UV photodissociation of the van der Waals dimer (CH$_3$I)$_2$ revisited: Pathways giving rise to ionic features

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The CH$_3$I $A$-state-assisted photofragmentation of the (CH$_3$I)$_2$ van der Waals dimer at 248 nm and nearby wavelengths has been revisited experimentally using the time-of-flight mass spectrometry with supersonic and effusive molecular beams and the “velocity map imaging” technique. The processes underlying the appearance of two main (CH$_3$I)$_2$ cluster-specific features in the mass spectra, namely, $I_2^+$ and translationally “hot” $I^+$ ions, have been studied. Transitionally hot $I^+$ ions with an average kinetic energy of 0.94±0.02 eV appear in the one-quantum photodissociation of vibrationally excited $I_2^+(	ilde{X}_{1\text{a}}^2\Pi_{3/2,}\text{g})$ ions ($E_{\text{vib}}=0.45\pm0.11$ eV) via a “parallel” photodissociation process with an anisotropy parameter $\beta=1.55\pm0.03$. Comparison of the images of $I^+$ arising from the photoexcitation of CH$_3$I clusters versus those from neutral I$_2$ shows that “concerted” photodissociation of the ionized (CH$_3$I)$_2$ dimer appears to be the most likely mechanism for the formation of molecular iodine ion $I_2^+$, instead of photoionization of neutral molecular iodine. © 2005 American Institute of Physics. [DOI: 10.1063/1.1909083]

I. INTRODUCTION

Van der Waals (vdW) complexes are the first step of complexity along the way from isolated molecules to molecules in the condensed medium. The study of the photophysics and photochemistry of van der Waals complexes is vital in understanding the effect of a weakly bound environment on photoinitiated processes. In spite of the weak binding of partner molecules in the vdW complex, there are several examples in literature in which the vdW complex at low temperatures, or its analog (the “collisional complex”) at higher temperatures, demonstrates “concerted” photochemistry, where new chemical channels open up as compared with the isolated molecule. Here we can refer to the iodine-containing dimers (RI)$_2$, giving rise to molecular iodine, which will be discussed in more detail below; dimers of OCS (Refs. 1 and 2) and CS$_2$, generating S$_2$ as a photofragment; and the O$_2$−O$_2$ complex, giving rise to O$_3$+$O^+$ as well as the O$_2$−N$_2$ complex, which gives two NO molecules as photoproducts. The best documented example of this concerted photochemistry is the photodissociation of iodine-containing clusters (RI)$_n$ and the dimer (RI)$_2$ as the simplest member of this series. The photochemistry of van der Waals complexes (RI)$_n$ has been extensively studied during the last 15 years. Special attention has been paid to (CH$_3$I)$_n$ (Refs. 6–31 and 36–38) and (HI)$_n$ (Refs. 20 and 31–35) clusters because of the large amount of data that is available concerning the photochemistry of the corresponding single molecules CH$_3$I and HI. Other kinds of R groups (such as CH$_3$CH$_2$, CF$_3$, etc.) have also been used$^{20}$ for cluster generation.

Various experimental approaches and detection techniques, such as time-of-flight mass spectrometry, laser-induced fluorescence (LIF), IR, and UV absorption, and cavity ring-down spectroscopy (CRDS), have been used for the investigation of (RI)$_n$ clusters. Several groups have performed experiments involving photoexcitation of jet-cooled clustered CH$_3$I molecules in combination with ion time-of-flight detection of the photofragment mass spectrum. Fan$^{10–21}$ carried out LIF studies, and Wang$^{22}$ performed resonance Raman scattering experiments. Donaldson et al.$^{23,24}$ carried out UV absorption studies of (CH$_3$I)$_n$ clusters, while Garvey and Bernstein$^{25}$ and Syage$^{27}$ reported on electron-impact investigations. One-quantum ionization of CH$_3$I clusters by vacuum ultraviolet (VUV) radiation was studied by Chen$^{28}$ et al.$^{18}$ The IR-absorption spectra of matrix-isolated CH$_3$I clusters were obtained by Momose$^{26}$ et al. and Ito et al.$^{29}$ The photodissociation of (HI)$_n$ clusters was studied by Young$^{32,33}$ and by Zhang et al.$^{34}$ using the time-of-flight technique. Ito et al. applied cavity ring-down spectroscopy (CRDS) in the region of the $v_1$ band of CH$_3$I molecule to study (CH$_3$I)$_n$ cluster formation using super-
sonic jet conditions\textsuperscript{39} and CRDS in visible has been applied for the study of I\(_2\) product appearance in UV-photodissociation of (CH\(_3\)I\(_n\))\(_n\) clusters.\textsuperscript{39}

Several groups have used the kinetic energy-time-of-flight (KETOF)\textsuperscript{12,13,32,33} analysis and ion imaging\textsuperscript{37} to obtain information about the speed and angular distribution of the photofragments resulting from UV photoexcitation of (CH\(_3\)I\(_n\))\(_n\) (Refs. 12, 13, and 37) and (HI)\(_n\).\textsuperscript{32,33} Ito et al. performed \textit{ab initio} calculations of the structure, binding energy, and vibrational wavenumbers of the dimer (CH\(_3\)I\(_2\))\(_n\) as well as the higher clusters (CH\(_3\)I\(_3\))\(_n\) and (CH\(_3\)I\(_4\))\(_n\).\textsuperscript{39} Bogdanchikov \textit{et al.}\textsuperscript{40} carried out an \textit{ab initio} study of the structure and binding energy of the isomers of the neutral dimer (CH\(_3\)I\(_2\))\(_n\) as well as its ionized form (CH\(_3\)I\(_2\))^\textvisiblesuper{+}.

