**Photodissociation of Methyl Iodide and Methyl Iodide Clusters at 193 nm**

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**ABSTRACT:** This study introduces the state resolved dynamics of CH$_3$I when clustered in a supersonic expansion using He and Xe as seeding gases. Following excitation at 193 nm (6.4 eV), state specific alterations in photodissociation dynamics are observed. Four vibrational levels ($\nu_2 = 0, 1, 2, 3$) of the CH$_3$ umbrella vibrational mode were probed, as were I($^2P_{3/2}$) and I($^2P_{1/2}$) atomic photofragments. For nascent CH$_3$ fragments the measured kinetic energy releases and angular distributions show enormous sensitivity to the clustering. Manifestation of the clustering dynamics include: (a) shifting to higher energies (by up to 0.5 eV) and significant broadening of the kinetic energy distribution; (b) vibrational dependence of this increase in product kinetic energy; (c) angular distribution changes from a characteristic perpendicular character observed in free-standing CH$_3$I into a parallel transition for the clustered moiety. Drastic effects of clustering are also observed when probing iodine-atom photofragments, namely the state resolved distribution observed when seeding in He is replaced by a broad structureless distribution when seeding in Xe.

1. **INTRODUCTION**

The plethora of studies on the photodissociation of CH$_3$I, especially in its first absorption band (A-band), have constituted CH$_3$I, a prototypical molecule for studying dissociation processes in polyatomic molecules. The diatomic-like breaking of the C–I bond combines the simplicity of unidimensional bond breaking with the complexity of polyatomic molecular dynamics, such as different absorbing states, nonadiabatic crossings, and energy partitioning between electronic, vibrational, and rotational states. The A-band ranges from 220 to 350 nm and is characterized by prompt direct dissociation, as indicated by its broad, weak, and diffuse spectrum lying below the lowest Rydberg state.$^{1,2}$

The B-band is not so thoroughly studied as the A-band, but it has begun attracting significant attention.$^{3−9}$ The origin of the B-band stems from the excitation of a lone pair ($\epsilon$5p) electron in the iodine atom to a 6s Rydberg orbital $\sigma$5p$\rightarrow \sigma$ covering the spectral range from 188 to 205 nm and shows clear vibrational structure. A recent study using high resolution VUV photoabsorption in the 6–10.5 eV (207–118 nm) region has returned more than 200 lines.$^{10}$ Its dynamics have been characterized featuring a fast predissociation (lifetime 1.5 ps) due to crossing with repulsive states from the A-band.$^{4,11,12}$

Two distinct dissociation channels lead to the production of ground state CH$_3$ with ground state iodine I($^2P_{3/2}$) and spin–orbit excited iodine I($^2P_{1/2}$), labeled from now on as I and I*, respectively. A discrepancy concerning the $\Phi^*$ quantum yield in the B-band, that is, how much I* is produced, arises from the relevant literature. For excitation at 193 nm, Hess et al. report a $\Phi^*$ = 0.70 ± 0.04,14 while Continenti et al. and Van Veen et al. estimate this quantum yield to be close to unity.$^{13,15}$ Gilchrist et. al.,$^3$ using two different diode laser methods, obtained two different values: $\Phi^* = 1$ and $\Phi^* = 0.68 ± 0.04$. More recently, velocity map imaging (VMI) and slice imaging studies$^{1−6}$ find $\Phi^* = 1$ at 201.2 nm$^4$, $\Phi^* = 1$ at 196.7 nm$^5$, and $\Phi^* = 0.95 ± 0.01$ at 199.1 nm.$^5$

In this study we investigate how the dynamics of CH$_3$I in the B-band are affected by clustering in supersonic expansions when using He and Xe as seeding gases. Recently large clusters such as HBr···Xe$_M^{16}$ and ICl···Xe$_M^{17}$ have been studied using slice imaging. Molecules such as HBr and ICl have well-known dissociation dynamics that change dramatically when clustered even with a single Xe atom. In certain cases, active reaction channels in the bare molecule can be switched OFF, as the

