Research paper

Oxygen-assisted excitation of methyl iodide as a test of double spin-flip transition in van der Waals complex CH$_3$I-O$_2$

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ABSTRACT

Photoexcitation of van der Waals (vdW) complex CH$_3$I-O$_2$ has been studied with velocity map imaging of I atoms arising in photodissociation. A new scheme of resonance-enhanced multiphoton ionization of iodine atoms has been applied with simultaneous use of UV and VIS radiation. The measured kinetic energy of I(^{2}P$_{3/2}$) atoms indicates photogeneration of precursor CH$_3$I molecules via complex-specific channel with excitation energy expected for double spin-flip transition in complex CH$_3$I-O$_2$. The angular distribution for recoil directions of I(^{2}P$_{3/2}$) atoms coming from vdW complexes also corresponds to that expected for double spin-flip transition.

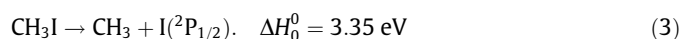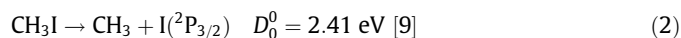© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Van der Waals (vdW) complex of oxygen is a very suitable model for experimental studies of the drastic effect of weakly bound environment on photoprocesses in oxygen [1–8]. In all these experiments with vdW complexes dramatic enhancement of oxygen atom photogeneration was observed when excitation above threshold of O$_2$ dissociation took place. Besides that the process of reactive singlet oxygen ^{1}O$_2$ photogeneration from complexes X-O$_2$ was revealed [5,6,8]. Existing data on singlet oxygen formation in photodissociation of vdW complexes X-O$_2$ were interpreted in terms of double spin-flip (DSF) transitions with simultaneous change of electronic spin of partner molecules [8]

$$^1X\text{-}^3O_2 + h\nu \rightarrow {}^3X + {}^1O_2. \qquad (1)$$

Conclusions in favor of this mechanism are based on observed correlation between the results of detection of singlet oxygen and estimated location of DSF absorption band [8]. Another argument is based on the fact of universally observed formation of vibrationally cold ^{1}O$_2$ in all detection cases that is just predicted for DSF mechanism [8]. Process (1) gives rise not only to singlet oxygen but also to a triplet state of partner molecule ^{3}X. The

energy of a radiation quantum absorbed in a supramolecular process (1) is split between oxygen and partner molecule X. A portion of about 1 eV goes to provide vibrationally cold ^{1}O$_2$. The internal energy of produced ^{3}X should fit this. In order to measure the internal energy of X molecule excited in supramolecular excitation of complex we investigate photodissociation of complex of methyl iodide CH$_3$I-O$_2$. It was earlier established that photodissociation of this complex and its deuterated analog (CD$_3$I-O$_2$) with UV-radiation at wavelengths around 226 nm (h$\nu \approx$ 5.5 eV) gives rise to singlet oxygen [8]. Excitation of this complex in a process (1) should provide excited CH$_3$I with internal energy levels of about 4.5 eV. This energy is sufficient for dissociation of CH$_3$I via two channels

$$CH_3I \rightarrow CH_3 + I(^2P_{3/2}) \quad D_0^0 = 2.41 \text{ eV [9]} \qquad (2)$$

$$CH_3I \rightarrow CH_3 + I(^2P_{1/2}). \quad \Delta H_0^0 = 3.35 \text{ eV} \qquad (3)$$

Photoexcitation of CH$_3$I to the energy level of about 4.5 eV is followed by prompt dissociation via processes (2) and (3) with excess energy released almost totally as the kinetic energy of the fragments CH$_3$ and I(^{2}P$_J$) [9]. So, measurement of the kinetic energy distribution of I atoms and so the total kinetic energy release (TKER) in dissociation of excited CH$_3$I via excitation of complex CH$_3$I-O$_2$ should allow us to verify this 1 eV shift in energy of excitation provided by double spin-flip process (1). In order to carry out these measurements with the use of velocity map imaging of I atoms we have applied new REMPI scheme for I atoms ionization

with simultaneous use of VIS- and UV-radiation provided by fundamental of dye laser and its second harmonic, respectively. This REMPI scheme has been tested for photodissociation of molecular iodine. This scheme allows us to excite the complex CH_3I-O_2 in the spectral region of singlet oxygen photogeneration and to ionize I atoms resonantly for velocity map imaging in a one-laser experiment.

