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Ultraviolet photodissociation of the van der Waals dimer $(\text{CH}_3\text{I})_2$ revisited.

II. Pathways giving rise to neutral molecular iodine

Konstantin V. Vidma and Alexey V. Baklanov

*Institute of Chemical Kinetics and Combustion, Institutskaja Street 3, Novosibirsk 630090, Russia and Novosibirsk State University, Novosibirsk 630090, Russia*Yongwei Zhang and David H. Parker^{a)}*University of Nijmegen, Toernooiveld, Nijmegen 6525 ED, The Netherlands*

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The formation of neutral I_2 by the photodissociation of the methyl iodide dimer, $(\text{CH}_3\text{I})_2$, excited within the *A* band at 249.5 nm is evaluated using velocity map imaging. In previous work [J. Chem. Phys. **122**, 204301 (2005)], we showed that the formation of I_2^+ from photodissociation of the methyl iodide dimer takes place via ionic channels (through the formation of $(\text{CH}_3\text{I})_2^+$). It is thus not possible to detect neutral I_2 by monitoring I_2^+ . Neutral I_2 is detected in this study by monitoring I atoms arising from the photodissociation of I_2 . Iodine atoms from I_2 photodissociation have a characteristic kinetic energy and angular anisotropy, which is registered using velocity map imaging. We use a two-color probe scheme involving the photodissociation of nascent I_2 at 499 nm, which gives rise to I atoms that are ionized by (2+1) resonance enhanced multiphoton ionization at 304.67 nm. Our estimate of the yield of nascent I_2 is based on the comparison with the signal from I_2 at a known concentration. Using molecular beams with a small fraction of CH_3I (1% in the expanded mixture) where smaller clusters should prevail, the production of I_2 was found to be negligible. An upper estimate for the quantum yield of I_2 from $(\text{CH}_3\text{I})_2$ dimers was found to be less than 0.4%. Experiments with a higher fraction of CH_3I (4% in the expanded mixture), which favor the formation of larger clusters, revealed an observable formation of I_2 , with an estimated translational temperature of about 820 K. We suggest that this observed I_2 signal arises from the photodissociation of several CH_3I molecules in the larger cluster by the same UV pulse, followed by recombination of two nascent iodine atoms is responsible for neutral I_2 production.

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INTRODUCTION

Van der Waals clusters are interesting media for studying the influence of a weakly bound environment on photoinitiated processes. Even though the average intermolecular distance is usually quite large, there are several examples in the literature of such clusters demonstrating “concerted” photochemistry, where monomer bonds are broken and new chemical bonds are formed synchronously across the weak van der Waals bond. This opens up new chemical channels that are not possible when starting from isolated molecules. One of the most documented and intriguing example of concerted photochemistry is the UV photodissociation of clusters of the type $(\text{RI})_n$ ($n=2,3,\dots$) where the formation of molecular iodine, I_2 , has been observed. The photochemistry of $(\text{RI})_n$ clusters has been extensively studied during the last 20 years. An overview of the literature concerning this topic is given in our recent paper.¹ Special attention has been paid to photodissociation of methyl iodide clusters, $(\text{CH}_3\text{I})_n$, which can be compared with the well-characterized photodissociation of the individual CH_3I molecule. The central question in this paper is whether photodissociation of the CH_3I dimer leads to neutral I_2 formation. When using dilute

molecular beam conditions where mainly $(\text{CH}_3\text{I})_2$ should be present, we find no evidence for production of neutral I_2 . We assume here that the amount of dimer present in the molecular beam expansion is not less than the amount of dimer present in the room temperature sample before the expansion. Under this assumption, we show that our sensitivity is high enough to detect neutral I_2 in observable quantities if the quantum yield for production of neutral I_2 by CH_3I dimer photodissociation exceeds $\sim 4 \times 10^{-3}$.

Evidence for the formation of molecular iodine after the UV photolysis of $(\text{CH}_3\text{I})_n$ clusters has been presented in a number of studies.¹⁻¹² These assignments were based on the observation of ionized molecular iodine I_2^+ as well as direct detection of neutral I_2 . In our recent paper¹ pathways giving rise to I_2^+ were investigated. It was shown that neutral molecular iodine is not the precursor of I_2^+ but that photodissociation of the ionized dimer, $(\text{CH}_3\text{I})_2^+$, is responsible for this ion product. The formation of neutral molecular iodine in the photodissociation of $(\text{CH}_3\text{I})_n$ clusters has been detected directly with the use of resonance Raman scattering,² laser-induced fluorescence (LIF),³⁻⁵ and cavity ring down spectroscopy.⁶ In the experiments of Wang *et al.*² a laser pulse of wavelength close to 200 nm was used for both photodissociation of clusters and for probing I_2 by resonance Raman scattering. In these experiments several anti-Stokes