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clusterings introduce significant changes in the excited potential energy surfaces.18

Previous experimental and theoretical studies on hydrogen halides have shown three main different photodissociation mechanisms for weakly bound clusters where the molecule under study is embedded in the cluster and surrounded by atoms such as Xe or Ar.19–21 First, the direct cage exit where the photofragments could escape without interacting inelastically with the surrounding atoms, and their kinetic energy resembles that of the free molecule. The second case is the delayed cage exit, where the photofragments are interacting with the surrounding atoms, resulting in significantly lower kinetic energy. The third case is the cage effect, where photofragments are interacting so many times that they are losing all their kinetic energy and are ready for recombination.

Using slice imaging, we have acquired photofragment images of I, I*, and CH3 (ν2 = 0, 1, 2, 3) from the photolysis of CH3I at 193 nm using both helium and xenon as seeding gases. We confirm previous work on the B-band dynamics (especially on the absence of the CH3 + 1 channel at 193 nm for the states probed) and observed significant changes in the dynamics when clustering in Xe. More specifically, CH3 fragment distributions for clusters exhibit a parallel character (compared to the perpendicular one of the CH3 from the CH3I monomer), they peak at higher KER than the monomer CH3 fragments, and their KER actually increases with ν2 quantum number, being 0.5 eV higher than the monomer for ν2 = 3. When probing iodine atoms, no ground state I fragments are observed, while the I* ones span a wide range of KERs.22–24

2. EXPERIMENTAL METHODS

The slice imaging technique used in the experiments has been described previously in detail.25, 26 A molecular beam (1000 mbar total backing pressure), with a mixture of CH3I ~ 2.5% in He or Xe, is used. The mixture is expanded through a homemade piezoelectrically actuated nozzle valve27 (1 mm diameter) and skimmed before it enters the detection chamber, where the ion optics are positioned. After passing through the 2 mm diameter orifice in the repeller electrode, the molecular beam is intersected at right angles by the photolysis and photofragment ionization lasers at the geometric focus position of a single-electrode repeller-grid arrangement.26

The timing of the dissociation and ionization lasers with respect to the gas pulse was very well selected during the experiments. Evidence of clustering typically manifests itself though structureless features (“blobs”) with small kinetic energy release, that appear at the center of a photofragment image. Even when using helium as seeding gas, (CH3I)x clustering is observed when photodissociating in the most dense part of the molecular beam (peak intensity). When so desired, to ensure that only monomers are present, it was necessary to operate in the early part of the molecular beam expansion, where gas density is low and gas cooling not as efficient. On the contrary, when clustering was desired, experiments were performed at the maximum intensity of the molecular beam.

For the slicing experiments reported here, the repeller is pulsed on (3 kV) at the appropriate time (typically 300 ns) following the photoionization. The photofragments traverse a field-free time-of-flight region and are detected by a position-sensitive detector (dual, imaging-quality MCP array coupled to a phosphor screen). The detector is gated such that the center slice of the photofragment Newton sphere is imaged. The image frame is recorded asynchronously every second (10 laser shots) by a CCD camera, and several thousand frames are averaged to form images. Each final image is appropriately integrated to extract kinetic energy release and the angular distributions of the photofragments. We recorded images with photolysis and ionization laser polarizations parallel to each other and to the imaging detector plane (XX geometry) as well as images where photolysis and ionization laser polarizations are parallel to each other but perpendicular to the imaging detector plane (ZZ geometry). The later are used to "normalize" the XX images for artifacts such as detector inhomogeneities, laser profiles, etc., especially in extracting the angular distributions.

