PHOTOFRAGMENT IMAGING: THE 266 nm PHOTODISSOCIATION OF CH₃I *

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Received 19 December 1988

We use photofragment imaging to study the internal-state and velocity distributions of methyl fragments following photodissociation of CH₃I molecules in a pulsed molecular beam by 266 nm radiation. The methyl fragments are state-selectively ionized via 2+1 resonance-enhanced multiphoton ionization (REMPI) through the 3p, Rydberg state. The velocity distribution for a particular internal state of the methyl radical is obtained from the images; this velocity distribution is then used to determine the branching of the methyl iodide into either the ground-state iodine, I(2P₃,2), or excited-state iodine I(2P₁/₂), channel or the selected state of the methyl radical. We find that the branching ratio, I(2P₃/₂)/I(2P₁/₂), increases with increasing vibrational excitation in the methyl fragment. In addition, we use a line by line analysis to extract populations from the observed spectra of the 0⁻ band of the 3p, –→ X transition of the CH₃ fragment. The fit reproduces the observed spectrum and represents conservation of the K quantum number (spin about the C₃ axis) upon dissociation. For internally cold parent molecules, the amount of rotational energy about the fragment figure axis is found to be about 8 cm⁻¹ and about 106 cm⁻¹ for rotational energy perpendicular to the figure axis.

1. Introduction

The photodissociation of methyl iodide by ultraviolet light is one of the most studied photochemical problems both experimentally [1-12] and theoretically [12-19]. Methyl iodide photodissociation has drawn considerable attention in part because it is an “instantaneous” pseudo-linear dissociation that may be described by a two-dimensional potential-energy surface. Despite all this effort there are still questions to be answered. Is only the umbrella vibrational mode, ν₂, of the methyl radical excited in the dissociation process? How is the branching ratio of ground state iodine, I(2P₃/₂), designated I, to excited-state iodine, I(2P₁/₂), designated I*, correlated with the state of the methyl radical formed in the dissociation process?

Some of these questions have been partially answered using neutral time-of-flight [1,4-7] and spectroscopic techniques [8,9]. Other questions are only now being answered by new laser-ionization/mass-spectrometric techniques [10,12,20] that measure simultaneously the velocity of a fragment and its internal state. We have developed a variation on these techniques using the position of the ions at the time-of-flight detector along with their arrival time to determine the velocity of the fragments for a given internal state [11,21]. Using the data obtained with this technique it is possible to reconstruct com-

* Work supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.
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0 009-2614/89/$ 03.50 © Elsevier Science Publishers B.V.
(North-Holland Physics Publishing Division)
completely the spatial distribution of the fragments at a specified time after the dissociation event.

The CH₃ fragments produced by the photodissociation of CH₃I by polarized 266 nm laser radiation are state-selectively ionized via 2+1 resonance-enhanced multiphoton ionization, REMPI [22-24]. The molecular-beam apparatus is arranged such that the selected fragments impact a position-sensitive ion detector a short time after ionization and create an image of the projected spatial distribution of the ionized fragments. Because the photodissociation process involves a parallel transition (the electronic transition moment is parallel to the molecular symmetry axis) to a dissociating state, the photofragments are distributed spatially with a nearly cos² angular distribution about the direction of the polarization axis of the photolysis laser beam.

The images have a double-ringed appearance, in which the inner ring correlates to slow moving methyl born in coincidence with electronically excited iodine and the outer ring correlates to the faster methyl coinciding with ground-state iodine. From the relative intensities of these rings we obtain the branching ratio of excited-state to ground-state iodine generated in coincidence with the selected state of the methyl fragment. Additionally, a photomultiplier tube is used to monitor the ion detector while the frequency of the ionization laser is scanned. In this manner a REMPI spectrum through the two-photon-allowed 3p→2A₂^* ←X₂^* electronic transition of the methyl fragment is recorded.