^{a)}Electronic mail: parker@science.ru.nl

transitions of I_2 were observed. The relative intensities of the anti-Stokes peaks yielded an estimated vibrational temperature of 925 K. Donaldson and co-workers^{3–5} performed a series of two-laser experiments using the first laser for dissociation of the $(RI)_n$ clusters and the second laser for excitation of the $B-X$ transition in the nascent I_2 molecules. Laser-induced fluorescence from the B state was detected. Donaldson and co-workers observed the formation of I_2 after the excitation of $(CH_3I)_n$ clusters at the wavelengths of 248 nm (Refs. 3–5) and 193 nm.⁵ The dependence of the I_2 LIF signal intensity on the photolysis laser power and on the pressure of CH_3I in the expanding mixture was measured.⁴ Comparison of the observed I_2 LIF spectra with simulations yielded an estimate of ~ 150 K for the nascent I_2 rotational and vibrational temperatures. Donaldson and co-workers also observed the formation of I_2 after photolysis of different types of clusters $(RI)_n$ such as $(HI)_n$, $(C_2H_5I)_n$, $(CH_3CH_2I)_n$, etc.⁵ Ito and Nakanaga⁶ observed the formation of I_2 after crossing a supersonic beam of CH_3I with tunable UV radiation in the 245–275 nm range. I_2 formation was detected by means of cavity ring down (CRD) spectroscopy. Their CRD spectrum recorded in the region of 560–570 nm was assigned to the $B-X$ band of I_2 molecule.

The present study is aimed at an evaluation of the quantum yield of neutral I_2 arising from the concerted photodissociation of methyl iodide dimer $(CH_3I)_2$. We determined earlier in our previous study¹ that the signal of I_2^+ cannot be used as a measure of the yield of neutral I_2 because the observed strong I_2^+ signal originates from the ionized dimer, $(CH_3I)_2^+$, instead of from I_2 . In this study we detect I_2 by velocity map imaging the iodine atoms arising from the photodissociation of I_2 at 499 nm. Together with its high sensitivity, this approach provides straightforward identification of I atoms from the I_2 precursor and allows us to probe all neutral I_2 molecules independent of their rovibrational state, because photodissociation takes place within the I_2 absorption continuum. Calibration of the yield of neutral I_2 uses the signal from neat I_2 at a known concentration, measured in the same apparatus conditions.

EXPERIMENT

The experimental setup is described in detail elsewhere.^{1,13,14} Here, a brief overview will be given. The setup is a molecular beam apparatus combined with velocity map imaging detection.¹⁴ A vacuum chamber equipped with a pulsed valve and a system of open electrodes works as a velocity mapping lens for extracting laser-produced ions from the photoexcitation region through a time-of-flight region towards a two-dimensional (2D) spatial detector, which is gated on for mass selection at the proper arrival time. The electrostatic lens is set to project all ions of the same mass and the same velocity to the same point on the 2D detector, independent of their point of origin. The distribution of ion density over the surface of 2D detector (the so-called “velocity mapped” 2D image) contains all information about the speed and angular distributions of photoproducts and can be reconstructed in three dimensions (3D) by applying the inverse Abel transform.¹⁵

A pulsed solenoid valve (General Valve) used for generation of the molecular beam was directed parallel to the time-of-flight axis. After flowing through a 0.2 mm nozzle, the molecular beam passes through a 2 mm skimmer mounted 20 mm downstream from the nozzle and propagates further in the direction of time-of-flight axis. About 100 mm downstream from the nozzle the molecular beam passes through a 2 mm hole in the center repeller plate electrode and into the region between the repeller and extractor electrodes, where photolysis takes place.

For generation of $(CH_3I)_n$ clusters, the valve was filled with a mixture of methyl iodide with argon as a carrier gas. The mixture was prepared by flowing argon through a bubbler filled with liquid CH_3I kept at the temperature of a slush bath. In our experiments two slush temperatures were used: -44 and -23 °C providing methyl iodide vapor pressures of 11.5 and 43 Torr, respectively. In experiments on the photolysis of neat I_2 , the argon carrier gas flowed through a vessel filled with beads of iodine crystals at room temperature, providing an I_2 vapor pressure of 0.2 Torr. The total backing pressure of the expansion in all experiments was 1.5 atm.

Photolysis was carried out using three successive laser pulses with wavelengths of 249.5, 499, and 304.67 nm. The duration of each pulse was about 6 ns. For experiments with $(CH_3I)_n$ clusters the sequence of laser pulses was as follows: First, the molecular beam was irradiated by the 249.5 nm laser pulse, then, 15 ns later, the beam was irradiated by a 499 nm laser pulse, and 35 ns afterwards the molecular beam was irradiated by the 304.67 nm laser pulse. In the experiments with neat I_2 only the 499 and 304.67 nm laser pulses were applied.

The laser radiation at 499 nm was generated by a pulsed dye laser (Quanta Ray PDL-2) pumped by the third harmonic of a Nd:YAG (yttrium aluminum garnet) laser (Continuum Surelite). The dye laser pulse energy used in our experiments was about 1 mJ, and the lasers, pulsed valve, and detection equipment operated at a 10 Hz repetition rate. The UV radiation at 249.5 nm was obtained by frequency doubling the 499 nm radiation in a beta barium borate (BBO) crystal. In order to provide a time delay of 15 ns between the 249.5 and 499 nm laser pulses, the two beams were separated with a dichroic mirror and the 499 nm beam was steered along an additional optical path. The two beams were then recombined on another dichroic mirror and copropagated into the chamber. These beams were focused with an UV fused silica lens, which had focal lengths of 40 cm at 499 nm and 37 cm at 249.5 nm. The lens was mounted at a distance of 34 cm from the photolysis region. The diameters of those two beams before the lens were about 2.5 mm, and the diameters of the beams in the photolysis region were estimated to be about 0.20 mm for the 249.5 nm and 0.38 mm for the 499 nm radiation.