The photolysis laser is an excimer laser (Lambda Physik COMPex 110) operating with an ArF mixture giving unpolarized light at 193 nm with a pulse duration of 25 ns. Brewster reflection is used to polarize the laser. The ionization laser is produced by a MOPO (master oscillator power oscillator) system (Spectra Physics MOPO 730D10) pumped by a Nd:YAG laser (Spectra Physics Pro Series 450). The photolysis and photoionization laser pulses (~0.5 mJ per pulse each) are separated in time by about 10 ns, in order to avoid multiphoton effects. The I and I* photofragments were ionized by (2 + 1) REMPI through the 6p(D7/2) ← ← (F3/2) at 304.504 nm and 6p(D9/2) ← ← (F1/2) at 303.984 nm transitions, respectively. The CH3...
photofragments are resonantly detected at the following Q-branch transitions: \((3p_{j}^{2}A'' \leftrightarrow 2p_{j}^{2}X^{2}A''), 0_{0}^{0} (333.500 \text{ nm}), 2_{1}^{1} (329.595 \text{ nm}), 2_{2}^{2} (326.162 \text{ nm}), \text{ and } 2_{3}^{3} (322.859 \text{ nm})\).

Background images are recorded with the photolysis laser off and subtracted from the signal images.

3. RESULTS AND DISCUSSION

3.1. CH₃ Photofragment Images. Shown in Figure 1 are photofragment images of CH₃(\(\nu_2 = 0, 1, 2, 3\)) from the photodissociation of CH₃I at 193 nm with either helium (top row) or xenon (bottom row) as seeding gases. When seeding in helium, three features are observed in each image: two rings and a central blob. The outer ring is assigned to photolysis of the monomer CH₃I by the 193 nm laser, while the second inner ring is assigned to photolysis of CH₃I by the probe laser (333–323 nm depending on the \(\nu_2\) state probed). For \(\nu_2 = 3\) we observe no inner ring. The structure-less “blobs” in the center of the image are attributed to (CH₃I)ₙ clusters. As mentioned earlier, when seeding in helium and using low stagnation pressures (1 atm), we do not expect a significant amount of clustering. However, as the absorption cross section of CH₃I at 193 nm is extremely weak, in order to obtain images with adequate signal-to-noise, the

Figure 2. Photofragment images of CH₃(\(\nu_2 = 0, 1, 2, 3\)) with the probe laser subtracted with either helium (top row) or xenon (bottom row) as seeding gases.

Figure 3. Kinetic energy (KE) distributions of CH₃(\(\nu_2 = 0, 1, 2, 3\)) photofragments with either helium (blue color) or xenon (red color) as seeding gases are shown in panels a–d, respectively.
experiments were performed in the densest part of the molecular beam, facilitating \((\text{CH}_3\text{I})_N\) cluster formation. Efforts to eliminate experimentally the photolysis contribution of the ionization laser proved unsuccessful, as sufficient photon flux is necessary to ionize via 2 + 1 REMPI, which makes the 1-photon photolysis of CH3I by the probe laser unavoidable. As shown in Figure 2, subtracting this "photolysis" contribution of the probe laser from the image eliminates the central blob, therefore suggesting that the 193 nm absorption of \((\text{CH}_3\text{I})_N\) clusters is negligible.

Similarly, in the lower panel of Figure 1, while seeding in Xe, a central blob feature and an outer ring are observed. Images where the probe laser contribution has been subtracted are shown in Figure 2. It is evident that only the probe laser contributes to the central blob, and residual "features" around the center of the image arise from incomplete subtraction of the probe laser because of the weak signal. However, in this case, the central blob may be \((\text{CH}_3\text{I})_N\) or \((\text{CH}_3\text{I})_N\cdots\text{Xe}_M\) clusters, as we cannot a priori rule out the existence of mixed clusters of the type \((\text{CH}_3\text{I})_N\cdots\text{Xe}_M\). In addition, as will be discussed below, assigning the outer ring solely to monomer CH3I photodissociation is not satisfactory, as it exhibits drastic differences from the He data images.

