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International Journal of Mass Spectrometry 225 (2003) 249–259
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Multielectron dissociative ionization of CH_3I under strong picosecond laser irradiation

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Received 4 November 2002; accepted 16 December 2002

Abstract

The multielectron dissociative ionization (MEDI) processes of methyl iodide (CH_3I) induced by strong ($I = 10^{15}$ W cm^{-2}) picosecond laser light at 532 and 1064 nm are studied by means of a time-of-flight mass spectrometer. The experimental results are compared to those reported from femtosecond experiments at similar laser intensities. The influence of the laser pulse duration is clearly reflected in the kinetic energy values of the ejected fragments, which were found to be significantly lower in the picosecond experiments. Multiple charged atomic fragments (up to I^{6+}) have been recorded in the mass spectra. It is suggested that the higher charged atomic ions (I^{n+}, $n \geq 3$) are produced by field ionization processes on atomic ions which have been liberated via Coulomb explosion within unstable multiple charged parent ion in the rising time of the laser pulse. The laser intensity thresholds for the appearance of the multiple charged atomic ions have been determined and found to be reasonably close to those predicted by the barrier-suppression ionization model. Nevertheless, the observed variation of the appearance intensity thresholds with the laser wavelengths used implies that there is a contribution to the ionization by electron tunneling processes, especially at 1064 nm.

Keywords: Strong laser fields; Field ionization; Mass spectrometry; Multiply charged ions

1. Introduction

The interaction of strong laser fields (10^{12}–10^{17} W cm^{-2}) with molecules has been the subject of much discussion in recent years. The research in this field is facilitated by the developments in laser technology and the availability of tabletop femtosecond lasers. Nevertheless, picosecond lasers can generate strong laser fields too and the early studies on multielectron dissociative ionization (MEDI) processes were performed in the picosecond time domain [1,2]. The influence of laser pulse duration on the ionization/dissociation processes has been studied in the past, in particular with respect to the abundance of the parent ion production [3–5]. Under strong laser irradiation, the molecular ionization can be induced through multiphoton processes (MPI) and/or field ionization (FI) mechanisms, depending on the laser wavelength and the intensity. For a series of molecules, it is found that in the MPI regime, the parent ion production increases as the laser pulse duration decreases [6–8]. This observation has been attributed to the increased probability of the "ladder climbing" mechanism—compared to that of the "ladder switching"—when femtosecond pulses are used.

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1387-3806/03/$ – see front matter
doi:10.1016/S1387-3806(03)00003-4

At high laser intensities—in particular with infrared lasers—FI mechanisms have an important contribution to the molecular ionization. Contribution from FI processes is expected theoretically for laser intensities where the Keldysh parameter (γ) takes values $\gamma \ll 1$ [9]. Nevertheless, this criterion is not universally valid, since FI characteristic spectral features have been found in experiments with $\gamma > 1$ also [10]. Therefore, it is believed that the description should take into account the molecular structure too [11–14].

Of course, even at high laser intensities (e.g., $\sim 10^{17}\,\mathrm{W\,cm^{-2}}$), the contribution of MPI to the molecular ionization cannot be excluded, especially from the temporal and spatial wings of the focused laser beam. Thus, the multiple electron ejection from the parent molecule under strong laser irradiation is a complex phenomenon and it is related to the molecular structure and the characteristics of the laser pulse (intensity, wavelength, duration, shape).

The removal of several electrons from the molecule leads to the generation of multiple charged—often unstable—ions that undergo Coulomb explosion resulting in multiply charged atomic ions production. The understanding of these processes, known as MEDI, is of great significance, because of their fundamental importance and their close relation with processes such as coherent control, molecular alignment, high harmonic generation, etc.

Methyl iodide (CH_3I) has been extensively studied in the past [15–18] and it is still the subject of many studies in recent years [19–24]. It is known that CH_3I exhibits a broad absorption band in the UV, centered at $\lambda_{max} = 260\,\mathrm{nm}$, which corresponds to a $\sigma^* \leftarrow n$ transition. Three dissociative excited electronic states, designated as $^3Q_0$, $^3Q_1$ and $^1Q_1$ are lying in this region [25]. The $^3Q_0$ state correlates asymptotically to $CH_3 + I(^2P_{1/2})$ while the other two states correlate to $CH_3 + I(^2P_{3/2})$.

Recently, the MEDI processes induced by 50 fs strong ($\sim 10^{16}\,\mathrm{W\,cm^{-2}}$) laser light have been reported by Graham et al. [24]. Multiple charged iodine fragment ions (up to I^{7+}) have been detected and the kinetic energies of the atomic fragments have been investigated. Moreover, the same authors compared their findings with those reported from studies on CH_3I clusters under strong femtosecond laser irradiation by Castelman and coworkers [20,21] and found that the maximum charged state of iodine ions and the kinetic energies of the fragments are higher in the clusters experiments.