The power of the 249.5 nm radiation was attenuated in order to avoid excessive photoion production, which could damage the detector. We used a pulse energy of 200 μ J at 249.5 nm in the experiments with 11.5 Torr pressure of CH_3I in the expanding mixture, and 70 μ J when the pressure of CH_3I was 43 Torr. The 304.67 nm laser light was ob-

tained by doubling the radiation of second pulsed dye laser (Quanta Ray PDL-2) in BBO. The dye laser was pumped by the second harmonic of a Nd:YAG laser (Quanta Ray GSR-11). The wavelength of this laser was tuned to a (2+1) resonance enhanced multiphoton ionization (REMPI) line of atomic iodine in the $^2P_{3/2}$ ground state.¹³ This 304.67 nm beam entered the chamber counterpropagating with the 249.5 and 499 nm beams and was attenuated to about 50 μ J. The beam was focused into the photolysis region by a 35 cm focal length lens. The diameter of the 304.67 nm beam in the photolysis region was much smaller than the diameters of the 249.5 and 499 nm laser beams. All three laser beams crossed the molecular beam at the same point. The radiation at all three wavelengths was linearly polarized in the direction parallel to the detector face.

I⁺ ions appearing in the three-color (249.5 nm+499 nm+304.67 nm) experiment with CH₃I seeded in argon may originate from various photochemical processes involving one, two, and three different lasers. The signal of interest is a result of a pure three-color process: the 249.5 nm laser dissociates the clusters and produces I₂, the 499 nm laser dissociates I₂ to produce specific velocity I($^2P_{3/2}$ and $^2P_{1/2}$) atoms, and the 304.67 nm laser state selectively ionizes the nascent I($^2P_{3/2}$) atoms. In all of the experiments the micro-channel plate (MCP) detector was gated by a pulsed high-voltage power supply with a pulse duration of less than 100 ns. The time position of this detector gating pulse was optimized to register only the charged particles that were created by the 304.67 nm laser pulse. Charged particles created by an earlier laser pulse in the sequence, such as the strong I⁺ signal from the 249.5 nm excitation of clustered CH₃I,¹ are fully suppressed by this gating.

In order to discriminate between the different sources of neutral I atoms produced in the three-color scheme and other possible processes, we performed a series of experiments where the excitation was provided by various combinations of 249.5, 499, and 304.67 nm laser pulses. We performed three one-color experiments (249.5, 499, and 304.67 nm) and three two-color experiments (249.5 nm+499 nm, 249.5 nm+304.67 nm, and 499 nm+304.67 nm). Expansion conditions, laser pulse energies, and time positions of the laser pulses in those experiments were identical to those of the three-color experiment. The 499 nm laser working alone does not create ions or cause photodissociation of CH₃I or its clusters. The 304.67 nm laser alone creates a weak I atom image from the photodissociation of CH₃I followed by ionization of the I($^2P_{3/2}$) fragment,¹³ and the two-color (249.5 nm+304.67 nm) experiment creates a strong I⁺ signal by excitation of monomer and clustered CH₃I at 249.5 nm, giving rise to atomic iodine which is then ionized by REMPI at 304.67 nm. The experimental challenge is to extract the true three-color signal in the presence of this strong (249.5 nm+304.67 nm) two-color signal.

RESULTS

Detection of I₂ by photodissociation

In Fig. 1(a) a raw I⁺ image is shown of I($^2P_{3/2}$) neutral fragments from the photolysis of I₂ (0.2 Torr) seeded in ar-

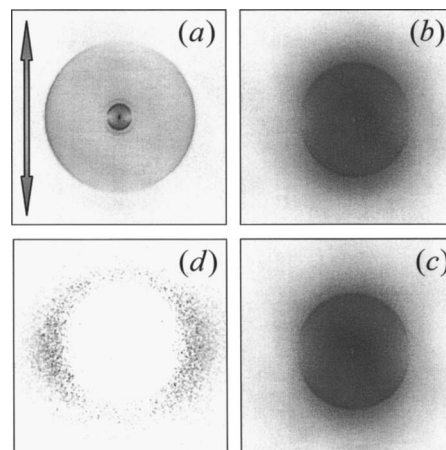
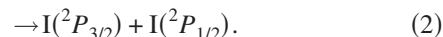
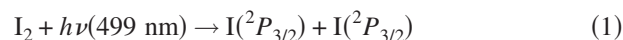


FIG. 1. Raw I⁺ images of I($^2P_{3/2}$) atoms. (a) Two-color experiment (499 nm+304.67 nm) with I₂ (0.2 Torr) seeded in argon (1.5 atm). (b) Three-color experiment (249.5 nm+499 nm+304.67 nm) with CH₃I (43 Torr) seeded in argon (1.5 atm). (c) Two-color experiment (249.5 nm+304.67 nm) with CH₃I (43 Torr) seeded in argon (1.5 atm). (d) Difference image [(c) minus (b)], represented with a higher sensitivity scale than images (b) and (c) for better visibility. The laser polarization direction is indicated by the double-headed arrow. The darker areas correspond to higher signals.

gon (1.5 atm) by the 499 nm-304.67 nm pulse sequence. At the excitation wavelength of 499 nm the I₂ molecule undergoes photodissociation via the channels,¹⁶