Figures 3 and 4 show the corresponding KERs for the photofragment images of Figures 1 and 2, respectively. Tick marks indicate the predicted KER positions of CH3(\(\nu_2\)) fragments using the relation

\[
\text{KER}_{\text{CH}_3} = \frac{m_i}{m_{\text{CH}_3}}(h\nu - D_0 + E_i(\text{CH}_3\text{I}) - E_{SO})
\]

where \(m_i\) is the mass of iodine, \(h\nu\) is the photon energy corresponding to the photolysis or ionization laser, \(E_i(\text{CH}_3\text{I})\) is the internal energy of CH3I (negligible), \(D_0 = 2.41\ \text{eV}\) is the dissociation energy of the parent molecule CH3I, and \(E_{SO} = 0.94\ \text{eV}\) is the spin–orbit energy in iodine.

In the CH3 KER distributions, for He expansions, the low energy \((\text{CH}_3\text{I})_N\) cluster signal is observed to be stronger for the \(\nu_2 = 1\) and \(\nu_2 = 2\) compared to the \(\nu_2 = 0\) and \(\nu_2 = 3\), while in all cases the monomer peak (2.5–3.5 eV) from the 193 nm photolysis dominates. This trend changes in the case of Xe, where the 2.5–3.5 eV peak is larger than the low energy cluster blob for \(\nu_2 = 1\) and \(\nu_2 = 3\) but smaller for \(\nu_2 = 0\) and \(\nu_2 = 2\). What is common in both Xe and He is that the central blob contribution is mainly from the probe laser, while the 193 nm photolysis gives rise to the faster, outer peak. The discussion on these two features will be done separately, in order to emphasize their differences.

**Probe Laser (323–333.5 nm) Dynamics.** Our observations indicate that the blob features in both He and Xe expansions have identical behavior, leading us to believe that this is due either to identical clusters or to clusters that follow similar photodissociation dynamics. Previous work on HBr, and ICl clustering, concluded that such features originate from a cluster cage-effect.\(^{16,17}\) According to this model,\(^{21}\) molecular photodissociation occurs inside a large cluster, and in the case of CH3I, the nascent CH3 undergoes a large number of collisions with cluster
elements, thus losing almost all of its kinetic energy. The methyl radical photofragment can either recombine with iodine to form again CH₃I with higher internal energy than the parent or remain caged with near zero kinetic energy that results in the central blob in our images. Typical KERs resulting from a classical cage-effect or delayed-cage-exit are peaking at or very close to 0 eV1,16,17,21 as in the case of (CH₃I)ᵣ seeded with He in Figure 3b–d (blue lines). However, the slow KER component for Xe as seeding gas (red line) corresponding to a probe laser (333–323 nm) is peaking at significantly higher energies, up to 1.2 eV for ν₂ = 1. Besides the mechanistic effects of the cage-effect, one could additionally suggest a number of different scenarios, such as statistical decay of the molecule inside the cluster where the direct dissociation of the molecule is hindered due to clustering with Xe atoms and could result in a hot CH₃I with higher dissociation energy. Subsequently, the cluster evaporates and the molecule decays with the KE of the nascent fragments to follow a statistical distribution. This assumption is supported by the Maxwellian-like shape of the slow component for Figure 3c and d.

**Pump (193 nm) Laser Dynamics.** The KER spectra for the 193 nm photolysis are shown in Figure 4. When seeding in Xe, the peak appears to broaden and to shift toward higher KER with respect to the He expansion, especially as the ν₂ excitation increases. This indicates that this peak in the case of Xe expansion either (a) corresponds to extremely different CH₃I internal energy or (b) must contain a contribution from clusters of the type (CH₃I)ᵣ−…Xeₘ. We expect expansion using Xe to lead to more efficient cooling, so we favor the second explanation. The energy shift in the KER to higher energy would mean weakening of the C–I bond because of the clustering, while in addition the heavier mass of the parent cluster will impart more kinetic energy in the light methyl radical, assuming an impulsive dissociation and that the internal rotational energy partitioning in daughter radicals remains about the same. This later assumption is contradicted by the broadening of Xe peak, which would mean that the CH₃ radical product is rotationally hotter. Alternatively, this increased width could simply be the fact that, unlike the photodissociation of the monomer CH₃I, where the sibling I-atom fragment can only have electronic energy,