In this work the MEDI processes in CH_3I induced by a 35 ps laser ($I \sim 10^{15}\,\mathrm{W\,cm^{-2}}$) are studied by means of a time-of-flight (TOF) mass spectrometer. The motivation for carrying out the present work is to explore the influence of the pulse duration on MEDI processes in CH_3I vis-à-vis the observations of the femtosecond experiments.

2. Experimental

The Nd-YAG picosecond laser system (Quantel YG-901C) used in these experiments produces 35 ps pulses at 1064 and 532 nm with a pulse energy of 80 and 40 mJ, respectively, and a repetition rate of 10 Hz.

A home-built TOF mass spectrometer based on Wiley–Mclaren design, with a 1.4 m long field-free tube was used for ion analysis. The ions that were produced in the molecule–laser interaction region were accelerated by a 12.5 cm long dual stage electrostatic field under a variable potential (0–3000 V). The two field stages were separated by an electrode with a 1 mm pinhole. After acceleration, the ions were focused by an einzel lens electrode, in conjunction with two pairs of parallel plates placed normal to each other, and were detected by a 2.5 cm diameter pair of multichannel plates. The electronic signal was recorded with a LeCroy 9310C digital oscilloscope. The mass resolution was typically 600 at 100 Da.

The vacuum chamber was evacuated by a rotary-backed diffusion pump equipped with a liquid nitrogen trap to ensure an oil-free interaction region. Furthermore, a small turbomolecular pump (Varian Turbo-V70) was used to evacuate the field-free region.

The background pressure of the system was below 10^{-7} Torr, while the molecular vapor was expanded through a needle valve into the interaction region. The

pressure in the chamber was kept below 10^{-6} Torr during the experiments in order to ensure that no space-charge effects were perturbing the mass spectrum measurements. The CH_3I, which was purchased from Aldrich, had a purity better than 99.5% and used after several repeated freeze thaw-degassing cycles under vacuum.

The laser light was focused with a 3.5-cm focal length spherical mirror at about 1 cm from the repeller electrode. Optimum spatial conditions were achieved using an xyz vernier-controlled mechanism attached to the focusing mirror. The polarization of the laser light was arranged with a Brewster angle polarizer and was rotated by using half-wavelength plates at the particular wavelengths of interest. In the present experiments the polarization angle is defined as the angle between the axis of the TOF and the polarization vector of the laser light. The intensities achieved at the focus were also checked through comparison with the intensities needed to produce multiple charged argon ions [26].

3. Results and discussion

In Fig. 1, the mass spectra of CH_3I, recorded at 532 and 1064 nm, are presented. As mentioned above, the excited states $^3Q_0$, $^3Q_1$ and $^1Q_1$, which are optically accessible from the ground state, are dissociative, leading to the production of CH_3 and I fragments. These states can be reached through absorption of two (532 nm) or four (1064 nm) photons, while more photons are needed for molecular ionization (IE = 9.54 eV).

The recorded mass spectra, at first glance, could be attributed to fragmentation (at the dissociative electronic levels of the neutral molecule) which is followed by ionization. On the contrary, El-Sayed and coworkers [15] have shown that the multiphoton ionization dissociation (i.e., ionization followed by dissociation) is the dominant mechanism involved in the ionization/dissociation processes in the CH_3I, when this molecule is irradiated by picosecond laser pulses (30 ps at 266 nm).

Our experiments at lower laser intensities with picosecond and nanosecond laser pulses (not presented) confirm the above interpretation. Therefore, the recorded mass spectra should be attributed to above ionization dissociation processes.

As it is shown in Fig. 1, the parent ion peak ($m/z = 142$) was clearly recorded in the mass spectra. Furthermore, multiple charged atomic ions have been also observed, while there is no spectral peak that could be assigned to a multiply charged molecular ion.

In the inset of Fig. 1, the spectral area around the I^{2+} ($m/z = 63.5$) ion is shown. The peak profiles have a complex structure. This observation is valid for all ionic fragments recorded and is attributed to the detection of ions ejected initially away and towards the detector.

In strong field femtosecond experiments, the observation of such ion peak profiles is considered as evidence of Coulomb explosion that is taking place within a multiply charged unstable precursor. Nevertheless, ion peaks with such profiles have been recorded in the mass spectra induced by low intensity picosecond and nanosecond lasers. Actually, this is the case for molecules with dissociation time much smaller than their rotational period. In these molecules, the excess energy goes into kinetic energy of the fragments, which have an anisotropic spatial distribution (depending on the laser polarization), and their detection results in complex ion peak profiles.