2. Experiment

As described in previous communications [11,21] and shown in fig. 1, the apparatus consists of a pulsed molecular beam that is skimmed and directed through a repeller plate toward a position-sensitive ion detector. The molecular beam is produced by flowing He at pressures between 1 and 7 bar over CH₃I in an ice-cooled sample holder and into a pulsed valve (Laser Technics) equipped with a 0.3 mm orifice. The 250 μs pulses forming the molecular beam are directed into the dissociation chamber through a 0.5 mm diameter skimmer (Beam Dynamics). A
quadrupled Nd:YAG laser beam at 266 nm (Quanta-Ray DCR-2) intersects the leading edge of the molecular-beam pulse. The laser beam is linearly polarized and the polarization axis is oriented perpendicular to the molecular-beam axis. A second counterpropagating linearly polarized laser beam intersects the photolysis region about 10 ns after the 266 nm laser beam. This laser beam is from a frequency-doubled dye laser operating near 334 nm. A single-mode Nd:YAG laser is used as a pump source for this dye laser. This Nd:YAG laser is injection-locked by a cw single-mode Nd:YAG laser (Lightwave Electronics). Both laser beams are focused into the chamber with 200 mm focal length lenses. Typically, 2 to 5 mJ/pulse of 266 nm light is used for photolysis and 1 to 3 mJ/pulse of 334 nm light is available for the REMPI. We avoid focusing the lasers at the molecular beam because of single-laser ionization of the molecular beam from such intense fields. The foci are moved such that the background from either laser is only a few percent of the total two-laser signal. The polarization axis of the 334 nm laser beam is oriented parallel to the polarization of the photolysis laser beam unless stated otherwise.

After the ions are formed by the REMPI process they are directed through an extracting grid and into a grounded time-of-flight tube (80 mm long and 40 mm diameter). The detector consists of a Chevron microchannel plate assembly backed by a phosphor screen (Galileo Electro-Optics). The P-47 phosphor has a lifetime of about 50 ns. When taking an image, the front face of the microchannel plate ion detector is held at ground potential until the appropriate time for the signal of interest, CH₃ ions, arrives. It is then gates (0 to –600 V with a 400 ns width) in order to accelerate the ions into the microchannel plates and to detect only the ion of interest. To record the REMPI spectra of the CH₃, a photomultiplier tube (Hamamatsu 955) is placed near the phosphor screen and its output is sent to a boxcar averager gated at the appropriate arrival time.

Gating the front face of the microchannel plate allows us to eliminate high- (CH₃I⁺ and I⁺) and low-mass (C⁺) background ions generated by the UV laser beams. Also appearing near the center of the detector are methyl ions formed from the photodissociation of methyl iodide dimers and polymers [10,25]. This methyl signal cannot be eliminated by background subtraction since it is a two-laser signal with the same frequency characteristics as the signal of interest. This two-laser background signal can usually be avoided by working at the leading edge of the molecular beam pulse where the dimer concentration is small.

During the flight time the methyl ions are spatially separating due to the differences in the velocities with which they were formed. Two rings corresponding to the two channels of the dissociation (I and I*) are easily resolved when the image appears on the detector, about 3 μs after the laser beams intersect the molecular beam. The recoil velocity distribution of the methyl fragment is determined by measuring the position and arrival time of the ions.

The image is recorded by using an electronic camera (Photometrics 200 thermoelectrically cooled electronic camera with a Thompson-CSF charge-coupled device (CCD) chip). By opening the shutter on the electronic camera for variable periods of time, we are able to average the signal from many laser shots. When taking data, an image is recorded at a given ionization laser frequency, and then a background image is recorded after turning off the molecular beam. This allows us to subtract scattered light and background methyl ion signals. The CH₃I dimer dissociation signal cannot be eliminated in this manner. This small amount of residual background is typically observed in the center of the image and does not affect our data analysis.

If the beams are not properly overlapped, a bias is introduced in ionizing fragments with certain velocities. This typically manifests itself as unequal brightness in the upper and lower halves of the image. The goal is to ionize equally all fragments in resonance with the ionization laser.

3. Results and discussion

We observe the 0⁰, 2| and the 1| transitions of CH₃ in our REMPI spectra following the 266 nm photolysis of CH₃I. The ν₁ mode is a C–H stretching mode and the ν₂ mode is the umbrella inversion mode. The 0⁰ and the 1| transitions overlap with each other. The 3p, 2A₂ electronic state of CH₃ is predissociative. Because of this predissociation the vibronic transitions are severely broadened and the
REMPI spectra are correspondingly weak. Rotational structure corresponding to excitation up to \( N=6 \) is observed on the origin band. The large extent of predissociation in the 3p\(_e\) excited electronic state makes quantitative analysis of the spectra and extraction of population information difficult.