2. Experimental

The Novosibirsk setup for velocity map imaging (VMI) was described earlier in paper [8]. Cold molecules and van der Waals complexes have been generated in a pulsed molecular beam. The supersonic beam with duration of 100 μs is generated by a home-made electrodynamic valve. The premixed gas is expanded into the vacuum chamber through a nozzle with an orifice diameter of 0.27 mm. The central part of the gas jet passes through the 2.5 mm skimmer mounted 60 mm downstream and so generated molecular beam enters the region between electrodes perpendicularly to the axis of VMI arrangement. Tunable VIS radiation is produced by a pulsed dye laser (Coumarine 120) pumped by an excimer XeCl laser. Dye laser radiation is doubled in frequency in a BBO crystal. Overlapped second harmonic (UV radiation) and fundamental (VIS) of dye laser are focused into molecular beam with a spherical mirror providing the same focus length of 25 cm for radiation at both wavelengths. Schemes with polarization of UV radiation perpendicular (VIS-parallel) to the axis of VMI setup and VIS-perpendicular (UV-parallel) have been used. Tunable half-wavelength plate (Alphalas) has been used for adjustment of polarization plane of laser radiation. Ions were detected by a microchannel plate (MCP) detector (F2225-21P MCP assembly by Hamamatsu). The images averaged over several thousand shots were inverted using the pBasex method [10].

To deliver I_2 vapor into the valve volume the helium carrier gas at a pressure of 1 atm flowed through a vessel filled with beads of iodine crystals at room temperature, providing I_2 vapor pressure of about 0.2 Torr. In experiments with methyl iodide and its vdW complex CH_3I-O_2 gas mixtures $CH_3I(0.125\%)$-He and CH_3I(0.125%)-O_2(5%)-He at the backing pressure from 1 to 5 atm have been used.

3. Results and discussion

3.1. REMPI [(1 + 1′) + 1(1′)] of I atoms arising in photodissociation of I_2

In Fig. 1 the scheme of REMPI of I atoms used in the current work is shown. This scheme can be classified as REMPI [(1 + 1′) + 1(1′)]. At a first step resonant two-photon excitation with the use of radiation of the fundamental of pulsed dye laser (VIS) and its harmonic (UV) takes place. Then one-photon ionization by VIS or UV radiation takes place giving rise to I^+ ions detected in our experiments.

Tuning of dye laser provides simultaneous change of both VIS and UV wavelengths. For finding of resonances appropriate for REMPI of I atoms the experiments with I atoms arising in photodissociation of molecular iodine I_2 have been carried out. In Fig. 2 two spectral profiles of I^+ signal in TOF mass-spectrum are shown which indicate two resonances of iodine atom.