The outer ring in Fig. 1(a) corresponds to channel (1) and the set of small-radius rings corresponds to channel (2). In the low fragment kinetic energy region the resolution is sufficient to separate channels due to the photodissociation of several vibrational states of molecular iodine which are populated in the molecule beam expansion.¹⁷ Nascent I₂ produced by cluster photodissociation can produce an image differing from Fig. 1(a) in two ways. First, a larger range of internal states may be excited than in the supersonically cooled sample. This will create a band of rings with the same angular distribution as in Fig. 1(a) shifted towards higher velocity. Secondly, the nascent I₂ could be born with a velocity distribution, which will be mapped onto every component of the velocity mapped image, creating a smearing towards both higher and lower radii. There is no information in the literature about the translational temperature of nascent I₂ produced at 249.5 nm from (CH₃I)_n clusters. An I₂ internal temperature of 150 K was reported by Donaldson and co-workers at this dissociation wavelength.³⁻⁵ Because there are other sources of I($^2P_{3/2}$) atoms from photolysis at 249.5 nm, particularly CH₃I monomer photodissociation, which create strong signals at smaller radius in the image, we use the region covered by the outer ring of the I⁺ image in Fig. 1(a) in this study as a fingerprint for molecular I₂ as a photodissociation product.

Photodissociation of clustered CH_3I at 249.5 nm using 3.8% CH_3I in Ar

In Fig. 1(b) a raw I^+ image is shown of $\text{I}(^2P_{3/2})$ atoms resulting from photolysis of the molecular beam expansion of a gas mixture containing CH_3I (43 Torr) seeded in Ar (1.5 atm). The three-pulse sequence 249.5, 499, and 304.67 nm is used here, where the additional pulse [compared to Fig. 1(a)] at 249.5 nm is strongly absorbed by methyl iodide clusters. All conditions including the energy and timing of the 499 and 304.67 nm pulses as well as the sensitivity of the detector were the same as those used to obtain the image shown in Fig. 1(a). In the image shown in Fig. 1(c) the 499 nm beam, used for photodissociation of nascent I_2 , is blocked. This results in an image which is by eye quite similar to Fig. 1(b), where the 499 nm beam is on. Subtraction of the two images, however, yields a distinctive difference image, shown in Fig. 1(d), with a shape similar to the outside ring of the I_2 image, Fig. 1(a). The inner part of the difference image, corresponding to channel (2), production of $\text{I}(^2P_{3/2}) + \text{I}(^2P_{1/2})$, was not reliable for detection of nascent I_2 due to the limited dynamic range of the detector. This part of the image is dominated by contributions from CH_3I which are much stronger than those from nascent I_2 , and the subtraction of two images yielded no discernable signal in the middle of the image. The outer I atom channel from I_2 photodissociation [Fig. 1(a), Eq. (1)], however, is relatively free of the background from the substantial I^+ produced by ionization of I atoms from CH_3I photodissociation and can be used to detect I_2 .

Our goal is to extract the signal from the images shown in Figs. 1(b) and 1(c) with a similar anisotropy and the same speed range as the outer ring in Fig. 1(a), and to measure the intensity (the total number of ions) of this signal. Analysis of the difference image, Fig. 1(d), directly leads to similar results as the analysis of the two original images, but with much more noise due to the pixilated nature of the image. We assume that the ratio of the intensity of the difference signal in Figs. 1(b) and 1(c) to the intensity of the outer ring from Fig. 1(a) is equal to the ratio of concentrations of I_2 in the photolysis region of these two experiments. This ratio will be denoted further as n_1/n_2 , where n_1 is the concentration of I_2 produced from clusters, and n_2 is the concentration of I_2 in the experiment with I_2 (0.2 Torr) seeded in Ar (1.5 atm). We take care that the pulse energies of the 499 and 304.67 nm lasers are the same in these two experiments. We neglect any difference between the absorption cross section at the wavelength of 499 nm for I_2 seeded in argon and I_2 produced from clusters, because the indicated vibrational temperature of the nascent I_2 is low and similar to that of the supersonically expanded I_2 -Ar sample. The vibrational temperature of I_2 seeded in argon was estimated in our previous work¹⁷ to be 240 ± 10 K. Fan and Donaldson⁴ reported an ~ 150 K vibrational temperature for nascent I_2 produced from photodissociation of methyl iodide clusters at the nearby wavelength of 248 nm.

Below we describe our method for extracting the intensity of the I_2 signal produced by photodissociation of CH_3I clusters formed at 249.5 nm in an expansion of 3.8% CH_3I