The low temperature necessary to generate van der Waals complexes is provided by the technique of supersonic jet cooling. The efficiency of cooling and the cluster size depend on many parameters such as the backing pressure, the composition of the expanding mixture, etc. The formation of clusters as large as (CH\(_3\)I\(_n\))\(_n\) (Ref. 16) or even larger\textsuperscript{40} has been detected. The effect of the backing pressure and the composition of the expanding mixture on the CH\(_3\)I cluster size distribution has been studied experimentally by Ito \textit{et al.}\textsuperscript{39}

As has been revealed in numerous previous studies, new photodissociation routes open up in clusters compared with the corresponding single molecules. The UV photodissociation of single CH\(_3\)I or HI molecules gives iodine atoms in the \(2P_{1/2}\) and \(2P_{3/2}\) states as well as CH\(_3\) and H fragments, respectively.\textsuperscript{41} Using conditions where the supersonic jet favors cluster formation, (CH\(_3\)I\(_2\))^\textvisiblesuper{+} ions have been observed in the mass spectrum of the ionized species arising from the photoexcitation of CH\(_3\)I or HI clusters. Sapers \textit{et al.}\textsuperscript{6} observed the appearance of (CH\(_3\)I\(_2\))^\textvisiblesuper{+} ions from clusters of CH\(_3\)I molecules when a nanosecond radiation of the KrF laser (248 nm) was used. Syage and Steadman\textsuperscript{10} also reported the presence of (CH\(_3\)I\(_2\))^\textvisiblesuper{+} ions in the mass spectrum of a cold beam of CH\(_3\)I molecules when a nanosecond or picosecond radiation at the wavelength of 266 nm was used. Strobel \textit{et al.}\textsuperscript{11} observed the appearance of (CH\(_3\)I\(_2\))^\textvisiblesuper{+} ions in the beams of CH\(_3\)I (Ref. 11) and HI (Refs. 32 and 33) molecules when excited at the 240-nm wavelength. Zhong \textit{et al.}\textsuperscript{14,15} and Poth \textit{et al.}\textsuperscript{16} observed a (CH\(_3\)I\(_2\))^\textvisiblesuper{+} formation from CH\(_3\)I clusters in femtosecond pump-probe experiments using laser pulses at wavelengths of 277 plus 304 nm (Refs. 14 and 15) and 270 plus 405 nm.\textsuperscript{16} Syage and Steadman studied these clusters with a picosecond pump-probe approach at wavelengths of 266 plus 532 nm.\textsuperscript{10}

After the first observation of the (CH\(_3\)I\(_2\))^\textvisiblesuper{+} formation by Sapers \textit{et al.}\textsuperscript{6} efforts were made to analyze the mechanism of the (CH\(_3\)I\(_2\))\(_n\) photochemistry. The photoexcitation of (CH\(_3\)I\(_2\))\(_n\) yields I\(_2\) (Refs. 19–22 and 36) and (CH\(_3\)I\(_2\))^\textvisiblesuper{+} (6,10,14–16,51) which are new chemical channels compared to the monomer. In addition, energetic I\(_2\) ions are observed.\textsuperscript{37} Using UV photons around 250 nm, possible mechanisms for I\(_2\), (CH\(_3\)I\(_2\))^\textvisiblesuper{+}, and I\(_2^+\) formation include the following:

\[
(CH_3I)_2 + h\nu \rightarrow I_2 + \text{other products}, \quad (1)
\]

\[
I_2 + 2h\nu \rightarrow I_2^+ + e^- , \quad (2)
\]

\[
I_2^+ + h\nu \rightarrow I^+ + I(2P) , \quad (3)
\]

\[
I_2 + h\nu \rightarrow I(2P) + I(2P), \quad (4)
\]

\[
I(2P) + (2 \text{ or } 3)h\nu \rightarrow I^+ + e^- , \quad (5)
\]

\[
(CH_3I)_2 + 2h\nu \rightarrow (CH_3I)_2^+ + e^- , \quad (6)
\]

\[
(CH_3I)_2^+ + h\nu \rightarrow I_2^+ + \text{other products}. \quad (7)
\]

Because I\(_2\) formation [process (1)] has been observed in the experiments with CH\(_3\)I clusters, the I\(_2^+\) and I\(_2^+\) ions were usually assumed to appear due to the photodissociation and photoionization of I\(_2\) [processes (2)–(5)]. However, these ions can be also formed via processes starting with the ionized dimer [process (7) followed by process (3)].

Some of the above-mentioned authors proposed that I\(_2^+\) is the product of \textit{dimer} photochemistry,\textsuperscript{6,11,14,15,51} while others concluded that larger clusters also contribute to I\(_2^+\) formation.\textsuperscript{10,16,32,33} Poth \textit{et al.}\textsuperscript{16} suggested that the I\(_2^+\) ion is produced via a dissociation of the ionic clusters (CH\(_3\)I\(_n\))^\textvisiblesuper{+} as in process (6) for \(n=2\). Syage and Steadman\textsuperscript{10} studied the photodissociation of (CH\(_3\)I\(_n\))^\textvisiblesuper{+} cluster ions at 532 nm [process (7)] and found that the photodissociation proceeds via the rupture of van der Waals bond and does not provide I\(_2^+\) ions at this wavelength.