By taking images while the ionization laser is resonant with a particular transition, we determine the branching ratio, \( I/I^* \), for methyl populating the particular ground-vibrational state from which the transition originates. Of particular interest is the intensity pattern on a vertical slice through the center of the image. Ions contributing to this portion of the image are moving perpendicular to the propagation axis of both laser beams. The \( I/I^* \) ratio is determined by comparing the magnitude of the outer ring's maximum to that of the inner ring's maximum. The inner ring's maximum sits on the tail of the outer ring; it is measured with respect to the extrapolated value of the outer ring at the position of the inner maximum. The magnitude of the outer ring at this point is approximately \( 1/3 \) of its value at the maximum. We use this technique because it is insensitive to the resolution of the laser and the Doppler width of the transition [21]. Because the faster fragments, correlating with the I channel, have spread in space further than the slower methyl fragment, correlating to the I* channel, they are discriminated against in the intensity pattern of the stripe through the center of the distribution. Because they are spreading as the square of the distance from the center and the outer-ring radius is 1.3 times larger than the inner-ring radius the population indicated by the intensity in the outer peak must be multiplied by \( (1.3)^2 = 1.69 \) in order to obtain a correct population ratio.

Fig. 2 displays the region of the origin band of the 3p\(_e\) \( 2A_e^+ \rightarrow X^2A_e^+ \) electronic transition of CH\(_3\) seen in 2+1 REMPI following CH\(_3\)I photolysis at 266 nm. To obtain pure rotational population information and to avoid alignment effects the polarization of the probe laser beam was set at the magic angle of 57.2° relative to the vertically polarized dissociation laser. The strong Q branch transition centered near 333.5 nm is expanded off scale in order to show the rotationally resolved O, P, R, and S bands. Images taken while the ionization laser is resonant with the Q branch gives an \( I/I^* \) ratio of about 0.12, see image a of fig. 2. At 334.0 nm the ratio abruptly changes to being greater than 2.0 as seen in image b of fig. 2. We take this abrupt change in the \( I/I^* \) ratio as an indication of a contribution from a transition originating from a level other than the vibrationless ground electronic state at this wavelength. The P(4) transition of the 0\(_0^g\) band lies at this wavelength and overlaps the transition with the large \( I/I^* \) ratio. Assigning this spectral feature as a Q branch band head would indicate a red-shift in fig. 2 of 45 cm\(^{-1}\) from the Q branch band head of the 0\(_0^g\) band. If we accept Hudgens et al.'s [22] measurement of the excited-state 3p\(_e\) \( 2A_e^+ \) vibrational energy separation between \( v_e=0 \) (\( v_e=0 \) of the \( v_1 \) mode) and \( v_e=1 \) of 2914 cm\(^{-1}\), and the ground-state spacing of Holt et al. [27] of 3004.8 cm\(^{-1}\), a shift of 90.8 cm\(^{-1}\) is expected between the Q branch of the 1\(_1^g\) band and the Q branch of the 0\(_0^g\) band. This shift corresponds with a one-photon energy of 45.4 cm\(^{-1}\), which is about the red-shift of the feature with the anomalous branching ratio of > 2.0. Because this transition overlaps the P(4) rotational line of the 0\(_0^g\) band and we do not know the Franck-Condon factors for these transitions, we are unable to determine the relative populations of the originating states.

The presence of two transitions manifests itself by the appearance of three rings in the image taken at this wavelength, image b of fig. 2. The outer ring corresponds to the production of CH\(_3\)(\( v_1=1 \)) + I. The inner ring corresponds to production of CH\(_3\)(\( v_1=0 \)) + I* and CH\(_3\)(\( v_1=1 \)) + I*. Assuming a dissociation energy of 2.30 eV [7] for the C–I bond, these three channels correspond to the velocities 4.78×10\(^3\), 4.04×10\(^3\) and 3.47×10\(^3\) m/s, respectively. The ratios of these velocities, 0.84 and 0.73, compare well to the ratios obtained from image b of fig. 2, 0.84 and 0.75. The CH\(_3\)(\( v_1=0 \)) + I product channel is not observed at 334.0 nm. Less than 10% is observed at the Q branch of the 0\(_0^g\) band, image a of fig. 2. Because of the overlapping transitions the \( I/I^* \) branching ratio reported for the 1\(_1^g\) band is only a lower limit. The source of excitation in the \( v_1 \) mode is not easily assigned. It is either a product of the dissociation dynamics of a vibrationless parent molecule or it reflects a small amount of population in a non-relaxed vibrational mode in the CH\(_3\)I parent. As can be seen by inspection of fig. 2 the signal at 334.0 nm is quite small relative to the Q branch of the 0\(_0^g\) band.
Fig. 2. (Top) 2+1 REMPI magic angle spectrum of CH₃ in the region of the 00 band of the 3p, 2A'_2 ← X 2A' electronic transition following photolysis of CH₃I with 266 nm radiation. Below the experimental spectrum is a computer-generated spectrum as described in the text. (Bottom) Images and intensity cross sections recorded vertically through the center of the images taken at 333.5 nm (a) and 334.0 nm (b). The image taken at 334.0 nm shows three rings due to overlap of the 11 Q branch with the P(4) line of the 00 band. The image at 333.5 nm shows only a small amount of outer ring reflecting the character of the 00 band. Each successive color change represents approximately 12% increase in intensity.
but its distinctive ratio (>2.0) and position mark it unmistakably as the 1\(^i\) band.