Central positions of the spectral profiles observed correspond to VIS wavelength values λ_{vac} = 447.34 and 456.04 nm. The first one provides energy of two quanta $h\nu(UV) + h\nu(VIS)$ = 67,063 cm^{-1} which corresponds to the allowed two-quantum transition from the ground state $I(^2P_{3/2})$ to the state $I\left((^3P_2)6p[1]_{3/2}\right)$ [11]. The second wavelength provides energy $h\nu(UV) + h\nu(VIS)$ = 65,784 cm^{-1} which corresponds to the allowed two-quantum transition from
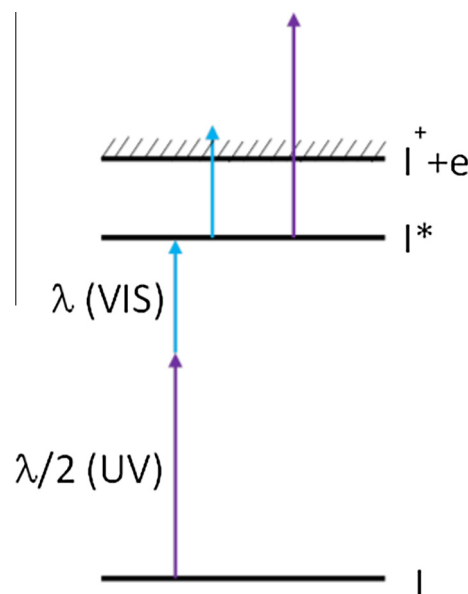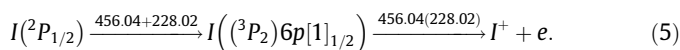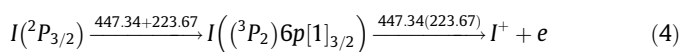

Fig. 1. REMPI scheme applied for I atom detection. Detected states of I atom were I $(^2P_{3/2})$ or $I(^2P_{1/2})$ with corresponding excited states I^* being $I((^3P_2)6p[1]_{3/2})$ and I $((^3P_2)6p[1]_{1/2})$, respectively.

the excited fine state $I(^2P_{1/2})$ to the intermediate state $I\left((^3P_2)6p[1]_{1/2}\right)$ [11]. This excitation with further one-photon ionization is shown below as the processes (4) and (5):

$$I(^2P_{3/2}) \xrightarrow{447.34+223.67} I\left((^3P_2)6p[1]_{3/2}\right) \xrightarrow{447.34(223.67)} I^+ + e \tag{4}$$

$$I(^2P_{1/2}) \xrightarrow{456.04+228.02} I\left((^3P_2)6p[1]_{1/2}\right) \xrightarrow{456.04(228.02)} I^+ + e. \tag{5}$$

3.2. VMI of I atoms arising in photodissociation of I_2

In Fig. 3 velocity map images of photoions I^+ provided by REMPI of $I(^2P_{3/2})$ and $I(^2P_{1/2})$ atoms arising in photodissociation of I_2 are shown. The images observed correspond to photodissociation of I_2 via one-photon excitation by blue radiation of the fundamental of dye laser (VIS).

In the blue region the absorption spectrum of I_2 is provided by overlapping of two continuous bands corresponding to the transitions $B\ ^3\Pi(0_u^+) \leftarrow X\ ^1\Sigma_g^+$ and $C\ ^1\Pi(1_u) \leftarrow X$ [12]. Photodissociation of I_2 in this spectral region proceeds via two channels