More information on the nature of the processes giving rise to ionic species in the photoexcitation of methyl iodide clusters can be gained from the energy distribution and angular anisotropy of the photofragments. In the current paper the ion time of flight and velocity map imaging techniques have been applied for the study of the cluster-specific pathways giving rise to ionic features under UV photoexcitation of methyl iodide dimer (CH\(_3\)I\(_2\)).

II. EXPERIMENT

A. Time-of-flight experiments

For the present study two different experimental setups were used. The setup used in Novosibirsk is a molecular-beam apparatus combined with a time-of-flight mass spectrometer in the Wiley–McLaren arrangement.\textsuperscript{32} The chamber is evacuated by a turbo-molecular pump and liquid N\(_2\) trapping down to a pressure of \(3 \times 10^{-7}\) Torr. Two different molecular-beam arrangements were used with this setup. One arrangement provided a cold supersonic beam (estimated translational temperature of the gas in the probing region was as low as 1 K), and another one provided an effusive beam of gas at room temperature. This allowed us to separately probe conditions favorable and unfavorable for the clustering of methyl iodide molecules. A home-built current-loop actuated valve similar to that one used in Ref. 43 generates the supersonic beam. The pulsed valve operates at 1 Hz with a pulse duration of 200 \(\mu\)s. Gas was expanded into the chamber through a 0.23-mm nozzle. The gas mixture was prepared by a flow of argon through a liquid CH\(_3\)I sample held at fixed temperatures provided by
different slush baths. This allowed us to vary the partial pressure of methyl iodide from 0.7 to 140 Torr. Mixtures of CH₃I (0.5%-1.5%) with a carrier gas (argon or helium) in a stainless steel vessel were also used. The valve backing pressure was varied within the interval of 0.2 to 2.5 bars. The gas jet passed through a 2.5-mm skimmer mounted 60 mm downstream and entered a homogeneous electric-field region created between the electrodes of the time-of-flight mass spectrometer (TOF MS), where it is crossed by a beam from a pulsed KrF excimer laser. Ions produced by laser radiation were accelerated by an electric field perpendicular to the directions of molecular and laser beams and detected by a microchannel plate (MCP) detector. The signal was then digitized, stored, and processed by a personal computer.

In the case of the effusive beam, the gas mixture flowed continuously into the chamber through a multichannel array (22 × 4 mm²) with 50-μm channel diameter. The molecular beam was intersected 30 mm downstream by the laser beam. The nozzle was filled with neat CH₃I at pressures up to 0.25 Torr. The efficiency of cooling was negligible since the typical pore size was less than the gas-free path. Therefore, the molecules in the effusive beam were at room temperature.

Special attention was paid to create similar CH₃I concentration conditions in the supersonic and effusive molecular-beam setups. For the supersonic beam, the concentration of the carrier gas in the photoexcitation region was estimated by calculating the radial spread of the molecular beam using the formalism given in the paper of Anderson and Fenn. In these estimations the effect of a small CH₃I admixture was neglected. The estimated concentrations of CH₃I molecules (the sum of clustered and unclustered species) in the supersonic beam were within the interval of 10¹¹-10¹³ cm⁻³ for the conditions used. The concentrations for the effusive beam were estimated with the use of the formalism for multichannel arrays given in the paper of Olander and Kruger. These estimated concentrations for the effusive beam were within the interval of 2.5 × 10¹¹-4.5 × 10¹² cm⁻³.

A separate experiment on molecular iodine photoexcitation in the effusive beam conditions was also carried out. The molecular iodine vapor pressure of about 0.1 Torr was provided by a solid sample of I₂ connected to the volume behind the multichannel array. Its concentration in the photoexcitation region was estimated to be about 10¹² cm⁻³.

The home-built pulsed KrF excimer laser (248 nm) operated at 1 Hz with 1-mJ pulse energy and pulse duration of 5 ns. The light polarization was parallel (“vertical polarization”) or perpendicular (“horizontal polarization”) to the static electric field in the supersonic region of the TOF MS where the photoexcitation took place. The laser beam was focused by a 53-cm focal length lens with a maximum laser-pulse energy fluence in the focal region of about 150 mJ/cm². The energy of the laser pulse was monitored by a UV-sensitive photodiode, which was mounted behind the output window of the chamber. Wire mesh or quartz filters were used to attenuate the pulse energy.

### B. Velocity map imaging experiments

The Nijmegen velocity map imaging setup has been described in detail elsewhere. The main feature of this setup is an electrostatic lens system using open electrodes for extracting nascent ions from the photoionization region through a time-of-flight region towards a two-dimensional (2D) spatial detector, which is gated at the proper arrival time for mass selection. The electrostatic lens is set to project all ions of the same velocity to the same point on the 2D detector, independent of their point of origin. The “velocity-mapped” 2D images contain all information about speed and angular distributions of photoproducts and can be reconstructed as three-dimensional (3D) by applying the inverse Abel transform.

A brief overview of the experiment follows. The vacuum chamber was equipped with two pulsed solenoid valves (General Valves) providing the generation of the molecular beam directed parallel to the TOF axis (on-axis beam) or perpendicular to the TOF axis (off-axis beam). The results obtained with both configurations were similar, therefore only the experiments with the off-axis beam are described here. The molecular beam passed through a 2-mm skimmer mounted 20 mm downstream from the nozzle and propagates further perpendicular to the time-of-flight axis. About 100 mm downstream from the nozzle, the molecular beam enters the region between the repeller and extractor electrodes where photoexcitation takes place. In the experiments with methyl iodide the gas mixture contained 15–140 Torr of CH₃I and 1–2 bars of argon. Two modes of pulsed valve operation were used in order to change the conditions for cluster formation in the molecular beam. The conditions unfavorable for clustering were provided with a short gas pulse, while favorable clustering conditions were provided with a longer gas pulse. In the experiments with molecular iodine, the carrier gas flowed through a glass cylinder filled with iodine and was then injected in the chamber. The maximum partial pressure of molecular iodine in the injected gas mixture is estimated to be about 0.1–0.2 Torr. The lasers, valve, and detection equipment operated at a 10-Hz repetition rate.