Since the dissociation of CH_3I (~166 fs [19]) is much smaller than the rotational period (~1 ps), the observed peak profiles do not a priori imply that a Coulomb explosion process is involved, because the recorded profiles for the highly charged atomic fragments could arise from multiphoton excitation of fragments ejected in the backwards and forward direction. In order to have more insight, the kinetic energies (E_{kin}) of the fragments have been calculated. The E_{kin} of the fragments can be estimated from the time separation between the backward and forward components of the ion peak according to the formula

$$E_{kin}\,(\mathrm{eV}) = 9.65 \times 10^{-7}\,\frac{\Delta t^2 n^2 F^2}{8m}$$

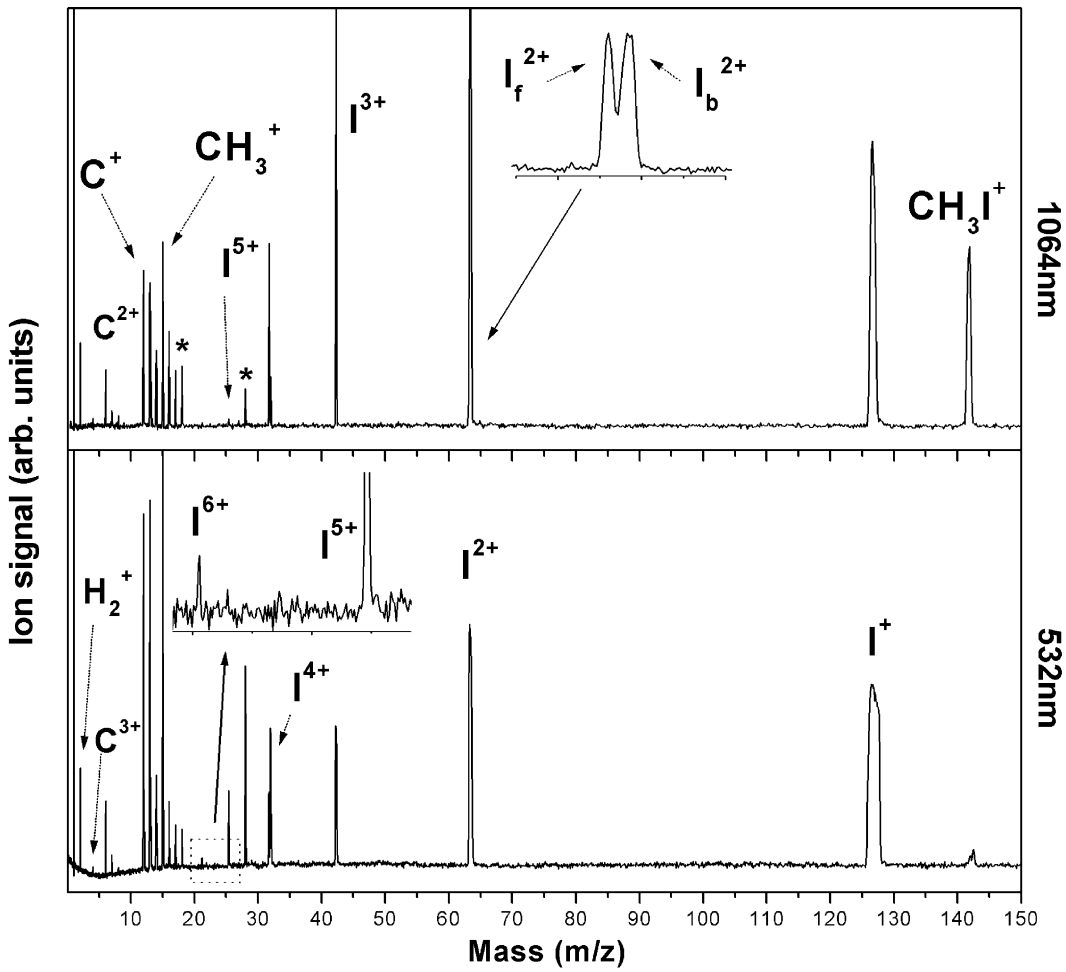

Fig. 1. The mass spectra of CH_3I recorded at 1064 ($I = 1.5 \times 10^{15}\,W\,cm^{-2}$) and 532 nm ($I = 5.8 \times 10^{15}\,W\,cm^{-2}$). The insert in the mass spectra recorded at 1064 nm shows the complex peak profile of I^{2+} ions (the $I_f{}^{2+}$ and $I_b{}^{2+}$ in the inset denote the forward and backward component of the I^{2+} ion peak). The stars denote impurities from H_2O and N_2.

where Δt represents the time difference in nanosecond between the split mass peaks, F is the static electric field for ion extraction in $V\,cm^{-1}$, n is the charge, and m the mass in amu of the fragment.

