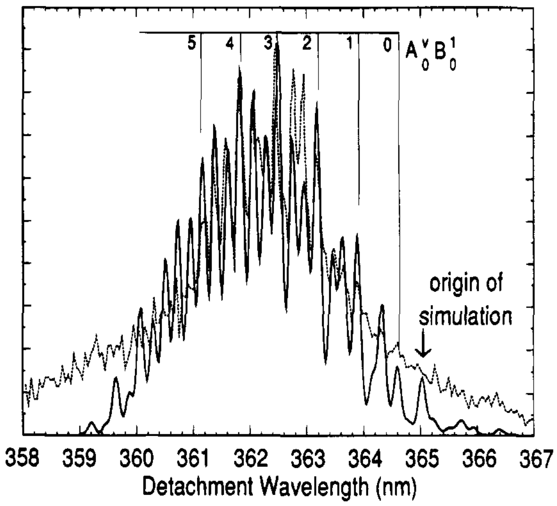

**Figure 2.** ZEKE spectrum of $\mathrm{I^-\cdot CH_3I}$ shown on an expanded scale near the origin of band X (dotted line) superimposed onto a spectral fit (solid line, see text).

There is likely to be some excitation of the low-frequency anion modes as well, but due to the overall congestion of the ZEKE spectrum, it is difficult to determine which structure is due to hot bands or sequence bands, making the choice of anion frequencies for the simulation somewhat arbitrary. However, we found that if the anion frequency corresponding to mode A is chosen to be approximately 100 cm$^{-1}$, the width of the simulated progression is in fairly good agreement with the observed progression. Moreover, if the anion frequency of mode B was made to be 53 cm$^{-1}$ (20 cm$^{-1}$ greater than the neutral frequency), the level of congestion due to hot bands and thus the intensities of peaks in the fit were closer to the experimental peak intensities. The choice of larger frequencies in the anion relative to the neutral is consistent with the stronger $\mathrm{I^-\!-\!(CH_3I)}$ interaction in the ion–dipole complex. For the particular simulation shown in Figure 2, the origin was placed at 365.04 nm, the anion wave function was displaced from the neutral wave function substantially and comparably along the coordinates of *both* the 33 and 55 cm$^{-1}$ modes, and anion vibrational levels were thermally populated at 50 K. It should be noted that even assuming zero vibrational temperature in the anion, most of the peak positions could be matched simply assuming a large activation in the two neutral frequencies. Including transitions from excited anion levels in the simulation serves primarily to fill in some of the intensity.[18]

Truhlar calculated the two lowest frequency modes of the anion to be 64 and 66 cm$^{-1}$; the 100 cm$^{-1}$ anion frequency used in our simulations is substantially higher than either of those. Simulations using Truhlar's anion frequencies gave profiles much more extended than in the experimental spectrum. In particular, when either the 64 or 66 cm$^{-1}$ frequency modes were taken as the anion mode corresponding to the neutral 55 cm$^{-1}$ mode, the peak of the extended progression could be appropriately simulated, but the simulated structure would tail much further to both the red and blue of the progression maximum than what is observed. However, because our treatment of what is likely a very complicated system is so simplified, our anion frequencies cannot be considered definitive. On the other hand, the two neutral frequencies are better determined as they correspond to observed peak spacings.

We now consider the electronic states of the anion and neutral and the observed vibrational structure in terms of these electronic states. The anion electronic structure is fairly straightforward: a closed-shell anion is bound to a closed-shell neutral molecule by both charge–dipole and dipole–induced dipole interactions in addition to some charge transfer between the I$^-$ and CH$_3$I.[3] The calculations by Truhlar[4] suggest that the $\mathrm{I^-\cdot CH_3I}$ complex

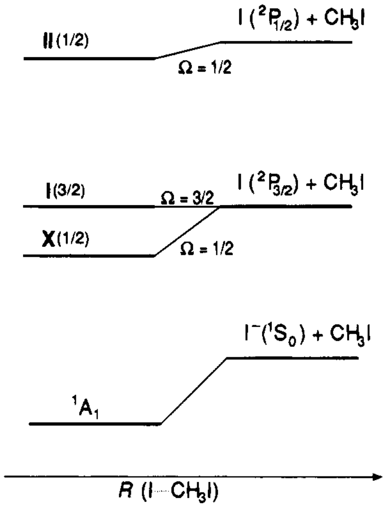

**Figure 3.** Schematic of the electronic states resulting from the electrostatic interaction between $I^-$ and I with $CH_3I$.

has $C_{3v}$ symmetry, and the anion electronic state is best described as a $^1A_1$ state. As mentioned above, Truhlar's vibrational frequency calculations found two low-frequency modes involving $I^-$—($CH_3I$) relative motion. The 66 cm$^{-1}$ mode is the $\nu_4$ ($a_1$) $I^-$—C stretch and the 64 cm$^{-1}$ frequency corresponds to $\nu_8$, a degenerate (e) rocking mode. The calculated anion frequencies are too close to suggest whether the neutral $a_1$ or e van der Waals mode should have the higher frequency.

