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Multielectron dissociative ionization of CH_3I clusters under moderate intensity ps laser irradiation

G. Karras, C. Kosmidis*

Atomic and Molecular Physics Laboratory, Department of Physics, University of Ioannina, University Campus, GR-45110 Ioannina, Greece

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ABSTRACT

The interaction of 35 ps laser pulses with methyl iodide clusters in the intensity region of 10^{12}–3×10^{13} W/cm^2 is studied at $\lambda = 266$, 532 and 1064 nm by means of time-of-flight mass spectrometry. At $\lambda = 532$ and 1064 nm the multielectron dissociative ionization (MEDI) of clusters results in highly charged atomic fragment (up to I^{7+}) ion production of high kinetic energy. The explosion of the multiple charged cluster ions is found to be isotropic, while an asymmetric charge distribution prior to their fragmentation is observed. Moreover, negative ion formation is observed. The MEDI of clusters exhibits a dependence on laser polarization and the intensity thresholds for the observation of the fragment ions are determined for linear and circular laser polarization. These intensity thresholds are found to be about three orders of magnitude lower than those reported by experiments with 35 ps laser pulses on CH_3I monomers.

For the observed MEDI of $(CH_3I)_n$ clusters a mechanism is proposed. According to this mechanism, the clusters are initially single ionized by multiphoton absorption and an internal electric field is created within the cluster, which distorts the potential barriers. This distortion increases the probability for electron tunneling even at relatively low laser intensities, giving thus rise to the formation of negatively charged moieties within the clusters, which prevent the cluster elongation and facile further the tunneling process. This procedure results in a higher distortion of the internal barriers and an increased ionization of the clusters, which, due to increased repulsive forces, finally fragment leading to multiple charged high kinetic energy fragment ion production.

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1. Introduction

The interaction of strong laser beams with clusters is a topic of significant research activity over the last years. This interest is related to the fact that clusters can be thought of as an intermediate step between gas and condensed matter. Nevertheless, the laser–cluster interaction results in some experimental observations that are interesting in their own right. The ejection of multiple charged ion fragments with high kinetic energy from molecular clusters has been repeatedly reported, while no such ions were observed, when the same molecular species (monomers) were irradiated under the same laser conditions [1–11]. Different mechanisms have been proposed for the interpretation of the interaction of fs laser pulses' with atomic and molecular clusters [12–20]. Due to the complexity of this kind of interaction the majority of the published work is dealing with atomic clusters and mainly those consisted of noble atoms.

Recently there have been some publications concerning the interaction of molecular clusters with ns laser pulses at relatively low intensities (10^9–10^{12} W/cm^2) which report the observation of multiple charged fragment ions ejected with high kinetic energies. At a first glance these observations seem unexpected, since the laser intensity is at least two orders of magnitude lower than that typically needed for multiple molecular ionization leading to fragment ion production via Coulomb explosion.

Multielectron dissociative ionization (MEDI) of clusters under relatively low laser intensities have been reported for species like NH_3, CS_2, CH_3I and benzene [8–11,21,22]. Two main mechanisms have been proposed for their interpretation.

The first one is that of Inverse Bremsstrahlung Scattering (IBS) which originally was proposed by Ditmire et al. for the case of atomic clusters under strong laser field irradiation [16]. Luo and co-workers [10] have attributed their experimental findings in the case of $(CH_3I)_n$ and $(NH_3)_n$ clusters (at 10^{10}–10^{12} W/cm^2) to this mechanism.

On the other hand, Sharma et al. [8] have reported on MEDI from $(CH_3I)_n$ using an 8 ns laser at $\sim 5 \times 10^9$ W/cm^2. They have suggested that the IBS model is inadequate and a plausible mechanism is that of «energy pooling» or excitation annihilation interactions.

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* Corresponding author. Tel.: +30 26510 08537; fax: +30 26510 08695.
E-mail addresses: kkosmid@uoi.gr, kkosmid@cc.uoi.gr (C. Kosmidis).

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It is of importance to note that they have found a dependence of MEDI on the laser wavelength and that the resonant excitation to a highly excited electronic state enhances the MEDI of methyl iodide clusters. The idea of «energy pooling» mechanism has been used extensively in various fields of Physics and Chemistry. One characteristic case is that of MALDI (Matrix Assisted Laser Desorption Ionization) where the ejection of molecular ions [23,24] and atomic fragments with significant kinetic energy [25] have been reported.

It is clear from the above that the multiple charged ion ejection from molecular clusters at relative low laser intensities (10^9–10^{13} W/cm^2) is not a well understood phenomenon and the methyl iodide clusters seem to be a case study.