Information on several aspects of the dissociation process is available from analysis of the rotational structure of the 3p->X origin band of CH\(_3\), including the overall amount of rotational excitation and the partitioning of rotational energy between tumbling about a C\(_2\) axis and spinning about the C\(_3\) axis.

Two-photon rotational selection rules for this transition, derived by Hudgens et al. [22], allow \(\Delta K=0, \Delta N=0, \pm 1, \pm 2\). Because the molecule is planar in the upper and lower states, the lower K bands of the O and S branches (\(\Delta N=2\)) are overlapped by bands of the P and R branches (\(\Delta N=1\)), respectively. In addition, \(\Delta K=0\) transitions from individual K\(^\prime\) levels of the same N\(^\prime\) level occur at similar energies. Due to our \(\approx 0.3 \text{ cm}^{-1}\) laser resolution, the low level of CH\(_3\) rotational excitation and line-broadening due to predissociation (c.f.) we do not resolve K\(^\prime\) structure. Even with these problems we are able to deduce an approximate rotational population distribution from the general appearance of the spectrum.

Black and Powis [12] have recently analyzed the rotational structure of the CH\(_3\) 4p->X origin with methyl radicals produced by 266 and 283 nm photolysis of CH\(_3\)I. They showed that a perpendicular (x, y axis) Coriolis coupling mechanism in the excited state causes predissociation, producing a rotational-level-dependent propensity for decay proportional to N\(^\prime\) (N\(^\prime\) + 1) -K\(^\prime\)^2. For a given N\(^\prime\) initial state the S branch bands, particularly those with low K\(^\prime\) levels, show the most rapid predissociation. This causes a rotational-level-dependent broadening of the transition plus loss of ionization signal due to competition with predissociation for the most rapidly decaying rotational levels. These factors must be taken into account in analyzing the spectrum of fig. 2.

Colson and coworkers [24] have reported a 2+1 REMPI methyl-radical 3p->X spectrum of the origin band for CH\(_3\) formed by flash pyrolysis in a supersonic expansion. Black and Powis [12] fitted this cold, but presumably Boltzmann spectrum, including the predissociation process plus an additional homogeneous linewidth term. In our rotational analysis we use a homogeneous linewidth of 4 cm\(^{-1}\) and a heterogeneous predissociation width of 0.2 cm\(^{-1}\).

We follow the rotational bandshape procedure of Hudgens et al. [22] to obtain the simulated CH\(_3\) spectrum, shown also in fig. 2. Our rotational energy level expression includes the B, C, and D rotational constants but no D\(_{NK}\) term since K structure is not resolved [28]:

\[
E(N^\prime, K^\prime) = B^\prime [N^\prime (N^\prime + 1)]
+ (C^\prime - B^\prime) K^\prime^2 - D^\prime [N^\prime (N^\prime + 1)]^2.
\]

Appropriate two-photon linestrength, nuclear spin and statistical weight factors are employed in both a state-by-state population analysis and a two-parameter temperature fit of the data. The line-by-line fit shown in fig. 2 reproduces the intensities on all the lines to within the signal to noise of the experiment and conserves the ortho/para ratio (equal to 1.0) of the parent CH\(_3\)I. The populations are given in table 1. The obvious conclusion is that for a given N quantum number the population is mainly in the low K states. The N=4, K=3 state anomaly may be explained by the overlap of the 1\(^i\) band with the P(4) line, which makes the fit of the N=4 populations uncertain. From this fit we find that the average energy of rotation about the figure axis is approximately 8 cm\(^{-1}\) (5 cm\(^{-1}\) if the N=5, K=3 population is lower) and the average energy perpendicular to the figure axis is 106 cm\(^{-1}\).