The frequency-doubled radiation of a dye laser (Coumarin 500) pumped by the third harmonic of a neodymium-yttrium aluminum garnet (Nd:YAG) laser has been used for the generation of UV radiation tuned around 250 nm. The resulting pulse energy of this radiation was about 1 mJ and the pulse duration was about 5 ns. A lens with a focal length of 20 or 40 cm focused the light at the molecular beam. In experiments with clusters the laser power was adjusted to minimize the concentration of ions and to avoid their Coulomb repulsion by shifting the laser focus away from the molecular beam by 2–3 cm.

I⁻ images were calibrated by the one-laser photodissociation of I₂ at different wavelengths used for (2 + 1) resonantly enhanced multiphoton ionization (REMPI) of I(2P₃/₂): at λᵥᵥ = 249.61 nm providing resonant two-quantum excitation to the intermediate level with an energy of 2hv = 80125.45 cm⁻¹ (Ref. 48) or at λᵥᵥ = 304.67 nm.⁴₇
FIG. 1. Time-of-flight mass spectra of fragments resulting from the photodissociation of CH$_3$I molecules in (a) supersonic beam and (b) effusive beam, at the wavelength 248 nm. The unassigned peaks are due to the background.

III. RESULTS

A. Mass spectra of CH$_3$I photodissociation fragments in effusive and supersonic beams

Time-of-flight mass spectra of ionized fragments of the photodissociation of CH$_3$I molecules at 248 nm (KrF laser) in supersonic and effusive beams are presented in Fig. 1. The laser power was the same for both spectra. The mass spectrum of the room-temperature effusive beam contains the parent ion CH$_3$I$^+$ as well as its photofragments I$^+$ and CH$_3$. In contrast, the mass spectrum with the supersonic beam shows the existence of strong I$^+$ and I$_2^+$ signal and the absence of CH$_3$I$^+$ and CH$_3$. Under clustering conditions a splitting of the I$^+$ peak [Fig. 2(a)] is seen, which disappears after changing the laser light polarization from parallel to perpendicular, relative to the static electric field. These features were also observed when helium, instead of argon, was used as a carrier gas. The mass spectrum did not change substantially when the laser pulse was scanned in time along the gas pulse. Data similar to those shown in Figs. 1 and 2 were observed for all concentrations of the precursor CH$_3$I molecules (estimated to be of $10^{11}$–$10^{13}$ cm$^{-3}$ for the supersonic beam and $2.5 \times 10^{11}$–$4.5 \times 10^{12}$ cm$^{-3}$ for the effusive beam).

A deconvolution of the time profile of the I$^+$ peak (Fig. 2) has been carried out. The form of the splitting is characteristic of a "parallel" photoprocess, and the peak separation corresponds to an I$^+$ ion kinetic energy of about 1 eV. Comparing the peak shape to one expected from a process with a purely parallel transition (anisotropy parameter $\beta=2$), it was determined that these "hot" ions provided about 70% of the total integral of the I$^+$ peak presented in Fig. 2(a). This contribution was dependent on the laser power, the backing pressure, and the CH$_3$I content in the molecular beam.

In Fig. 3, the laser-power dependence of the integrated I$^+$ and I$_2^+$ peaks as well as the sum of these peaks is shown. A drop in the I$_2^+$ signal due to the photodissociation is observed at higher pulse energy. This photodissociation gives rise to I$^+$ ions. The summed signal of I$_2^+$ and I$^+$ rises approximately with the square of the laser-pulse energy (the slope is equal to 2.36±0.23). Taking into account that the hot component is the major component of the I$^+$ peak, we suppose that the hot I$^+$ ions arise primarily from the photodissociation of I$_2^+$.

To elucidate the size of the clusters that are the source of the cluster-specific features (I$_2^+$ and hot I$^+$) we have varied the expansion conditions in order to change the cluster size composition. The critical parameter for the cluster size composition is the CH$_3$I content in the expanding mixture. In Fig. 4 the experimentally measured ratio of the amplitudes of

FIG. 2. Time-of-flight profiles of the I$^+$ peak arising from 248 nm photoexcitation of CH$_3$I molecules under the conditions of (a) supersonic beam and (b) effusive beam. Solid lines (—) correspond to the signal obtained with the laser radiation polarized parallel to the static electric field in the region of photoexcitation and the dotted line (···) corresponds to perpendicular polarization. The double peaking in signal observed for the supersonic beam (a) is due to hot I$^+$ ions with kinetic energy of about 1 eV. Monomer splitting [see also Fig. 6(a)] is too small to resolve under condition (b).

FIG. 3. The dependence of the integrals of I$^+$ and I$_2^+$ peaks on laser (248 nm) pulse energy in supersonic beam is shown. The symbol ■ corresponds to the I$_2^+$ peak; ○ corresponds to the I$^+$ peak; ▲ corresponds to the sum of the integrals of I$^+$ and I$_2^+$ peaks. Solid line indicates the linear fit for the ▲ dependence. The slope of fitted line is 2.36±0.23. The expanded mixture was CH$_3$I (0.65%) in argon (2.5 bars).