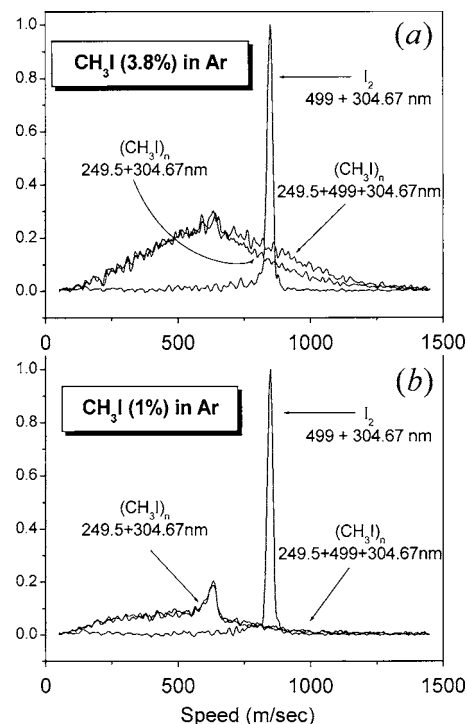


FIG. 2. Speed distributions of I^+ ions taken in the range of polar angles from 75° to 105° . (a) Two-color (499 nm+304.67 nm) experiment with I_2 (0.2 Torr) seeded in argon (1.5 atm), three-color (249.5 nm+499 nm+304.67 nm) experiment with CH_3I (43 Torr) seeded in argon (1.5 atm), and two-color (249.5 nm+304.67 nm) experiment with CH_3I (43 Torr) seeded in argon (1.5 atm). (b) Two-color (499 nm+304.67 nm) experiment with I_2 (0.2 Torr) seeded in argon (1.5 atm), three-color (249.5 nm+499 nm+304.67 nm) experiment with CH_3I (11.5 Torr) seeded in argon (1.5 atm), and two-color (249.5 nm+304.67 nm) experiment with CH_3I (11.5 Torr) seeded in argon (1.5 atm).

in Ar from the images shown in Figs. 1(b) and 1(c). The same approach will then be applied in experiments where a gas mixture with a lower fraction (1%) of CH_3I was used for preparation of the clusters. The outer ring in Fig. 1(a) has its maximal amplitude in the direction perpendicular to the photolysis laser polarization direction. Speed distributions in the range of the polar angles from 75° to 105° , where the angle θ is referenced to the polarization direction, which were obtained from the images shown in Figs. 1(a)–1(c) are plotted in Fig. 2(a). The speed distribution for I atoms resulting from excitation of I_2 seeded in argon has a sharp narrow peak around 850 m/s, as expected for the low translational temperature of I_2 in the beam. The speed distributions obtained from the image of three-color experiment (249.5 nm+499 nm+304.67 nm) and the two-color experiment (249.5 nm+304.67 nm) show a broad additional feature in the region centered around 850 m/s [see also Fig. 1(d)]. We suggest that this signal originates from internally cold but translationally excited I_2 produced from clusters $(\text{CH}_3\text{I})_n$ at the wavelength of 249.5 nm.

We used two different methods to estimate the ratio of signal coming from I_2 seeded in argon to the signal coming from I_2 produced in the cluster photodissociation. In the first method we analyzed directly the angle-selected speed distributions shown in Fig. 2(a). The two curves from $(\text{CH}_3\text{I})_n$ were integrated in the range from 700 to 1200 m/s and sub-

tracted, yielding difference we label Y_1 . The integral under the narrow peak in the I_2 curve is labeled Y_2 . We assumed the ratio Y_1/Y_2 to be the estimation of the ratio of concentrations of I_2 in the photolysis region n_1/n_2 . This method gives the value of $Y_1/Y_2=0.57$.

An alternative method for extraction of the relative intensity of the signal from I_2 produced from clusters is based on the analysis of polar angular distributions of the signals. In this method we performed the following procedure. Angular distributions were extracted for speeds in the range of 700–1200 m/s from the images shown in Figs. 1(a)–1(c). The angular distributions from the image of two-color excitation (499 nm+304.67 nm) of I_2 were fitted with the function

$$f = A(1 + \beta(\frac{3}{2} \cos^2 \theta - \frac{1}{2})), \quad (3)$$

where A and β are fitting parameters. This function describes the angular distribution of fragment recoil resulting from one-quantum photodissociation.^{18–20} Note that formula (3) is not valid when the photodissociation process produces aligned $I(^2P_{3/2})$ atoms. The effects of alignment in I_2 photodissociation imaging have been fully analyzed in a previous paper¹⁷ and are expected to be minor in this comparative study. The anisotropy parameter β was determined from the fit to be equal to -0.60 .

- (1) In the same manner we determined the anisotropy parameter β of the speed-specific angular distributions from the image of two-color excitation (249.5 nm + 304.67 nm) of CH_3I seeded in Ar. The extracted value of β was found to be 0.82.
- (2) We fit the angular distribution obtained from three-color experiment (249.5 nm+499 nm+304.67 nm) on CH_3I seeded in Ar with the function

$$f = A_1(1 + \beta_1(\frac{3}{2} \cos^2 \theta - \frac{1}{2})) + A_2(1 + \beta_2(\frac{3}{2} \cos^2 \theta - \frac{1}{2})), \quad (4)$$

with the fixed parameters $\beta_1=0.82$ and $\beta_2=-0.60$, and the amplitudes A_1 and A_2 as fitting parameters. In this fit there are two components of the angular distribution, one with the same anisotropy as the signal in two-color experiment with CH_3I seeded in argon, and another with the same anisotropy as the signal in two-color experiment with I_2 seeded in argon. The result of this deconvolution is represented in Fig. 3(a).

Using this deconvolution we calculated the relative contribution of the signal with the anisotropy of -0.60 to the total ionic signal in the range of the angles from 75° to 105° . We then multiplied this relative contribution with the integral of the three-laser curve in Fig. 2(a), which was taken over the speed interval with the limits from 700 to 1200 m/s, and denoted the obtained value as Y'_1 . Then we compared this value with the integral of the sharp peak on the I_2 curve (denoted earlier as Y_2). The ratio Y'_1/Y_2 was attributed to be another estimate of the n_1/n_2 concentration ratio. The obtained value is $Y'_1/Y_2=0.47$. For the images represented in Figs. 1(a)–1(c) both of the described methods provide similar values for the concentration ratio.