A two-parameter temperature fit has also been used to simulate the experimental spectrum. To account for the predominance of the population in low K lev-

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<th>Best-fit populations from a line-by-line analysis of the spectrum shown in fig. 2</th>
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\(^{\text{a})\text{ Overlaps with 1\( ^i\) Q branch. See text.}\) | N  | K  | Best-fit population |
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156
els the population of a level \((N, K)\) is simulated by
the normal Boltzmann factor \(\exp\left[-E(N, K)/kT_N\right]\)
times an extra factor \(\exp\left[-E(K, K)/kT_K\right]\), includ-
ing the appropriate statistical degeneracy factors. To
conserve the original ortho:para population ratio of
1:1 of the parent \(\text{CH}_3\text{I}\) beam which should be re-
lected in the fragment's rotational distribution, each
\((N, K)\) level is weighted by the total partition sum
of the spin species of the two-parameter fit to which
the level belongs. The same predissociation line-
width parameters as used for the line-by-line analysis
were included.

An \(N\) temperature \(T_N=120\) K and a \(K\) tempera-
ture \(T_K=30\) K reproduce the overall shape of the
spectrum quite reasonably. Mainly the higher \(O\) and
\(S\) lines are slightly underestimated as well as the \(P(4)\)
line. Similar \(NK\) distributions are found for the \(0^0\)
rotational band of the \(3p_\pi^+X^2\Sigma^+\) spectrum of \(\text{CD}_3\)
produced in the 266 nm photolysis of \(\text{CD}_3\text{I}\) [29].

The REMPI spectrum in the region of the \(2^1\) band
near 329.6 nm is shown in fig. 3 along with an image
taken at the \(Q\) branch band head. Due to predisso-
ciation of the upper electronic state this transition
shows no assignable rotational structure. The \(I/I^*\)
ratio observed on the \(Q\) branch band head at 329.6
nm is 0.38.

Both Loo et al. [10] and Sparks et al. [41 have
reported measurements of the \(I/I^*\) branching ratio
using different techniques. We find that the ratios
are approximately \(0.12 \pm 0.05\) and \(0.38 \pm 0.05\) for
\(v_2=0, 1\) of \(\text{CH}_3\), respectively. Loo et al. report ratios
of 0.08 and 0.037 for these transitions. Sparks et al.
[4] have used conventional time-of-flight tech-
niques to measure the velocity distribution of the \(\text{CH}_3\)
following \(\text{CH}_3\text{I}\) photolysis. They found \(I/I^*\) ratios of
0.03, 0.09, 0.09, and 0.48 for \(v_2=0-3\) of \(\text{CH}_3\). New
time-of-flight data from their laboratory yield dif-
ferent ratios [30], and we therefore do not attach
significance to the comparison between our data to
the older measurements.

Chandler and Houston [11] in their initial report
of ion imaging technique reported an \(I/I^*\) ratio of

Fig. 3. 2+1 resonance-enhanced multiphoton ionization spec-
trum of \(\text{CH}_3\) in the region of the \(2^1\) band of the \(3p, 2\Delta^+\rightarrow X, 2\Delta^+\)
electronic transition following photolysis of \(\text{CH}_3\text{I}\) with 266 nm
radiation. The image taken at 329.6 nm, the \(2^1\) band \(Q\) branch,
is also shown along with the intensity cross section recorded ver-
tically through the center of the image. Each successive color
change represents approximately 12% increase in intensity.
about 0.5 when ionizing the Q branch of the 00 band of the 3p-2A'+X 2A" transition. The factor of (1.3)^2 was inadvertently neglected in the calculation of this ratio, and it should be correctly reported as \( \approx 0.09 \).

4. Conclusions

We use the technique of photofragment imaging to study the photochemistry of CH₃I after absorption of 266 nm radiation. We observe excitation both in the \( \nu_2 \), umbrella bending mode, and \( \nu_1 \), the symmetric C-H stretching mode. For the CH₃I photolysis the I/I* branching ratio for the \( v_2 = 0 \), \( v_2 = 1 \) and \( \nu_1 = 1 \) vibrational levels of the CH₃ fragment are found to be 0.12, 0.38, and > 2.0, respectively. In addition, REMPI spectra of the origin band show that rotational excitation up to only \( N = 6 \) is induced in the methyl fragment from the photodissociation event when 266 nm radiation is used. The origin band can be adequately reproduced using a population analysis incorporating inhomogeneous predissociation and conservation of the parent ortho/para ratio in the fragment’s distribution. The photodissociation is found to induce about 100 cm⁻¹ of rotational energy about the fragment’s \( C_2 \) axis.

Acknowledgement

We would especially like to thank Dr. Steven Stolte for his interest and for many valuable discussions concerning this work. We would like to acknowledge the expert technical assistance in the laboratory by Mark Jaska and Mitch Williams and Diane Atwood for help with the figures. DHP and MHMJ gratefully acknowledge the National Science Foundation, Grant 8619803 for support.

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