FIG. 4. The dependence of the integrals of I$^+$ and I$_2^+$ peaks on laser (248 nm) pulse energy in supersonic beam is shown. The symbol ■ corresponds to the I$_2^+$ peak; ○ corresponds to the I$^+$ peak; ▲ corresponds to the sum of the integrals of I$^+$ and I$_2^+$ peaks. Solid line indicates the linear fit for the ▲ dependence. The slope of fitted line is 2.36±0.23. The expanded mixture was CH$_3$I (0.65%) in argon (2.5 bars).
hot I+ and I2+ signals due to cluster dissociation is shown as a function of the partial pressure of CH3I (PCH3I) in the expanding mixture. When PCH3I decreased, the ratio stabilized to a constant value corresponding to the predominant dimers (CH3I)2. When PCH3I=200 Torr (carrier gas argon, backing pressure P=1.6 bar),10 Poth et al.16 observed clusters with n up to 8 with PCH3I=200 Torr (carrier gas argon, backing pressure P=3.3 bars). Zhong and Zewail15 used a lower pressure PCH3I=7-8 Torr (carrier gas helium, backing pressure P=1.3 bar) and observed only the dimer (CH3I)2 without any traces of higher clusters. As it is shown in Fig. 4, we observed the cluster-specific features even for PCH3I lower than 7-8 Torr. We can thus conclude that in the low CH3I pressure extrapolation in our conditions (Fig. 4) the cluster features, I2+ and translationally hot I+ in the TOF mass spectrum, are due to the photodissociation/photoionization of the (CH3I)2 dimers.

A separate experiment on the photoionization of pure molecular iodine at the wavelength of 248 nm was also performed to investigate the possibility that process (2), the two-photon ionization of the neutral I2, provides the precursor of I2+ for our experimental conditions. Molecular iodine was introduced into the chamber under effusive beam conditions. The laser power and estimated concentration of I2 molecules (1013 cm−3) was similar to the concentration of CH3I (1011−1013 cm−3) in the supersonic beam experiment. The signals of I2+ and I+ ions were negligible when using neat I2 as a precursor.

**B. Velocity map imaging**

The velocity map imaging technique allowed us to obtain a detailed information on the speed and angular distributions of the I+ and I2+ products of the (CH3I)2 photodissociation. The I2+ signal was observed only for conditions favorable for clustering in the molecular beam. A raw I2+ image is presented in Fig. 5(a) and its reconstructed 3D speed distribution is shown in Fig. 5(b). The reconstructed speed distribution was fit to a Maxwell distribution function, yielding a I2+ translational temperature of approximately 650 K. The angular distribution was found to be isotropic.

Figures 6(a) and 6(b) show I+ images obtained under conditions favorable and unfavorable for cluster formation. The image corresponding to monomer dissociation [Fig. 6(a)] contains two main features: an outer ring and an inner structure. This image is very similar to the one reported by Samartzis et al.,49 who studied the photodissociation of unclustered methyl iodide with a similar technique. They assigned the outer ring to the nonresonant two-photon ionization of I(2P1/2) atoms arising from the one-photon dissociation of CH3I, and the lower-energy features arise from higher-order multiphoton processes. On tuning our laser to an I(2P1/2) resonance at 249.619 nm (vacuum) the outer ring is indeed greatly enhanced. Off-resonance, the I3+ image obtained at 248 nm under conditions favorable for cluster formation and low laser intensity (lens 2−3 cm out of focus) is shown in Fig. 6(b). Two main differences from the monomer image are: a smeared central "blob" instead of the sharp structure seen for the monomer and a large blurred outer ring of parallel character, which appears under the same molecular beam conditions as the I2+ signal. The origin of this outer ring will be discussed later in the text.

The radial speed distribution extracted from Fig. 6(b) is shown in Fig. 7(a). The two modes of this distribution were approximated by Gaussian functions. The best fit shows that the center of the outer ring distribution is located at
$E_t = 0.94 \pm 0.02$ eV, where the uncertainty is determined from averaging four experimental images. The angular distribution, Fig. 7(b), for this ring is fit by an anisotropy parameter of $\beta = 1.55 \pm 0.03$. The tuning of the UV-radiation wavelength over 1 nm to the blue and 6 nm to the red from 248.6 nm did not affect this hot-ion signal. The use of radiation resonantly enhancing the $I(I^*)$ and $I(2P_{3/2})$ signals (249.61 nm and 249.619 nm, respectively) did not affect the image of the hot $I^+$ ions. This result indicates that the neutral $I(I^*)$ atoms are not the precursors of the hot $I^+$ ions.

C. Photodissociation of $I_2$ and $I_2^+$ around 248 nm

In order to identify the $I_2^+$ photodissociation channels giving rise to the observed hot $I^+$ ions, we have studied the photodissociation of $I_2^+$, which was generated via the two-photon ionization of the molecular iodine $I_2$. A one-laser setup was used with the laser wavelength $\lambda_{\text{vac}} = 248.6$ nm. It is known that $I_2$ shows only continuous absorption in this region. The two-quantum ionization of $I_2$ [process (2)] provides $I_2^+$, which absorbs an extra photon and gives rise to an $I^+$ ion. In all the experiments with molecular iodine, $I^+$ images were observed only when the laser focus was set at the molecular beam. The image of $I^+$ appearing in the process $I_2^+ + h\nu \rightarrow I^+ + I(I^*)$ is presented in Fig. 8(a). The reconstructed total kinetic energy release (TKER) distribution is shown in Fig. 8(b).