The time intervals between the two peak components have been measured from mass spectra recorded with low acceleration field ($F = 150\,V\,cm^{-1}$) while the Einzel lens was switched off. The calculated values for the E_{kin} of the ion fragments are shown in Table 1 and the quoted error margins are determined by the sampling capabilities of the digital oscilloscope used.

As expected from momentum conservation, the E_{kin} values of $CH_3{}^+$ are higher than those corresponding to I^{n+}. But on the other hand, all E_{kin} values (Table 1) are an order of magnitude higher than those observed by El-Sayed and coworkers and those predicted by Franklin's approximate formula which is based on a statistical dissociation model. Assuming that the transfer of energy between the oscillators in the activated state is much faster than the dissociation into products so that the oscillators reach energy equilibrium, Haney and Franklin have shown that the average

Table 1
Estimated kinetic energy values (in eV) of the fragment ions which have been recorded at $I = 10^{15}\,\mathrm{W\,cm^{-2}}$ (1064 nm)

λ (nm)	I^+	I^{2+}	I^{3+}	I^{5+}	CH_3^+	C^+	C^{2+}	H^+
1064[a]	0.42 ± 0.06	0.9 ± 0.2	0.5 ± 0.2	0.5 ± 0.3	2.2 ± 0.4	2.3 ± 0.5	3 ± 1	1.0 ± 0.8
532[a]	0.42 ± 0.04	0.42 ± 0.08	0.4 ± 0.1	0.2 ± 0.1	1.0 ± 0.2	1.2 ± 0.2	1.7 ± 0.5	1.9 ± 0.9
266[b]	0.05 ± 0.03				0.2 ± 0.1			
795[c]		91	205					
795[d]	34.8	120	239	524		117	330	
Franklin's formula prediction[e]	0.04				0.22			
	0.04				0.43			
	0.06							

[a] This work.
[b] From [15].
[c] From [24].
[d] From [21].
[e] From [27].

kinetic energy of a fragment ion is given by [27]

$$E_{\mathrm{kin}} = \left(\frac{m}{m_{\mathrm{p}}}\right)\left(\frac{3kT}{2}\right) + \left(\frac{m_{\mathrm{n}}}{m_{\mathrm{p}}}\right)\left(\frac{E^*}{N'}\right)$$

where m, m_{p}, m_{n} are the masses of the fragment ion, the parent ion and the corresponding neutral fragment, respectively, T is the temperature, k is Boltzman's constant, E^* is the excess energy above the threshold for fragment formation, and N' is the number of effective oscillations (∼0.44 times the $(3N - 6)$ vibrations).

Moreover, E_{kin} values for I^{2+} at 1064 nm were found to be higher than those of I^+ ions, which implies that I^{2+} were not generated by further excitation of I^+ fragments ejected from the parent ion during the rising time of the laser pulse. Therefore, the Coulomb explosion mechanism within a multiple charged unstable precursor should be invoked. This precursor should be a transient multiple charged parent ion. It should be mentioned that stable multiple charged parent ions have not been observed even under femtosecond irradiation [24].

In Table 1, the E_{kin} values reported by femtosecond experiments on CH_3I [24] and on CH_3I clusters [21] are also presented. As it can be seen, there is a huge difference between these values and those estimated by the present work. By applying proper voltages on the ion-optics, the acceptance volume of the TOF spectrometer was increased to such a value that ions of high kinetic energies ($E_{\mathrm{kin}} \geq 50$ eV) could be detected. Nevertheless, no signal corresponding to such ions has been recorded.

Since our picosecond experiments were performed under similar laser intensities (∼$10^{15}\,\mathrm{W\,cm^{-2}}$) with those used in the femtosecond ones, the differences in E_{kin} values imply that the pulse duration affects dramatically the ionization/dissociation processes.

It is believed that, under strong femtosecond laser irradiation, highly charged transient parent ions are generated, which fragment because of the strong repulsive Coulomb forces, thus producing highly charged atomic ions. The kinetic energies of these atomic ions depend also on the elongation of the molecular skeleton prior the explosion. For polyatomic molecules it has been reported that the molecular elongation becomes smaller as the charged state of the ion increases [28,29]. For diatomic molecules it has been found that the dissociation takes place at R_{cr} distances, which are almost twice the length of the molecular bond in the equilibrium [30–32].