Our group have reported on the interaction of CH_3I monomers with strong ($\geq 10^{14}$ W/cm^2) 35 ps and 50 fs laser pulses [26,27]. We found that although the multiple charged states of the released atomic ions are similar, the involved ionization mechanism is different when the laser pulse duration varies. Excitation of CH_3I monomers at the A band ($\sim$4.6 eV) with ns laser pulses is known to result in molecular dissociation and the released neutral fragments can be ionized by further photon absorption from the same laser pulse [28,29]. When ps laser pulses are used for the excitation to the same electronic state, it has been shown that the molecular dissociation proceeds mainly after the molecular ionization (ionization followed by dissociation) [30] although, the dissociation from neutral states cannot be excluded.

The interaction of $(CH_3I)_n$ clusters with ps pulses at low laser intensity (<10^{13} W/cm^2) has been studied extensively. Syage and Steadman [31] have reported on the dissociation/ionization of methyl iodide clusters induced by a 18 ps laser at 266 nm but no multiple charged fragments have been observed for the laser intensity used in their experiments.

In the present work the interaction of $(CH_3I)_n$ clusters with 35 ps laser pulses in the intensity region of 10^{12}–3×10^{13} W/cm^2 is reported. The mass spectra have been recorded at three laser wavelengths and their dependence on laser polarization is explored. The aim of the present work is to explore the possibility for multiple charged ion production from $(CH_3I)_n$ clusters at lower laser intensity than the intensity thresholds determined previously from the interaction of ps pulses with CH_3I monomers. Moreover, we study the dependence of MEDI on laser parameters (wavelength, intensity, polarization) in order to elucidate the associated mechanism involved.

2. Experimental details

The time-of-flight mass spectrometer (TOF-MS) used in the experiments is a Wiley–McLaren setup with a 1.4 m field free region. High vacuum conditions are met by the combined use of a turbo molecular pump (100 l/s), evacuating the field free region of the TOF, and a diffusion pump (2400 l/s), pumping the interaction chamber and equipped with a liquid nitrogen trap which kept the stagnation pressure below 10^{-7} Torr.

Two different molecular beam arrangements are feasible with this setup. One provides an effusive beam of gas at room temperature along the time-of-flight axis using a needle valve and the other provides a supersonic molecular beam perpendicular to the flight axis, which is produced via the expansion through a pulsed valve. The pulsed valve (General Valve Corp, Iota One) has a 750 μm diameter orifice and is operated at 10 Hz with a pulse duration of 185 μs. The time delay between the pulsed valve and the laser beam was controlled by a digital delay generator (DG535, Stanford Research). During the jet operation the stagnation pressure inside the chamber was approximately 2×10^{-6} Torr.

The gas mixture was prepared inside a bubbler using liquid methyl iodide of high purity (Fluka purity > 99.5%) at room temperature although in some experiments the vapor pressure of the liquid sample was reduced by using a slush bath of ice and methanol/ethanol. He was used as a carrier gas, with the valve backing pressure held at 2 bars. The expanding molecular beam entered the interaction region where a homogeneous electric field of 690 V/cm was applied by two circular electrodes, the repeller and the extractor. The produced ions passed in the field free region through a 1 mm diameter hole on the extractor. This results in a decrease of the acceptance angle of the TOF system, but increases the angular resolution for the polarization dependence measurements. The jet pulse is intersected perpendicularly by the laser beam, approximately 7 cm downstream from the orifice of the pulsed valve. The ionic signal, produced by the laser–matter interaction, was detected by a chevron type micro channel plate detector (Photonics, G10-10SE) and the resulting electronic signal was recorded with an Agilent 54830B (600 MHz, 4 Gs/s) digital oscilloscope.

Laser pulses were provided by an Nd:YAG mode locked laser (Quantel YG-901C), operating at 10 Hz and producing 35 ps pulses at 1064, 532 and 266 nm with a pulse energy of 80, 40 and 11 mJ, respectively. The laser beam had a 7 mm diameter and was focused inside the vacuum chamber by a 50 cm focal length lens. The energy of the output beam was controlled by using a Brewster angle polarizer and a half wave plate, while polarization control was achieved by inserting half and quarter wave plates specific to each wavelength used. The intensities achieved at the focus were also checked through comparison with the intensities needed to produce multiple charged argon ions [32].

3. Results and discussion

In Fig. 1 the mass spectra of CH_3I seeded in a He supersonic jet, recorded at 266 nm for various delays between the laser beam and the valve's opening, is presented. It is clear that the production of cluster ions $(CH_3I)_n{}^+$ is dependent on the delay between the laser pulse and the valve's opening. The experimental conditions (delay time, CH_3I concentration in the expanded gas mixture) have been adjusted in order to maximize the cluster ion signal. Ion peaks of $(CH_3I)_n{}^+$ up to $n = 4$ and cluster ion fragmentation have been observed. It is worth mentioning the observation of an ion peak that is attributed to the molecular iodine ($I_2{}^+$) ion, which is indicative of molecular formation within clusters under laser excitation [33,34]. The observation of ions $(CH_3I)_n{}^+$ up to $n = 4$ does not necessarily imply that this is the maximum cluster size existing in the molecular beam. Under similar experimental conditions the formation of slightly bigger clusters ($n = 5$) has been reported [35]. The absence of cluster ions with $n \geq 5$ from Fig. 1 can be attributed to the small acceptance angle of the TOF used (there is a small orifice with $2R = 1$ mm in the first ion optic and the length of the field free region is 1.4 m) and the laser intensity region covert in the present experiments (10^{12}–3×10^{13} W/cm^2).