At the wavelength $\lambda_{\text{vac}} = 248.6$ nm ($h\nu = 4.99$ eV), a two-quantum photoionization can produce molecular ion $I_2^+$ in its two lowest spin–orbit $^3\Pi_{3/2, g}$ and $^3\Pi_{1/2, g}$ substates, with an adiabatic ionization energy determined by Cockett et al.\textsuperscript{50} to be 9.31 and 9.95 eV, respectively. When the photon energy was tuned below the threshold for the two-quantum ionization into the $^3\Pi_{1/2, g}$ state of the $I_2^+$ ($\lambda_{\text{vac}} > 249.2$ nm), peak 1 from Fig. 8 changed slightly in energy but peaks 2 and 3 with the TKER centered at 2.08 and 3.02 eV disappeared. This allowed us to identify peaks 2 and 3 as belonging to channels of the $I_2^+\left(^3\Pi_{1/2, g}\right)$ photodissociation. The anisotropy parameter for channel 1 was found to be $\beta = 1.58 \pm 0.03$. Fig-
FIG. 8. (a) Raw image of I+ ions resulting from the photoexcitation of I2 at the wavelength 248.6 nm. (b) Reconstructed total kinetic energy distribution (TKER) for the process I₂+hν→I+I+. Channel (1) corresponds to 1.61-eV TKER at maximum, channel (2) corresponds to 2.08-eV TKER, and channel (3) corresponds to 3.02-eV TKER. Several unassigned rings in the central part of the image correspond to the TKER below 0.4 eV.

Figure 9 shows an energy diagram for the I3(v = 0) photodissociation at 248 nm. Peaks 2 and 3 from Fig. 8 coincide well with the TKER expected for I3 ions produced from low v-state vibrationally excited I2 dissociated to [I3(3Pj 0) 3I(2P3/2)3] and [I3(3P2)3I(2P3/2)3] products, respectively, while peak 1 corresponds to production starting from I3(23/2g) dissociated to [I3(3Pj 0) 3I(2P3/2)3].

To check the possibility that I2 is a precursor of the I3 observed in the experiments with clusters of CH3I, we tuned the laser to the wavelength λvac = 249.61 nm, which is in resonance with a two-photon transition from the ground-state I(2P3/2) to the (2Σg⁺) state (E = 80 125.45 cm⁻¹). Figure 10 shows images of I+ due to (2+1) REMPI of I(2P3/2) [Fig. 10(a)] arising from the photodissociation of molecular iodine,

I2(2Σg⁺) → I(2P3/2) + I(2P1/2), ΔE = -1.50 eV, (4')

and from the photoexcitation of CH3I clusters [Fig. 10(b)]. The anisotropy parameter of process (4') was found to be β = -0.89±0.01. A comparison of the two images in Fig. 10 shows that the I+ outer ring from the (CH3I)2 dimer does not come from the neutral I2 molecules. The strong signal at lower kinetic energy in this image [Fig. 10(b)] results from the resonant detection of I(2P3/2) atoms arising from the dissociation of CH3I monomers in the beam.

IV. DISCUSSION

A. Translationally hot I+ ions

The translationally hot I+ ions shown in Figs. 6 and 10 arise from a precursor with a rather broad absorption spectrum, which could be I3. They cannot be a result of resonant ionization of fast neutral I atoms because the signal of hot I+ ions was not affected by tuning the laser to the resonant transitions of I(I*) atoms. As seen from Fig. 3, the photodissociation of I3 takes place at higher laser-pulse energy values and is accompanied by a rise in the I+ signal. As we have found above, about 70% of the I+ signal in the TOF experiments is contributed by hot I+ ions. In the imaging experiments, the hot I+ ions appear only together with an I2 signal. Another argument comes from the shape of the image of these hot I+ ions [outer ring on Fig. 6(b)] which is rather blurry. The most probable reason for the image broadening is the effect of velocity distribution of the precursor. The translational temperature of 650 K of I3 extracted from the image in Fig. 5 was then used for the simulation of the image of I+ arising from this precursor. The result of the simulation is shown in Fig. 6(c) and is very similar to the image observed experimentally for hot I+ ions [outer ring in Fig. 6(b)]. We
below 0.5 eV (Fig. 8) involves the channels corresponding to the photodissociation process (3) \( I^+ + I(I^*) \rightarrow I^+(I^+) \), two fragments of equal mass appear. The total kinetic energy release (TKER) in this process is equal to double the value of \( E_n \), i.e., TKER = 1.88±0.04 eV.

In order to establish the channel giving rise to these hot \( I^+ \) ions we consider the experimental results of the photodissociation of \( I_2 \) generated via the two-quantum photoionization of the neutral \( I_2 \) (process (4)) in the text. The region of the TKER values can thus conclude that \( I_2^+ \) is a precursor of the hot \( I^+ \) ions with an average translational energy of \( E_n = 0.94±0.02 \) eV. In the photodissociation process (3) \( I_2^+ + h\nu \rightarrow I^+(I^+) \), two fragments of equal mass appear. The total kinetic energy release (TKER) in this process is equal to double the value of \( E_n \), i.e., TKER = 1.88±0.04 eV.