In the present case, therefore, the reduced E_{kin} values, with respect to those from femtosecond experiments, suggest that the Coulomb explosion is taking place within relatively lower charged molecular ions and/or the molecular elongation prior the dissociation is larger.

The stretch of the C–I bond prior to the explosion can be estimated from the formula

$$E_{Cb}\,(\text{eV}) = 14.4\frac{pq}{r}$$

where r (Å) is the distance between the charges p and q of the fragments and E_{Cb} is the total kinetic energy [33].

Calculations using the above relation have been made assuming two point charges, localized on the CH_3 group and the I atom. Albeit this assumption is inadequate and a charge distribution should be used, it can provide a first-order semiquantative approximation of the length of the C–I bond prior the dissociation.

From the kinetic energies measured for I^+ and $CH_3{}^+$ at 532 nm the C–I bond for the doubly charged parent ion (P^{2+}) prior to explosion was estimated to be $r = 10 \pm 2$ Å, which is almost five times longer than the molecular bond in equilibrium.

The kinetic energies for the $CH_3{}^+$ and I^{2+} ions at 1064 nm were found to be higher than those measured from the 532 nm spectra suggesting that the former ions were generated by explosion of a higher charged unstable, P^{3+}, parent ion. Using the same formula the distance r in this case was estimated to be once again ∼10 Å. Nevertheless, if it is assumed that the I^{2+} ions at 532 nm were also produced from explosion of P^{3+} ions, then the E_{kin} values suggest a much longer (20 ± 4 Å) stretching of the C–I bond which implies that the parent ion had reached the separated atom limit. It should be mentioned that the laser pulse duration (35 ps) is long enough to allow large molecular elongation to take place even before the peak laser power is reached, which can also be supported by the estimated velocity (∼12 Å ps^{-1}) of the ejected I^{2+}.

E_{kin} values for the I^{n+} ($n \geq 3$) ions were found to be not higher from those of I^{2+} ions. This is different from the experience gathered from femtosecond experiments, where the higher kinetic energy values have been measured for the higher charged ionic species. Obviously, the generation of the I^{n+} ($n \geq 3$) ions cannot be attributed to Coulomb explosion within higher charged ($n \geq 3$) parent ions, since in that case higher E_{kin} are expected.

The estimated r and E_{kin} values for the I^{n+} ($n \geq 3$) ions indicate thus that these ions were produced by further excitation of the iodine atomic ions liberated from the molecule in the rising time of the laser pulse.

From the spectra presented in Fig. 1, it can been seen that multiple charged atomic ions have been detected. For the carbon atomic ions the highest charged state observed is $n = 3$ (C^{3+}, $m/z = 4$), while for iodine atoms is $n = 6$ (I^{6+}, $m/z = 21.17$).

In order to explore the ionization mechanism, involved in the molecular and atomic ion production, the power dependence of the ionic signal has been studied. In Table 2 the ionization energies (IE) for the observed iodine atomic ions and the number of photons needed for their production by MPI processes are shown.

The first striking observation from the comparison of the mass spectra recorded at the same intensity ($I = 10^{15}$ W cm^{-2}) for the two wavelengths used is that the parent ion abundance is higher in the 1064 nm mass spectra. This implies that at these laser intensities, at least for the 1064 nm, the dominant ionization mechanism for the parent molecule could be not MPI, but FI process (tunneling and/or barrier-suppression ionization (BSI)). It should be noted that the Keldysh parameter was smaller than 1 for both wavelengths used, but as it is known, the FI mechanisms are favored at the longer wavelengths.

Such an interpretation is in agreement with the relatively higher E_{kin} of the I^{2+} ions measured in the 1064 nm spectra, since the multiple ionization of the CH_3I, the generation of P^{3+}, for instance, is more probable in this wavelength.

From the power dependence plots (Fig. 2), the intensity thresholds for the appearance of I^{n+} ($n \geq 3$) have been determined (Table 2). A general remark is that the trend of the threshold intensities for the I^{n+} ($n \geq 3$) ions is not consistent with that expected for MPI processes, since they are found to be higher at 532 nm. This suggests that FI mechanisms are involved in ion production.

Atoms in strong laser fields can undergo BSI and the intensity thresholds for the appearance of the multiple

Table 2
Ionization energy and number of photons required for the production of multiple iodine ions by MPI processes. The intensity threshold values predicted by the BSI model and those determined by the present work are also depicted.