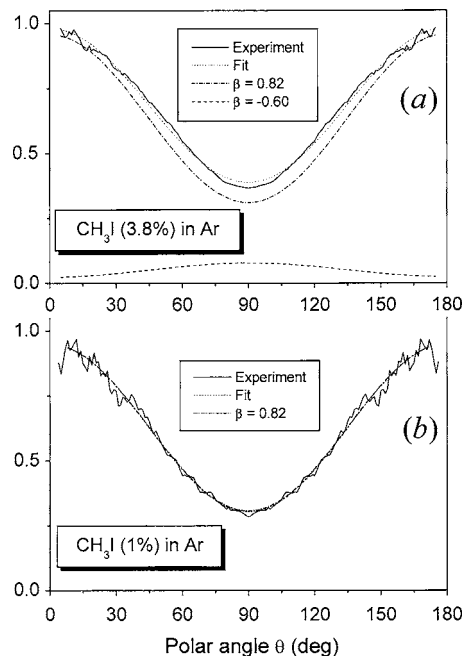


FIG. 3. Deconvolution of the angular distribution of I^+ ions arising in the three-color (249.5 nm+499 nm+304.67 nm) experiment with CH_3I seeded in argon. The angular distribution was taken in the speed interval around 850 m/s (see text for details). (a) CH_3I (43 Torr) seeded in argon (1.5 atm); (b) CH_3I (11.5 Torr) seeded in argon (1.5 atm). Solid line—experimental angular distribution; dashed line—fitting curve [the sum of two functions with anisotropies of 0.82 (dash-dot line) and of -0.60 (dashed line)]. In (b) the dashed curve is not shown because it is indistinguishable from the horizontal axis.

We have also estimated the translational temperature of the observed I_2 produced from clusters. This I_2 is assigned to be a source of I atoms providing the peak [difference between curves 2 and 3 on Fig. 2(a)], centered at around 850–900 m/s. The width of this peak allows us to estimate the translational temperature of precursor I_2 to be about 820 K.

Photodissociation of clustered CH_3I at 249.5 nm using 1% CH_3I in Ar

The same analysis procedure has also been applied to a series of experiments with a lower CH_3I fraction (1.0%) in the expansion mixture (11.5 Torr of CH_3I in 1.5 atm of Ar). The images obtained in those experiments look similar to the corresponding images shown in Fig. 1. The speed distributions obtained from the images of two-color (249.5 nm + 304.67 nm) and three-color (249.5 nm+499 nm + 304.67 nm) experiments with clustered CH_3I and two-color (499 nm+304.67 nm) experiment with I_2 , taken in the range of the polar angles from 75° to 105° , are represented in Fig. 2(b).

Unlike the higher concentration experiments, the distributions obtained in the three-color (249.5 nm+499 nm + 304.67 nm) versus two-color (249.5 nm+304.67 nm) experiments with 1.0% CH_3I seeded in argon do not demonstrate a discernible difference in the region around 850 m/s, indicating that the nascent I_2 signal is very small. For extraction of this signal we have applied the second method described above, based on the analysis of the angular distribu-

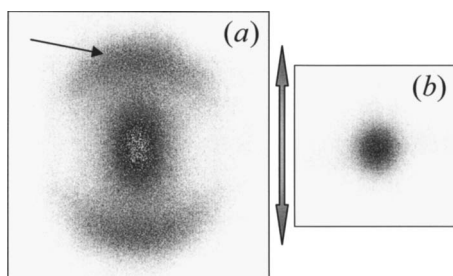


FIG. 4. Raw images resulting from one-color excitation at 249.5 nm of CH_3I (11.5 Torr) seeded in argon (1.5 atm): (a) $-\text{I}^+$ and (b) $-\text{I}_2^+$. The double-headed arrow shows the direction of the 249.5 nm laser polarization. The arrow in (a) indicates transitionally “hot” ions I^+ with kinetic energy of about 0.94 eV. The origin of these ions is discussed in detail in Ref. 1. The positions of the time gates of the MCP detector in these experiments were optimized for the detection of the ions produced by the 249.5 nm laser pulse, unlike the other experiments described in the paper.

tions. This method involves the deconvolution of two components with anisotropy parameters $\beta_1=0.82$ and $\beta_2=-0.60$ for the angular distribution extracted from the three-color experiment. The result of this deconvolution is represented in Fig. 3(b). As is seen from the figure, the contribution of the curve with the anisotropy of -0.60 is negligible. The extracted amplitude A_2 of the component is slightly negative but the error interval includes zero. The estimated ratio of I_2 concentrations resulted from photodissociation of CH_3I clusters and neat I_2 is found to be $Y'_1/Y_2 = -0.004 \pm 0.004$. This is zero within the experimental error.

In order to make sure that the mixture with the lower CH_3I fraction (11.5 Torr of CH_3I and 1.5 atm of Ar) in the expanded mixture does produce $(\text{CH}_3\text{I})_n$ clusters, we performed an experiment with this mixture where the molecular beam was irradiated by the 249.5 nm laser pulse alone. The expansion conditions and the 249.5 nm laser power were the same as in other experiments with the mixture of CH_3I (11.5 Torr) and Ar (1.5 atm). The images of I^+ and I_2^+ obtained in that experiment are shown in Figs. 4(a) and 4(b), respectively. The images look identical with images reported in our earlier paper.¹ They revealed the formation of I^+ with a specific speed and angular distribution including the so-called “hot” I^+ ions with a kinetic energy 0.94 eV [indicated by arrows in Fig. 4(a)], and thus the formation of I_2^+ . All these features were observed in the paper¹ and were attributed to the photochemistry of clustered CH_3I . In the present experiment qualitatively similar images were also obtained for experiments with higher CH_3I fractions than 43 Torr CH_3I in 1.5 atm Ar.