$$I_2 + h\nu \rightarrow 2I(^2P_{3/2}), \tag{6}$$

$$I_2 + h\nu \rightarrow I(^2P_{3/2}) + I(^2P_{1/2}) \tag{7}$$

correlating with B and C states, respectively [13]. In the image of I $(^2P_{3/2})$ atoms from Fig. 3a both channels are seen. According to this image ratio of integrals of channels (6) and (7) is equal to $\frac{S_5}{S_4} \approx 5.1 \pm 0.4$. This number fits the ratio $\frac{S_5}{S_4}$ = 5.2 expected on the basis of ratio of absorption cross-sections for transitions to C and B states found to be of 2.6 by Tellinghuisen (see supplementary material to Ref. [12]). Angular anisotropy of recoil directions of channels (6) (anisotropy parameter $\beta = -1.01 \pm 0.04$) and (7) ($\beta = 1.75 \pm 0.09$) giving rise to $I(^2P_{3/2})$ at 447.34 nm in our experiments is close to that observed for photodissociation of I_2 at the nearby wavelength 451.34 nm (see Fig. 10 in Ref. [13]). In Fig. 3b the image of excited fine state $I(^2P_{1/2})$ arising from I_2 is also presented. Its energy corresponds to channel (7) for photodissociation at wavelength 456.04 nm. Anisotropy parameter found
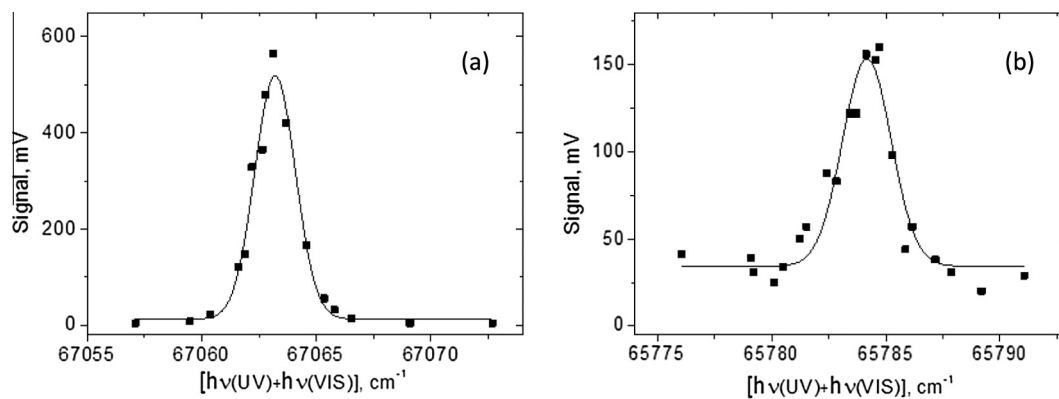
Fig. 2. Spectral profiles with the center at wavelengths (a) – λ_{vac} = 447.34 nm and (b) – λ_{vac} = 456.04 nm for REMPI [(1 + 1′) + 1(1′)] signal of I atoms arising in photodissociation of I_2.

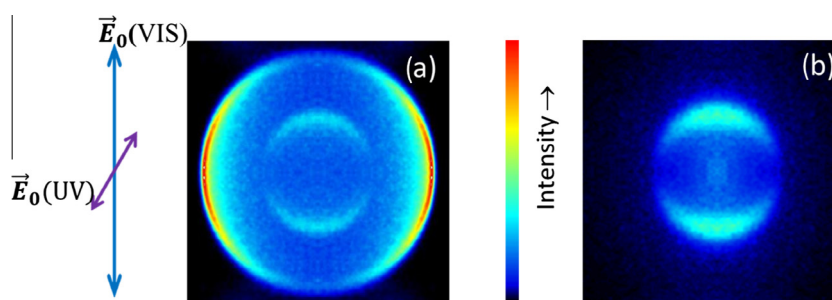**Fig. 3.** Images of (a) – $I(^2P_{3/2})$ and (b) – $I(^2P_{1/2})$ atoms, arising from photodissociation of molecular iodine at wavelengths λ_{vac}(VIS) = 447.34 and 456.04 nm, respectively, probed by REMPI [(1 + 1′) + 1(1′)] with simultaneous use of radiation at wavelengths λ(VIS) and λ/2(UV).

β = 1.47 ± 0.04 is close to that observed for $I(^2P_{3/2})$ appearing in this channel at the nearby wavelength. So the use of VMI with ionization of iodine atoms with REMPI [(1 + 1′) + 1(1′)] gives results coinciding with literature data for photodissociation of I_2 by VIS radiation. We didn't observe any contributions provided by photodissociation of I_2 by UV radiation. This is explained mainly by much weaker absorption of I_2 at UV wavelength (223.67 nm, extinction coefficient $\varepsilon \approx 5$ l mole^{-1} s^{-1} [14]) as compared with VIS wavelength (447.34 nm, extinction coefficient $\varepsilon \approx 70$ l mole^{-1} s^{-1} [12]).