In principle, the measurements analogous to those shown in Fig. 10, when carried out under similar laser power conditions for \( I_2 \) and for \( CH_3I \) clusters, could allow us to estimate the yield of molecular \( I_2 \) via process (1), which was observed earlier experimentally.\(^{19-22,36}\) We should mention again that in our experiment with neutral \( I_2 \) [Fig. 10(a)] the laser radiation was tightly focused, but that in the experiment with clusters [Fig. 10(b)] we had to lower the laser intensity by shifting the laser focus away from the molecular beam in order to obtain an image that was not distorted by Coulomb repulsion of the abundantly formed ions from \( CH_3I \) and \( CH_3I^+ \) photodissociation/collision [central part in Fig. 10(b)]. This did not allow us to use the same laser power conditions in these experiments, and thus we could not estimate the yield of \( I_2 \) via process (1).

**B. Dissociation of the ionized \( \text{(CH}_3\text{I)}_2^+ \) dimer**

An alternative source of \( I_2^+ \) is the dissociation of the ionized \( \text{(CH}_3\text{I)}_2^+ \) dimer, process (7). There is no reason to expect...
a reduction of the photoionization yield in the dimer as compared with the free CH$_3$I molecule. The results of our experiments with supersonic and effusive beams show that the total yield of ions under clustering conditions is higher than for the unclustered case. At a UV photon energy close to two quanta of the KrF laser ($\approx 10$ eV), Chen et al.\textsuperscript{18} observed a parent ion (CH$_3$I)$_2^+$ as the main product among the ions appearing from the photoionization of the neutral (CH$_3$I)$_2$ dimer. However, we do not observe any (CH$_3$I)$_2^+$ ions in the case of dimer photoionization. We suspect that the photoionization of the dimer is followed by a spontaneous or photo-initiated decay of the ionized dimer, giving rise to I$_3^-$. The energy of two UV quanta of the KrF laser ($2hv=9.97$ eV) is higher than the energy of the fragments of the spontaneous decay of (CH$_3$I)$_2^+$ via

$$(\text{CH}_3\text{I})_2 + 2hv \rightarrow [(\text{CH}_3\text{I})_2^+] \rightarrow \text{I}_3^- + \text{C}_2\text{H}_6, \quad \Delta E = -1.09 \text{ eV}. \quad (8)$$

The calculated $\Delta E$ value has been obtained with the use of the enthalpy data for CH$_3$I, C$_2$H$_6$ and I$_2$ molecules\textsuperscript{55} and the ionization potential (IP) of I$_2^+$ as well as the $ab$ initio calculated binding energy (0.096 eV) in the (CH$_3$I)$_2$ van der Waals dimer.\textsuperscript{65} In spite of the exothermicity of process (8), the formation of I$_3^-$ was not observed by Chen et al., who studied the photoionization of CH$_3$I clusters in a one-quantum process with the quantum energy tuned within the range of 8–35 eV. This result of Chen et al. does not exclude process (8) in our case because a two-quantum ionization of (CH$_3$I)$_2$ can yield (CH$_3$I)$_2^+$ ions with higher vibrational excitation, and thus a different decay rate than one-quantum ionization. The absence of (CH$_3$I)$_2^+$ and presence of I$_3^-$ can also be due to the photodissociation of (CH$_3$I)$_2^+$ ions by a photon of the same laser pulse

$$(\text{CH}_3\text{I})_2^+ \rightarrow \text{I}_3^+ (\Pi_{3/2}) + 2\text{CH}_3, \quad \Delta E = -2.27 \text{ eV}, \quad (7')$$

$$hv \rightarrow \text{I}_3^+ (\Pi_{3/2}), \quad \Delta E = -6.08 \text{ eV}. \quad (7'')$$

The enthalpy value for CH$_3$I is taken from Ref. 55. An absorption cross section at 248.6 nm higher than 3 $\times 10^{-17}$ cm$^2$ will result in photodissociation of more than 99% of the (CH$_3$I)$_2^+$ precursor ions. This value of the cross section implies saturation of the third photon absorption step and a near-quadratic pulse-energy dependence of the I$_3^-$ yield, as found in our experiments (the total yield of I$_3^-$ and I$^-$ arising from I$_2^+$ increased at a power of 2.36$\pm$0.23 pulse energy).

C. Discussion of the previous data on hot $^+$ ions

The previous results of Tanaka et al.\textsuperscript{37} can be interpreted using the same line of reasoning as above. Tanaka et al. used ion imaging for the study of the photofragments of CH$_3$I cluster photodissociation at 266 nm and observed the formation of hot $^+$ ions with translational energy $E_t = 0.69$ and 1.08 eV appearing via parallel processes with $\beta = 2\pm0.6$ and 2$\pm$0.5, correspondingly. The authors\textsuperscript{37} suggested that these hot ions are due to fast I atoms arising from the photodissociation of the CH$_3$I moiety in small clusters. Taking into account our results, we can interpret these hot ions as due to the one-quantum photodissociation of I$_3(\Pi_{3/2},g)$ via the lowest channels shown in Fig. 9(b). The difference of 0.39 eV (an experimental uncertainty is not given in Ref. 37) in the values of $E_t$ for the channels observed by Tanaka et al. corresponds to a difference of 0.78 eV in the TKER values, which is very close to the energy gap of 0.8 eV for these channels [Fig. 9(b)]. The channel with $E_t = 0.69$ eV (TKER = 1.38 eV) in the experiments of Tanaka et al. is similar to the channel we observed (TKER = 1.88$\pm$0.04 eV). The difference in the TKER values is partially due to the difference in the quantum energy ($hv=4.66$ eV at 266 nm versus $hv=4.99$ eV at 248.6 nm). An extra 0.17 eV in the TKER difference can be due to a variation in the vibrational excitation of I$_3^-$ with the dissociation wavelength. We should also mention that at 248.6 nm the lowest channel of Fig. 9(b) was also observed in the case of I$_2^+$ dissociation (a weak parallel ring with $E_t$ about 2.4 eV between rings 2 and 3 in Fig. 8). This gave a rather low contribution and was not distinct in our experiments with clusters (Fig. 6). Probably, the ratio of the product channels of I$_3^-$ photodissociation is wavelength dependent. The formation of hot $^+$ ions with $E_t = 0.924$ eV and a high anisotropy ($\beta = 1.5$) was also observed by Young, who studied the photodissociation of the clusters (H$_3$I)$_2$ at 240 nm.\textsuperscript{37} The similarity of $E_t$ and anisotropy with our observations suggests that the I$_3(\Pi_{3/2},g)$ ion is a precursor of hot I$^+$ ions in the cited experiments of Young as well.