DISCUSSION

Gas mixture with 1.0% CH_3I in Ar

The images shown in Fig. 4 prove that the amount of CH_3I in the valve of 11.5 Torr is sufficient for the formation of clusters. Our experiments reveal that the production of I_2 following photolysis of CH_3I seeded in argon using these expansion conditions is too low to be observed. An upper estimate of the nascent I_2 yield in the experiment with 1.0% CH_3I in Ar is the experimental uncertainty associated with the Y'_1/Y_2 ratio, which is equal to 0.4%. The concentration n_1

of nascent I_2 produced in the photolysis region is thus less than 0.4% of the concentration n_2 of neat I_2 in the experiment with I_2 (0.2 Torr) seeded in argon (1.5 atm). This upper estimate corresponds to the signal which would be provided by I_2 if its concentration in the beam would be $\approx 7 \times 10^{-5}$ of the concentration of CH_3I . To find the quantum yield of I_2 in the photodissociation of the $(\text{CH}_3\text{I})_2$ dimer we should estimate the fraction of dimers in the total concentration of CH_3I in the photolysis region and the fraction of those dimers absorbing the UV quantum under our experimental conditions. Zhong and Zewail¹⁰ characterized the cluster $(\text{CH}_3\text{I})_n$ size composition for a CH_3I content (7–8 Torr in the valve) most close to what we used. They observed only monomers and dimers of CH_3I without observable traces of higher clusters. We have also observed signals (I_2^+ and “hot” I^+) due to photoionization/photodissociation of clusters (Fig. 4). We do not know the actual fraction of dimer $(\text{CH}_3\text{I})_2$ in our expanded mixture but we can assume that the fraction of clustered CH_3I molecules only increases after the expansion as compared with the conditions before expansion (the mixture behind the valve). It is normally the case that supersonic expansion increases the clustering of molecules. Before expansion the concentration of dimer is at least 4% of the CH_3I monomer concentration. This number is obtained with the use of dimerization equilibrium constant determined by Waschewsky *et al.*²¹ These authors extracted the equilibrium constant (K) for dimer formation of CH_3I molecules in the gas phase on the basis of the measured temperature and pressure dependence of the CH_3I absorption spectrum. Using the range of the equilibrium constant values reported in paper²¹ ($K=0.004$ – 0.043 at 298 K) we calculated that at a pressure of CH_3I of 11.5 Torr in the valve, the concentration of dimer $(\text{CH}_3\text{I})_2$ should be at least 4% of monomer concentration before expansion. This 4% means that the concentration of I_2 arising from the photodissociation of $(\text{CH}_3\text{I})_2$ is not higher than $7 \times 10^{-5}/0.04 \approx 0.0018$ of the dimer concentration. The actual concentration of the dimer should be higher and so the last number can be even lower.

The probability of a dimer absorbing the 249.5 nm UV quantum in our experimental conditions is

$$P = \left(1 - \exp\left(-\frac{f \cdot \sigma}{\hbar \cdot \omega}\right) \right). \quad (5)$$

In this equation f is the laser fluence, σ is the absorption cross section of $(\text{CH}_3\text{I})_2$ at the wavelength of 249.5 nm, and $\hbar\omega$ is the energy of photon at 249.5 nm. We assumed the dimer absorption cross section to be the same as the cross section of the CH_3I monomer at this wavelength [for the monomer $\sigma_{249.5} = 9.5 \times 10^{-19} \text{ cm}^2$ (Ref. 22)]. This assumption is based on the results of Donaldson *et al.*²³ who studied UV absorption spectra of CH_3I over a range of clustering conditions. They reported the spectrum of clustered CH_3I to be very similar to the unclustered spectrum, with slight blueshift of the A-band maximum. Taking into account that our wavelength is close to the center of the band, the use of monomer cross section seems to be reasonable. The exciting laser beam cross section and pulse energy were measured and the fluence value was calculated to be $f \approx 500 \text{ mJ/cm}^2$. This

yields an estimated probability of $P \approx 0.45$. This value, together with the previously estimated upper limit for the I₂ yield (0.0018) per one dimer molecule, provides an estimate of the upper limit for the quantum yield (ϕ) of I₂ in the photodissociation of the dimer (CH₃I)₂ as $\phi \leq 0.0018/0.45 \approx 0.004$.

Gas mixture with 3.8% CH₃I in Ar

When the expanded mixture contains a higher fraction of CH₃I (43 Torr in 1.5 atm of Ar) a distinctive signal attributed to the formation of I₂ is observed. This CH₃I content is higher by 3.8 times as compared with the previously described “more diluted” mixture but the increase in signal from I₂ exceeded a factor of 140. The exciting UV pulse (249.5 nm) energy in this experiment was lower by 2.9 times as compared with the experiment where more the diluted mixture (1% of CH₃I) was irradiated (see Experiment section). The fraction of dimers absorbing the UV quantum [Eq. (5)] in this experiment was thus equal to 0.19. This means that a factor of 140 is necessary to multiply by the ratio of P ($0.45/0.19=2.4$) in these cases. When recalculated to the same laser power conditions, the increase in signal from I₂ exceeds a factor of about 340 when the CH₃I content is increased from 1% to 3.8%. The increase in this content by 3.8 times can result in an increase in dimer concentration (and thus the signal due to dimer photodissociation) by no more than 14.5 times (square of 3.8). We can thus conclude that at least a major part ($\geq (1 - 14.5/340) \approx 0.96$) of the observed I₂ is due to photoexcitation of clusters (CH₃I)_{*n*} with $n > 2$. This suggests that clusters larger than dimers give rise to nascent neutral I₂. In the previous literature, the formation of larger clusters has been confirmed when using expansions with a high fraction ($> \sim 3\%$) of CH₃I.