In contrast to the simple closed-shell/closed-shell interaction of the anion, the interaction between an open shell, anisotropic neutral halogen and a closed-shell moiety is complicated by spin—orbit and orientation effects. These considerations have been discussed in our previous work on $I^-{\cdot}CO_2$[11] and $Rg{\cdot}X^-$ (Rg = Ar, Kr, Xe; X = I, Br, Cl).[12,19] Figure 3 shows a schematic correlation diagram with the three electronic states of the neutral resulting from this interaction. Approximating $I{\cdot}CH_3I$ as a point dipole ($CH_3I$) interacting with an iodine atom, the electrostatic interactions cause a splitting of the $^2P_{3/2}$ ground spin—orbit level of iodine into an $\Omega = {}^1/_2$ X state, and an $\Omega = {}^3/_2$ I state, where Ω is the projection of the electronic orbital and spin angular momentum onto the C—I axis. In the Hund's case (c) limit, the X state is composed of $^1/_3$ Π and $^2/_3$ Σ character, and the I state has only Π character.[20] The $^2P_{1/2}$ level is not split; the resulting $\Omega = {}^1/_2$ II state has $^2/_3$ Π and $^1/_3$ Σ character in the case (c) limit. The well depth of the X state is the deepest, with the smallest equilibrium internuclear ($r_{C-I}$) separation, and the I state is the shallowest of the three states with the largest equilibrium internuclear separation. From the extent of the structure in the $I^-{\cdot}CH_3I$ ZEKE spectrum, we can determine a lower limit of the well depth of the X state of $I{\cdot}CH_3I$ to be 250 cm$^{-1}$. The true well depth is likely to be considerably larger; the well depth of the $I{\cdot}CO_2$ X state was more rigorously determined to be 359 cm$^{-1}$,[11] and the $I{\cdot}CH_3I$ well depth is likely to be greater than this due to the stronger interaction with the $CH_3I$ dipole moment.

The open-shell nature of the neutral is also important in considering the vibrational structure associated with the X state. Our analysis shows that at least two van der Waals modes are active, but only one of these (the $\nu_4$ mode) is totally symmetric in the $C_{3v}$ point group. A progression in the degenerate $\nu_8$ mode (with e symmetry) would normally not be expected if both the anion and neutral have $C_{3v}$ symmetry; although transitions in which $\Delta\nu$ is even are allowed by symmetry, an extended progression in this mode is highly unlikely based on Franck—Condon factors alone.[21] Since Π states correlate to degenerate E states in $C_{3v}$ symmetry, the X state (and the other two electronic states) of $I{\cdot}CH_3I$ should possess some E character. These states can then undergo Jahn—Teller distortion, thereby activating the low-frequency degenerate vibrational mode. This effect is well-known in E ← A electronic transitions[22] but is less well-characterized for systems with large spin—orbit coupling such as $I{\cdot}CH_3I$.

The ZEKE spectra of $I^-{\cdot}CO_2$ and several rare-gas halides show transitions to the I state of the neutral lying quite close to the X band; the X—I splitting varies from 225 cm$^{-1}$ for $I{\cdot}CO_2$[11] to 30—40 cm$^{-1}$ for rare-gas halogen dimers containing Ar or Kr.[12] However, no distinct I band is observed in the ZEKE spectrum of $I^-{\cdot}CH_3I$. The likely reason for this is that the potential energy minimum for the van der Waals stretch in the neutral I state lies at a considerably larger internuclear distance than the minimum in the corresponding anion potential. This means that a vertical transition from the anion accesses the repulsive wall of the I state, and the resulting broad and featureless band would be very difficult to observe in the ZEKE spectrum. Two factors favor this explanation. First of all, the dissociation energy of $I^-{\cdot}CH_3I$ is substantially higher than that of $I^-{\cdot}CO_2$, 0.39 eV vs 0.212 eV. Second, comparing the neutral complexes, one expects the I atom to interact more strongly with $CH_3I$ than with $CO_2$ because of the permanent dipole moment in $CH_3I$. This should result in an increased splitting between the X and I states, along with a larger difference in the equilibrium internuclear distances. Thus, compared to $I^-{\cdot}CO_2$, one expects a larger difference in the equilibrium internuclear distances between the anion and I states for $I^-{\cdot}CH_3I$ photodetachment. A preliminary analysis indicates that the I band is missing in the $XeBr^-$ ZEKE spectrum for the same reason.[19]

The above discussion offers an explanation of an interesting result observed by Cyr et al.[2] They found that the fast neutral peak resulting from photodetachment of $I^-{\cdot}CH_3I$ at 266 nm was somewhat broader than the parent ion peak, indicating the production of *neutral* I + $CH_3I$ photofragments with nonzero relative kinetic energy. These clearly must come from unbound states of the neutral complex that have Franck—Condon overlap with the anion. Transitions to the continuum of the I state could certainly account for their observation. It is also possible that they were observing vibrational predissociation from the $\nu_3 \geq 1$ levels of the X and I states.

To summarize, ZEKE spectroscopy of the $S_N2$ intermediate $I^-{\cdot}CH_3I$ has been used to probe the open shell $I{\cdot}CH_3I$ van der Waals complex. The band corresponding to transitions of the X state of the neutral shows vibrational structure from progressions in two low frequency van der Waals modes of the complex. As only one of these is totally symmetric, this suggests that the neutral complex undergoes Jahn—Teller distortion, activating the second (degenerate) mode. Transitions to the I state of the neutral complex were not apparent in the anion ZEKE spectrum. This was attributed to a significantly larger C—I bond distance in the I state compared to the anion, resulting in transitions to the continuum levels of the I state. The II state is observed, but no vibrational structure is resolved, possibly due to spectral congestion.

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