3.3. VMI of I atoms arising in photodissociation of CH_3I and CH_3I-O_2

In Fig. 4 images of $I(^2P_{3/2})$ atoms arising in photodissociation of methyl iodide CH_3I and its complex with oxygen CH_3I-O_2 at 223.67 nm are shown. Excited fine state $I(^2P_{1/2})$ is not revealed in

our experiments at the wavelength of its REMPI [(1 + 1′) + 1(1′)] because it is weaker than the signal of non-resonant two-photon ionization of the ground $I(^2P_{3/2})$ at this wavelength. Parallel quite broad image in Fig. 4a has maximum corresponding to translational energy of $I(^2P_{3/2})$ atom E_t = 0.29 eV. This energy corresponds to a total kinetic energy release (TKER) in a process

$$CH_3I + h\nu \rightarrow CH_3 + I(^2P_{3/2}) \tag{8}$$

to be of TKER = 2.78 eV. Energy and angular distributions of photofragments arising in photodissociation of CH_3I at the nearby wavelength of 225 nm were studied earlier in paper by Hu et al. [15]. These authors used a two-laser experiment with probing of appearing I atoms via REMPI (2 + 1) transitions at wavelengths close to 304 nm. The kinetic energy distribution was obtained with measurement of the time of I^+ ions arriving to the detector. They
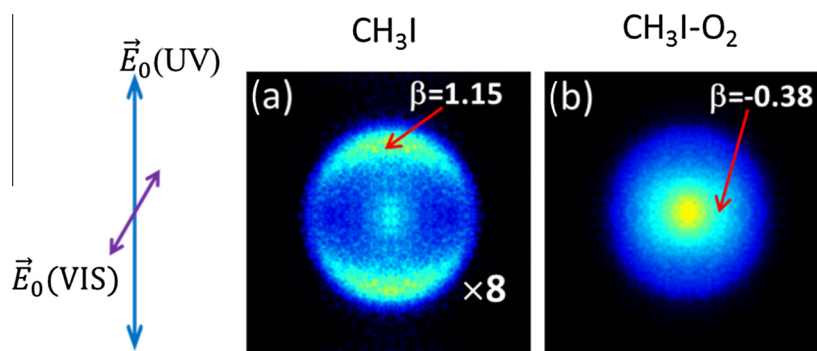

Fig. 4. Velocity map images of $I(^2P_{3/2})$ atoms arising in photodissociation of methyl iodide CH_3I and van der Waals complex CH_3I-O_2 by UV-radiation at wavelength 223.67 nm. Image (a) is obtained with molecular beam generated by expansion of mixture CH_3I(0.125%)-He at the backing pressure P = 5 atm; (b) – mixture CH_3I(0.125%)-O_2(5%)-He at the backing pressure P = 5 atm, in presented image contribution of image (a) is subtracted (see text).

observed a broad kinetic energy distribution for $I(^2P_{3/2})$ atoms indicating excitation of stretching and umbrella modes in CH_3 fragment. Our value of TKER is in agreement with the position of the maximum of the energy distribution at about 2.6–2.7 eV measured by Hu et al. Angular anisotropy $\beta = 1.15$ of the image in Fig. 4a is in accord with presumably parallel character ($\beta = 0.84$) of excitation giving rise to $I(^2P_{3/2})$ found in paper [15]. This parallel character was interpreted to be due to domination of $^3Q_0 \leftarrow X$ transition which is one of three active transitions ($^3Q_0$, $^3Q_1$ and $^1Q_1$) providing A-band of absorption in CH_3I [15]. Lower index corresponds to $\Omega = 0, 1$ (Hund's case (c)). Small spot in the center of image 4a corresponds to formation of slow ions I^+. Formation of slow ions was assigned earlier to be due to photodissociation of photoionized methyl iodide CH_3I^+ [16].