Syage and Steadman⁸ performed experiments on the photolysis of clustered CH₃I using picosecond laser pulses and expansion conditions similar to ours. With a mixture of CH₃I (60 Torr) and Ar (1.6 atm) they observed (CH₃I)_{*n*} clusters with $n \geq 10$. Ito *et al.*²⁴ performed a study on the IR spectra of clustered CH₃I by means of cavity ring down spectroscopy. Their expansion conditions were also similar to ours (38 Torr of CH₃I in 1 atm of helium). They observed two broad absorption features that were attributed to the clusters with the average size of $n=6$ and 10, respectively. In our experiments using a similar CH₃I fraction and stagnation pressure, clusters with about the same size range should also be produced.

Previous observations of neutral I₂ formation were made using expansion conditions with a rather high pressure of CH₃I in the valve. Donaldson and co-workers³⁻⁵ observed the formation of I₂ when the pressure of CH₃I was 35 Torr and higher. Wang *et al.*² used a mixture of 60 Torr of CH₃I seeded in 2 atm of argon or helium. Ito and Nakanaga⁶ observed the formation of I₂ with a lower pressure of CH₃I, in an expansion mixture of 17 Torr of CH₃I seeded in 0.5 atm of He. They reported in a preceding paper²⁴ that these conditions allow the formation of clusters (CH₃I)_{*n*} with the sizes up to $n=5$.

Our results thus allow us to conclude that the production of neutral I₂ in the photodissociation of methyl iodide dimers (CH₃I)₂ at the wavelength around 250 nm is negligible and that the dominate source of nascent I₂ formation is the photodissociation of larger clusters (CH₃I)_{*n*} ($n > 2$). We suggest that the photodissociation of several CH₃I molecules in the cluster by the same laser pulse followed by recombination of two nascent iodine atoms is the mechanism responsible for the observed nascent I₂ production.

Equation (5) gives the probability of absorption of a quantum of 249.5 nm radiation during the pulse action time. In the experiments with 3.8% CH₃I in Ar this factor is equal to about 0.20. The probability of the absorption of radiation by at least two molecules from a (CH₃I)_{*n*} cluster is estimated to have a value of about 0.04 for $n=2$, 0.10 for $n=3$, 0.18 for $n=4$, 0.26 for $n=5$, 0.34 for $n=6$, etc. If, for example, we suppose that clusters with $n=5$ or higher are responsible for I₂ formation via this mechanism, then a simple estimation shows that about 4.5% of CH₃I molecules should be formed in clusters of the size $n \geq 5$ in order to provide the formation of I₂ at the levels observed in our 3.8% CH₃I in Ar experiment.

Because we have not directly characterized our cluster distribution we do not categorically rule out the creation of I₂ by “concerted photochemistry” taking place in the CH₃I dimer. Our sample conditions are to our knowledge identical to those of previous studies where the cluster distribution was characterized. One could argue, however, that by increasing the CH₃I content when going from the dilute 1% CH₃I/Ar to the more concentrated 3.5% CH₃I/Ar, we have simply increased the amount of dimers present in the beam above a threshold necessary for nascent I₂ detection. Because our sensitivity to a small amount of “cold” I₂ is excellent [Fig. 1(a)], this implies that our sensitivity to “hot” (nascent) I₂ [Fig. 1(d)] is much lower. The nascent I₂ detected in Fig. 1(d), however, is actually internally colder than our cold I₂ sample—its translational energy is higher but low and high translational energy species are detectable with equal sensitivity by imaging. Imaging sensitivity is also linear over a large range up to saturation. While the region of the (I+I^{*}) channel in our image from CH₃I clusters is saturated, the region for the (I+I) channel is quite reliable. We believe that the highly nonlinear dependence of the nascent I₂ signal on the CH₃I sample pressure is also a strong indication that the nascent I₂ arises from larger clusters, and not from CH₃I dimers.

CONCLUSION

The formation of neutral molecular iodine in the photodissociation of clustered CH₃I at the wavelength of 249.5 nm has been investigated. Using the expansion conditions with 1.0% CH₃I in Ar, which favors the formation of small clusters, we observe no evidence for the formation of I₂. The quantum yield of I₂ formation in the photodissociation of (CH₃I)₂ at 249.5 nm was estimated to be less than 0.4%. Experiments with 3.8% CH₃I in Ar, which favor the formation of larger CH₃I clusters, revealed an observable formation of internally cold nascent I₂, in agreement with previous

results,³⁻⁵ with an estimated translational temperature of about 820 K. The steep dependence of the yield of this I₂ on CH₃I content shows that it comes mainly from clusters higher than the dimer. We suggest that photodissociation of several CH₃I molecules in the larger clusters takes place during the same UV pulse and is followed by recombination of two nascent iodine atoms to form the nascent I₂ observed in this work and in the previously reported experiments.

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