\[
\text{CH₃I} \rightarrow \text{CH₃}(ν₂) + I(ε)
\]

in the case of the clusters, the extra degrees of freedom in the cluster fragment allow for a wider range of KER even when a single ν₂ quantum state of the CH₃I is probed, that is,

\[
(\text{CH₃I})ᵣ₉−…Xeₘ \rightarrow \text{CH₃}(ν₂) + (\text{CH₃I})ᵣ₋₉−…Xeₘ(ν, J, ε)
\]

Further support of this assignment stems from the angular distribution of this peak, where the anisotropy parameter (Table 1) is increased from ~0.4 in the case of CH₃I(ν₂ = 1)/He to ~0.1 in the Xe expansion, indicating that species other than CH₃I monomer are contributing to this feature. The effect just described for ν₂ = 1 becomes even more drastic for ν₂ = 2 and ν₂ = 3, but what is even more remarkable for these vibrational states is that the angular distributions for the Xe peak become positive, β ≈ +0.1, from the initial value, ~0.4, in the CH₃I monomer.

Angular distribution expresses the change in electronic state symmetry between ground and excited states, and in the cases where photodissociation is not prompt, the lifetime of the excited state "reduces" the anisotropy parameter. However, in the long lifetime limit, a maximum reduction by a factor of 4 is expected. A change in sign of the β anisotropy parameter signifies completely different dynamics or electronic states; that is, the fast peak in the Xe case must be primarily photodissociation of clusters. The drastic changes of β could be explained by considering the dissociation process on some excited potential energy surfaces, but the process would have to be of parallel character, as suggested by Figures 1 and 2. This scenario also justifies the existence of mixed species in the molecular beam.

The 193 nm excitation clearly shows different dynamics than the 333 nm excitation (probe laser/central blob), so a different mechanism must be used to explain this feature. In a recent study on ICl−Xeₘ clusters,17 one such alternative approach was shown to explain similar behavior. In particular, if we assume that CH₃I molecules lie on the surface of a cluster (CH₃I)ᵣ−…Xeₘ, the slightly higher KE of the methyl photofragments from such surface bound CH₃I molecules could be understood from eq 1, where the mass scale factor is different in the case of the cluster, given by \( m_{(\text{CH₃I})ᵣ−…Xeₘ}/m_{(\text{CH₃I})Xeₘ} \). However, in the case of the monomer this mass ratio is already 0.90, so even in the extreme limit of very large clusters, with all other factors remaining the same, a maximum shift of only 10% is expected. Hence, this could explain small shifts in the KER, such as those in ν₂ = 1 or ν₂ = 2, but not the difference of 0.5 eV observed in the case of ν₂ = 3.

To explain the high KER shift of 0.5 eV in CH₃(ν₂ = 3)/Xe, one could suggest a multiphoton mechanism as in the case of acetylene,30 where the molecule is excited by the first photon but quenches to a vibrationally excited level of the ground electronic state and is dissociated by a second photon. These studies showed that the absorption of the second photon by the decaying molecule is possible even at low photon fluxes where only single-photon processes are observed for the isolated molecule.

Total caging of the photofragments and recombination back to the parent molecule with higher internal energy, as in the case of HBr−Xeₘ;31 is not likely because there are no extra rings as like in the HBr case. More theoretical treatment is needed to have a complete understanding of the clustering mechanism of CH₃I with rare gases such as Xe, and several considerations have to be made, such as the vibrationally dependent and the different dynamics of each absorption band of CH₃I.