	λ (nm)	I^{3+}	I^{4+}	I^{5+}	I^{6+}
Ionization energy (eV)[a]		32.20	44.01	55.32	78.84
Number of photons required for the production of the ions by MPI	532 1064	14 28	20 39	24 48	35 69
Intensity thresholds according to the BSI model (10^{14} W cm^{-2})		4.6	9.4	15	43
Experimental intensity threshold values for linear polarized light (10^{14} W cm^{-2})	532 1064	1.7 ± 0.3 1.7 ± 0.1	6.3 ± 0.4 3.7 ± 0.1	15 ± 1 9.9 ± 0.3	42 ± 3 13.4 ± 0.6
Experimental intensity threshold values for circular polarized light (10^{14} W cm^{-2})	532 1064	5.9 ± 0.3 2.8 ± 0.1	15.3 ± 0.8 5.5 ± 0.4	32.7 ± 0.8 11.7 ± 0.4	– –

[a] From [21].

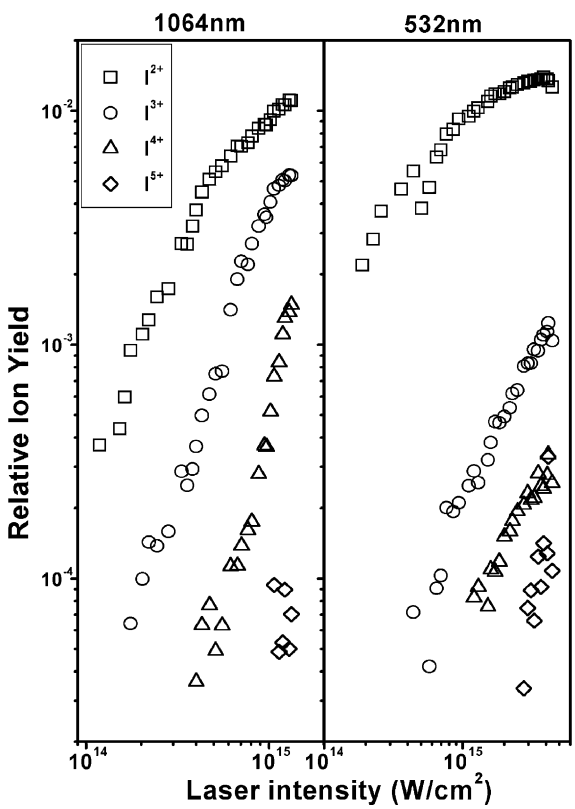

Fig. 2. The intensity dependence of the multiple charged iodine ions yield for linear polarized laser light.

charged ions can be predicted by the simple formula suggested by Auguste et al.

$$I\,(\mathrm{W\,cm^{-2}}) = 4 \times 10^{9}\,\frac{E_i^4}{z^2}$$

where E_i is the ionization energy (eV) of the atom (ion) and z is the ionic charge state [34]. The calculated intensity thresholds according to this model are given in Table 2. It can be seen that these values are close to those determined from the present experiments. Nevertheless, the experimental intensity threshold values raise questions. If the ionization, for both wavelengths used, was due to a pure BSI mechanism, then the appearance thresholds should be the same, since the BSI predictions are wavelength independent. But obviously this is not the case.

In order to gain more information, the mass spectra at 532 and 1064 nm have been recorded using circularly polarized laser light. It should be noted that I^{6+} ions were impossible to be detected in these spectra even at the higher laser intensities used ($I \sim 6 \times 10^{15}$ W cm^{-2}) in the present work. Fig. 3 shows the dependence of the ionic signal on laser intensity, for circularly polarized light. In the BSI model, the ionization threshold intensities depend only on the electric field amplitude which implies that the intensity thresholds for a circularly polarized beam are expected to be twice those obtained using linear polarization.

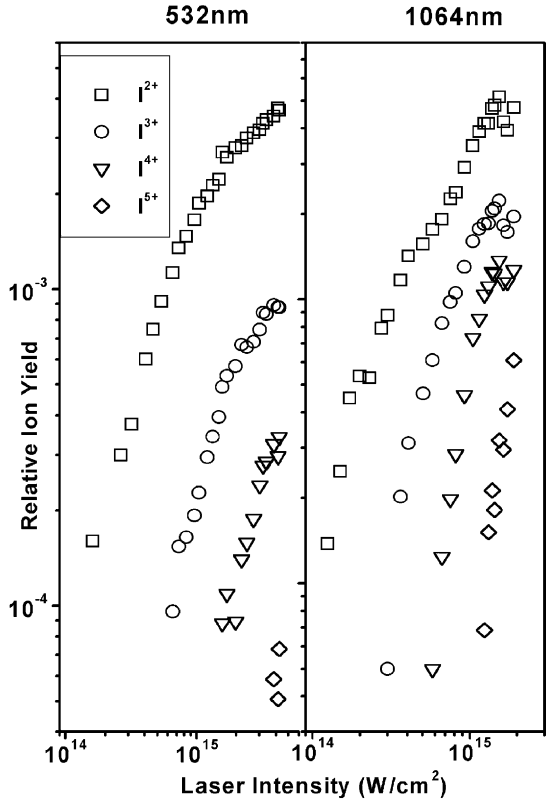

Fig. 3. The intensity dependence of the multiple charged iodine ions yield for circular polarized laser light.