Image 4b is obtained with oxygen added in the expanded mixture. The intensity of this image demonstrates wavelength dependence corresponding to REMPI $[(1 + 1') + 1(1')]$ signal of $I(^2P_{3/2})$. This image doesn't contain the contribution of dissociation of free CH_3I molecules shown in Fig. 4a which was subtracted. The image 4b didn't change qualitatively when backing pressure of expanded mixture was reduced down to 1 atm. We assign image 4b to $I(^2P_{3/2})$ atoms arising in photodissociation of van der Waals complex CH_3I-O_2. Participation of dimers of methyl iodide $(CH_3I)_2$ or higher clusters can be excluded on the basis of investigation of formation of clusters of methyl iodide carried out in paper [17]. Results of that paper show that at currently used very low partial pressure of CH_3I (1–5 Torr) formation of dimers is negligible. Earlier studies of O atoms photogeneration from van der Waals complexes as a function of expanded mixture composition allowed the authors of papers [5,8] to conclude that complexes CH_3I-O_2 and CD_3I-O_2 are the source of complex-specific photochemistry for expanded mixtures with similar content of oxygen.

In Fig. 5 velocity distributions of $I(^2P_{3/2})$ atoms obtained by inversion of images from Fig. 4 are presented. The energy distribution of I atoms arising in photodissociation of the complexes CH_3I-O_2 is shifted as compared with decay of free CH_3I molecules. The higher energy front is shifted by 0.11–0.12 eV to the lower values. Taking into account that I atoms arise in photodissociation of CH_3I molecules we can estimate that TKER of photofragments arising in photodissociation of excited CH_3I molecules provided by excitation of the complex is lower by about 1–1.1 eV than that characteristic for photodissociation of free CH_3I molecules by the same radiation. Excess of photoexcitation energy over thresholds of CH_3I dissociation channels (2) and (3) is released mainly as TKER of the photofragments. Eppink and Parker measured the kinetic energy distribution of I atoms arising in photodissociation of CH_3I excited
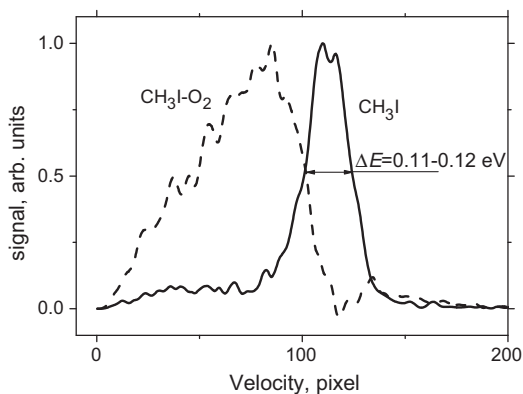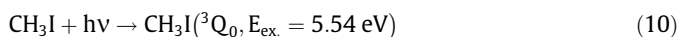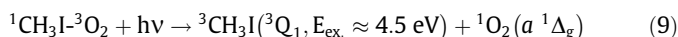
in the spectral range from 240 to 305 nm [9]. Maxima of these distribution profiles correspond to TKER values equal to about 95% of excess energy. Data by Hu et al. obtained in upper discussed experiments at 225 nm [15] indicate TKER values at a level of 85–87% of excess energy. All these data allow us to conclude that shift to lower TKER values by 1–1.1 eV indicates close numbers for a shift in excitation energy of CH_3I for the case of complex CH_3I-O_2 photodissociation as compared with excitation of free molecule. This difference is close to the expected value for the case of excitation of complex via double spin-flip transition (9). In DSF transition excitation of oxygen $a\,^1\Delta_g \leftarrow X\,^3\Sigma_g^-$ giving rise to vibrationally unexcited singlet oxygen takes 0.98 eV. So we should expect excitation level of CH_3I molecule arising in process (9) to be decreased by about 1 eV as compared with excitation of free CH_3I (10) by the same radiation.