### Table 1. Anisotropy Parameter β Obtained by Fitting Angular Distributions Obtained from the Images Shown in Figures 1 and 5 by Appropriate Integration

<table>
<thead>
<tr>
<th>193 nm photolysis</th>
<th>helium</th>
<th>xenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(ν₂ = 0)</td>
<td>β ≈ −0.37 ± 0.02</td>
<td>β ≈ −0.30 ± 0.03</td>
</tr>
<tr>
<td>CH₃(ν₂ = 1)</td>
<td>β ≈ −0.36 ± 0.02</td>
<td>β ≈ −0.10 ± 0.02</td>
</tr>
<tr>
<td>CH₃(ν₂ = 2)</td>
<td>β ≈ −0.53 ± 0.03</td>
<td>β ≈ 0.10 ± 0.02</td>
</tr>
<tr>
<td>CH₃(ν₂ = 3)</td>
<td>β ≈ −0.32 ± 0.02</td>
<td>β ≈ 0.13 ± 0.01</td>
</tr>
<tr>
<td>( \beta^{(\text{P}_3,2)} )</td>
<td>β ≈ 0.67 ± 0.01</td>
<td>β ≈ 0.09 ± 0.04</td>
</tr>
</tbody>
</table>

"The angular distributions were fit to the function 1 + βP₂(cos(θ)), to obtain the anisotropy parameter. The "four-leaf clover" shape observed in the ν₂ = 1 XX image (Figure 1) distribution disappeared when normalized with the ν₂ = 1 ZZ image distribution. This was confirmed by fitting the distributions with an expanded set \( \{β_2, β_0, β_6\} \) of β parameters which showed all \( β_2, β_6 \) values to be essentially zero."
where cluster contributions from \((\text{CH}_3\text{I})_N\) become evident (Figure 5, top left). In Figure 6a, we assign the 0.2 eV peak to the “monomer” photodissociation at 304.5 nm:

\[
\text{CH}_3\text{I} \rightarrow \text{CH}_3 (\nu, J) + \text{I}
\]

On the contrary, when probing I* in He, two rings are present (Figure 5, top right), with the outer one attributed to the 193 nm and the inner one to the 304 nm photolysis of CH₃I. Figure 6b (blue line) indicates that the dominant feature in the KER is the 193 nm photolysis. The lack of \((\text{CH}_3\text{I})_N\) clustering in the He signal is due to the fact that the strength of the I* REMPI line allows image recording at very early beam times where no clusters are yet formed. In the Xe expansion, the I* image shows essentially a center-peaking blob; however, the KER distribution features a slow and fast part in that blob consistent with I* production at 304 and 193 nm photolysis, respectively. It is safe
to conclude that the yield ratio $I^*/(I + I^*)$ is essentially unity at 193 nm; that is, when photodissociating CH$_3$I at 193 nm using a nanosecond laser no ground state iodine atoms are generated.

When probing CH$_3$I we attributed the KER shift to the surface bound clusters. The fact that this is absent when probing the large iodine atoms (either ground or spin–orbit excited) is reminiscent of the behavior reported in our previous study on ICI-Xe$_M$ clusters. In order to explain this behavior, we assumed that the surface molecule, in this case CH$_3$I, is preferentially attached to the cluster moiety via the large iodine atom. In such a geometry, following prompt (impulsive) photodissociation, the I-atom photofragment would collide with the cluster main body and, hence, the probability of prompt dissociation would be eliminated. Hence, we are seeing a very similar behavior in the case of the pseudodiatomic CH$_3$I and the ICl molecule when forming clusters in Xe mediated expansions.

4. CONCLUSION

Our results indicate that photodissociation of CH$_3$I at 193 nm yields exclusively I-atoms in their excited spin orbit state I* and a second where the precursor CH$_3$I molecule is embedded in a large cluster of Xe$_M$ and (CH$_4$I)$_N$, and a second where the precursor is mounted on the surface of the cluster. In addition, the KER spectra provide evidence that the surface mounted methyl iodide anchors to the cluster moiety via the iodine atom.

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Notes

The authors declare no competing financial interest.

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