The experimental laser intensity thresholds for the appearance of the I^{n+} ($n \geq 3$) ions, although were found to be higher, they are not twice (at least for all the ionic species) than those determined by using linear polarization. In particular for the I^{n+} ($n = 4, 5$) the discrepancy were found to be significant.

The relatively lower appearance thresholds at 1064 nm, could imply a contribution from another FI mechanism, i.e., tunneling ionization. It is known, that tunneling ionization is facilitated in longer wavelengths (longer optical cycle). Thus, it is reasonable to assume that, especially at 1064 nm, ionization occurs via tunneling at laser intensities lower than those required for the total suppression of the atomic barrier (BSI mechanism). The observed increase of the laser intensity thresholds with circularly polarized light is expected since the tunneling rate is dependent on the laser polarization and it is lower for circularly polarized light [35].

However, the BSI process cannot be categorically excluded as a plausible ionization mechanism at 532 nm. For linear laser polarization the intensity threshold values for I^{n+} ($n = 4$–6) ions are in reasonable agreement with those predicted by the BSI model. Moreover, under circular polarized laser irradiation the intensity threshold values, especially for I^{n+} ($n = 4, 5$) ions, are twice—within the experimental error—those obtained using linear polarization. Therefore, it is believed that the I^{n+} ($n \geq 3$) ions are most probably generated via different ionization mechanisms at these two wavelengths and that the contribution, if any, of electron tunneling ionization is relatively limited at 532 nm.

As far as the production of the I^{+} and I^{2+} ions is concerned, it should be noted that they were detected in all mass spectra even at the lower laser intensities used. Thus, the contribution of MPI processes, especially from the spatial and temporal wings of the focused laser beam cannot be excluded.

Further insight for the ionization processes involved can be gained from the dependence of the ionic signal on the laser polarization. Fig. 4 shows the mass spectra recorded at 1064 nm ($I = 10^{15}\,\mathrm{W\,cm^{-2}}$), for parallel and vertical laser polarization with respect to the TOF axis.

In the mass spectra recorded with vertical polarization only one ion peak component is appearing, while the complex peak structure (corresponding to backward and forward ion ejection) were detected when horizontal polarization was used. The spectra of Fig. 4 were recorded by adjusting the ion optic voltages in a manner that restricts the acceptance volume of the TOF spectrometer. The estimated acceptance angle by computer simulation was about 30° for ions having $E_{\mathrm{kin}} = 0.5\,\mathrm{eV}$. The spectral resolution facilitates the distinction of ions produced with small kinetic energy (SKE; the peaks recorded with vertical laser polarization) from those ejected backwards—towards the detector with $E_{\mathrm{kin}} \sim 0.5\,\mathrm{eV}$ (parallel polarization).

The origin of the peak components corresponding to ions ejected towards and away from the detector