D. Previous experiments concerning the dissociation of the ionized (CH$_3$I)$_2^+$ dimer

Syage and Steadman\textsuperscript{10} studied the 532-nm photodissociation of (CH$_3$I)$_2^+$ dimer ions prepared from the neutral dimer by electron impact. They observed the photodissociation of the ionized dimer only via the van der Waals bond (CH$_3$I)$_2^+$ + $hv$ $\rightarrow$ CH$_3$I$^+$ + CH$_3$I and concluded that the photodissociation of dimer ions does not contribute substantially to the production of ionized fragments such as I$_3^-$. Because the result of Syage and Steadman was obtained at 532 nm, far from the UV region, it does not contradict our conclusion that the ionized dimer is the source of I$_3^-$ in the UV photochemistry of CH$_3$I clusters.

The difference in energy of the products of process (7') and the neutral dimer (CH$_3$I)$_2$ is 12.69 eV. The process of dissociative ionization of the dimer,

$$[(\text{CH}_3\text{I})_2^+] \rightarrow \text{CH}_3\text{I}^+ + \text{CH}_3\text{I}, \quad \Delta E_{\text{thresh}} = 9.64 \text{ eV}, \quad (9)$$

has a $\Delta E_{\text{thresh}}$ value calculated on the basis of IP (CH$_3$I) = 9.54 eV (Ref. 56) and a binding energy of 0.096 eV for the vdW dimer (CH$_3$I)$_2^+$.\textsuperscript{46} The (CH$_3$I)$_2^+$ ions prepared by electron impact\textsuperscript{10} that survived until the arrival of the dissociation laser pulse should have an internal energy close to or lower than $\Delta E_{\text{thresh}}$. The sum of $\Delta E_{\text{thresh}} = 9.64$ eV and energy of the quantum of radiation at 532 nm $hv=2.33$ eV gives the value 11.97 eV, which is less than the 12.69 eV required for channel (7'). But channel (7') is a four-centered reaction which should have a
large activation barrier according to the Woodward–Hoffman correlation rules. For this reason channel (7') could probably not compete with the dissociative ionization [process (9)] in the experiments of Syage and Steadman, if the dissociation of ionized dimer was “statistical” as supposed by the authors. Due to the same reason we are in doubt about spontaneous decay [channel (8)] as the source for I$_3^-$ formation.

Channel (7') lies higher in energy than the dissociative ionization [channel (9)] and probably higher than the activation barriers for channel (7'). This channel can become accessible when using UV photoexcitation. The photodissociation of (CH$_3$I)$_2$ ions in the UV region could be nonstatistical, particularly if the excited state is repulsive. We suggest that the source of I$_3^-$ ions observed in the UV photochemistry of CH$_3$I dimers involves photodissociation of the ionized dimer (CH$_3$I)$_2^-$ via channel (7'). In our previous paper ab initio calculations have been carried out on the energetics and geometry of the neutral and ionized dimers of CH$_3$I. These calculations have shown that the strong binding between the ionized pair of I atoms exists in the most stable head-to-head configuration of the ion (CH$_3$I)$_2^-$, In this ion the spin density is already uniformly distributed over two I atoms and the distance $r_c(1-1) = 3.14$ Å is quite close to the distance in the ion I$_3$ (2.57 Å). The structure of the (CH$_3$I)$_2^-$ ion thus favors the formation of I$_3^-$ as a product.

V. CONCLUSIONS

The CH$_3$I A-state-assisted photofragmentation of the van der Waals dimer (CH$_3$I)$_2$ has been investigated with the use of the time-of-flight and “velocity map imaging” techniques for excitation around 248 nm. The main features in the mass spectrum of the dimer (CH$_3$I)$_2$ photofragments as compared with the photodissociation of single CH$_3$I molecules were observed: molecular ions I$_3^-$ (translational temperature, 650 K) and translationally hot I$^+$ ions ($E_t = 0.94 \pm 0.02$ eV, anisotropy parameter $\beta = 1.55 \pm 0.03$). It was found that hot I$^+$ ions arise from the photodissociation of I$_3^-$ ions in their electronic ground state ($\tilde{2}I_1^+(2,2,2)$), and the vibrational energy of the nascent I$_3^-$ ions was determined to be 0.45±0.11 eV. A comparison of the images of I$^+$ arising in the photoexcitation of CH$_3$I clusters with the neutral I$_3$ has allowed us to neglect the molecular iodine as the precursor of I$_3^-$ in the mass spectrum of the photofragments. The concerted photodissociation of the ionized dimer (CH$_3$I)$_2^-$ was concluded to be the most probable source of the molecular iodine ion I$_3^-$.

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Photodissociation of $(\text{CH}_3\text{I})_2$

52C. E. Moore, NBS Circular No. 476, 1958.