$$^1CH_3I\text{-}^3O_2 + h\nu \rightarrow {}^3CH_3I(^3Q_1, E_{ex.} \approx 4.5\ eV) + {}^1O_2(a\,^1\Delta_g) \qquad (9)$$

$$CH_3I + h\nu \rightarrow CH_3I(^3Q_0, E_{ex.} = 5.54\ eV) \qquad (10)$$

Double spin-flip transition (9) gives rise to triplet excited state of CH_3I. Opposite to the excitation of free CH_3I the triplet state generated from the complex is assigned to be $^3Q_1$. The reason is that dissociation of free $CH_3I(^3Q_0$, $E_{ex} = 4.5$ eV ($\lambda \approx 275$ nm)) gives rise mainly to the excited fine state of iodine atom $I(^2P_{1/2})$ [9]. But we don't see appearance of $I(^2P_{1/2})$ in photodecay of the complex. In turn the state $^3Q_1$ correlates with ground $I(^2P_{3/2})$ formation and "vertical" excitation to this state just corresponds to excitation level of about 4.5 eV [18]. Presumably negative anisotropy of angular distribution of appearing $I(^2P_{3/2})$ atoms fits double spin-flip excitation (9) as well. According to the results of *ab initio* calculations there are two most stable configurations of CH_3I-O_2 complex where C—I and O—O bonds are in one plane and oriented perpendicular or at an angle of 35 degrees to each other [19]. With neglecting of CH_3 group structure the first configuration corresponds to point group C_{2v} and the second – to group C_s. Orbital symmetry consideration shows that in C_{2v} structure transition $CH_3I(^3Q_1)$-$O_2(a\,^1\Delta_g) \leftarrow CH_3I(X)$-$O_2(X\,^3\Sigma_g^-)$ is allowed with radiation polarized perpendicular to C—I bond, and for C_s case-perpendicular and parallel to C—I bond. So this transition can provide presumably negative angular anisotropy of I atom recoil directions which is observed in our experiments.

4. Conclusions

Photodissociation of van der Waals complex of methyl iodide with oxygen CH_3I-O_2 has been investigated to test the contribution of the double spin-flip (DSF) transition with change of spin of both complex partners $^1CH_3I$-$^3O_2 + h\nu \rightarrow {}^3CH_3I + {}^1O_2$. Excitation of the complex has been provided by radiation in wavelength region ($h\nu \approx 5.5$ eV) where previously formation of singlet oxygen was observed. DSF transition should provide excitation of both partner molecules with expected excitation of $^3CH_3I$ to the energy level of about 4.5 eV. To determine the excitation energy of the CH_3I kinetic energy of iodine atom $I(^2P_{3/2})$ arising from dissociation of excited CH_3I has been measured. To ionize $I(^2P_{3/2})$ atoms a new scheme of resonance-enhanced multiphoton ionization REMPI $[(1 + 1') + 1(1')]$ has been applied where two colors are provided by fundamental of pulsed dye laser and its second harmonic. This scheme has allowed us simultaneously to excite complex CH_3I-O_2 in spectral region under study and to measure kinetic energy of I atoms in one-laser experiment. Experimentally measured kinetic energy of $I(^2P_{3/2})$ atoms indicates excitation energy of $^3CH_3I$ provided by complex-specific excitation to be lower by 1–1.1 eV as compared with excitation of free CH_3I by the same radiation. This shift corresponds to the energy consumed by excitation of oxygen

Fig. 5. Velocity distribution for $I(^2P_{3/2})$ atoms arising in photodissociation of CH_3I (solid line) and van der Waals complex CH_3I-O_2 (dashed line). Shift in kinetic energy (ΔE) of the high energy wing of $I(^2P_{3/2})$ velocity distribution between two shown profiles is shown by doubled arrow.

into singlet (a $^1\Delta_g$) state and so it is just in agreement with the expected one for the DSF transition in the complex $CH_3I\text{-}O_2$. The observed, presumably negative, angular anisotropy of $I(^2P_{3/2})$ atom recoil directions differs from the positive one for excitation of free CH_3I and is also in agreement with expected one for DSF transition.

Acknowledgement

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