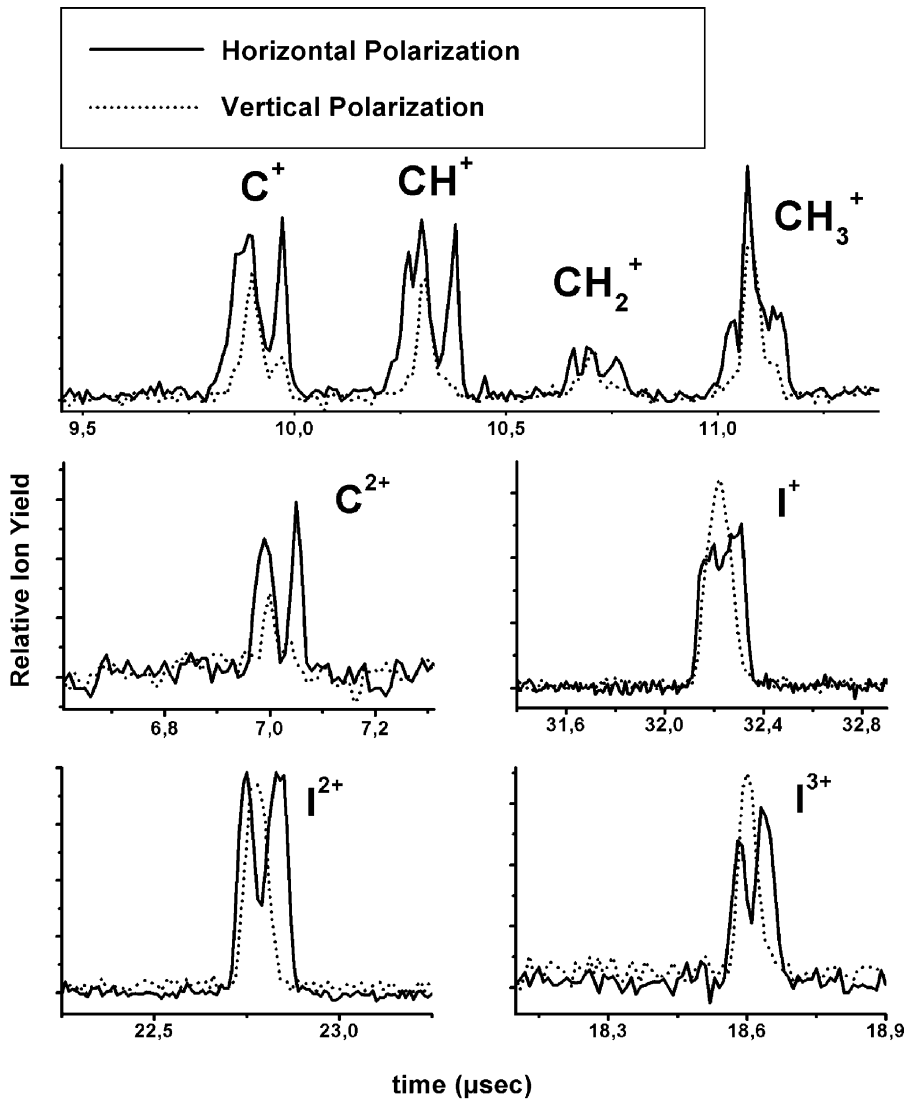

Fig. 4. The peak profiles of CH_3I fragment ions recorded at $I = 10^{15}\,W\,cm^{-2}$ (1064 nm) with horizontal and vertical linear laser polarization.

can be attributed to fragments liberated by Coulomb explosion. As far as the SKE ions are concerned, it is believed that these ions are produced by MPI processes. The fact that the corresponding to SKE ion peaks are decreasing for the higher charged atomic ions (for $n \geq 3$) supports such an explanation. In Fig. 4, it seems that the abundance of the SKE I^{3+} ions is not reduced compared to that observed for the I^{2+} ions. This is attributed to the fact that the acceptance angle for the I^{3+} ions is about 1.5 times larger than the one for I^{2+}, as it has been found by computer simulations.

The observation of SKE could also account for the decrease, with increasing ion charge, of the isotropic component appearing in the angular distribution measurements reported in femtosecond strong field experiments by Graham et al. [24]. The isotropic component of the angular distributions of the I^{n+} ($n \leq 6$) atomic

ions is attributed to soft fragmentation of a singly charged parent CH_3I^+ producing low kinetic energy ions. These ions, in addition to the high kinetic energy ones arising from higher charged parent molecules, have increased probability to be detected, resulting in more isotropic angular distributions. It has also been proposed, in the case of the dynamic alignment of molecules with the laser polarization axis, that the decrease of the isotropic component could be attributed to the torque exerted on the molecules by the laser electric field. This torque becomes stronger for higher charged parent molecules which thus tend to align more efficiently with the field, producing fragments with narrower angular distributions and vanishing isotropic components as their charge state increases [32,36]. The observations of the present work offer a complementary explanation for the decrease of the isotropic component in the angular distribution of multiple charged species.

4. Conclusions

The irradiation of CH_3I with strong ($\sim 10^{15}$ W cm^{-2}) 35 ps laser pulses at 532 and 1064 nm results in MEDI of this molecule. Highly charged atomic ions appear in the mass spectra and their charged states are slightly lower than those reported from 50 fs experiments performed under slightly higher laser intensities. The main difference between the present and the 50 fs experiments [24] has to do with the kinetic energy values of the ejected ionic fragments and reflects the influence of the pulse duration on the MEDI processes. In the femtosecond experiments, it is believed that the multiple charged atomic ions are generated by a Coulomb explosion mechanism that takes place in even higher multiple charged parent ions. For the present picosecond experiments, it is proposed that the ions (with charged state $n \geq 3$) are produced mainly by field ionization of ions ejected, in the rising time of the laser pulse, from unstable multiple charged parent ions via Coulomb explosion. The laser intensity thresholds for the appearance of these ions support the field ionization rather than the MPI processes.

Acknowledgements

We would like to express our thanks to the Central Laser Facility of the University of Ioannina, where the experiments have been performed. We also thank Dr. A. Lyras for useful discussions.

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