We observed that by reducing the laser intensity the abundance of the $(CH_3I)_n{}^+$ ions and especially those corresponding to $n = 4$ increased, which implies that at laser intensities >10^{11} W/cm^2 the ionization of the heavier clusters is followed by dissociation. For the determination of the maximum cluster size of noble atoms produced via a supersonic expansion the Hagena formula is frequently used [36]. Nevertheless, this formula is not applicable in this case, as explained by Sharma and Vatsa [37], because under the present conditions the resultant cluster size depends on the saturated vapour pressure of CH_3I in the He carrier gas.

The mass spectra at 532 nm have been also recorded under the expansion conditions for which the maximum cluster ion signal was observed at 266 nm irradiation (Fig. 2) but cluster ion peaks

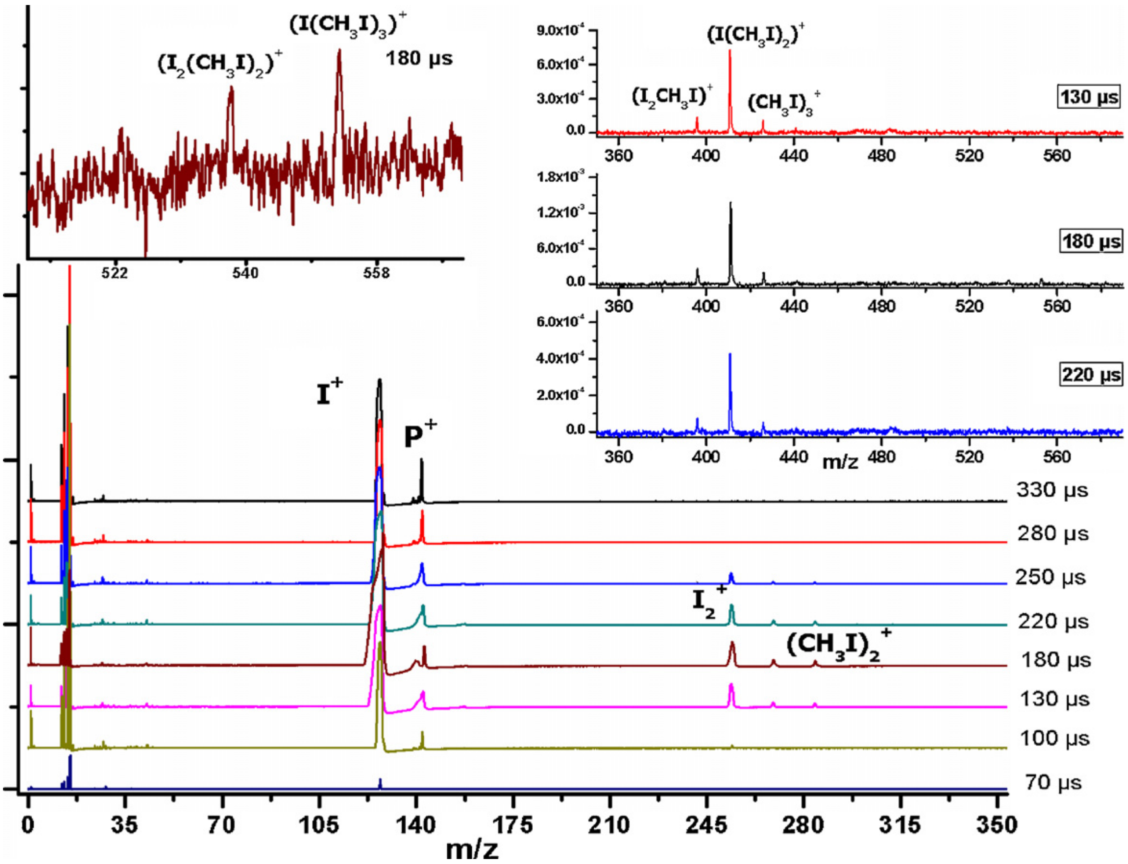

Fig. 1. Mass spectra of (CH_3I) clusters recorded at 266 nm ($I = 3.3 \times 10^{12}$ W/cm^2) for various delays between laser beam and valve opening.

are not observed there. Instead, ion peaks attributed to atomic fragment ions (up to I^{5+}) have been clearly recorded and their appearance is related to the laser intensity. Their intensity thresholds have been determined by recording the mass spectra at various laser intensities. The intensity threshold (I_{th}) is defined as the lower laser intensity where the particular ion has been clearly detected. Obviously these I_{th} values are closely related to the specific TOF mass spectrometer used (by increasing the collection efficiency of

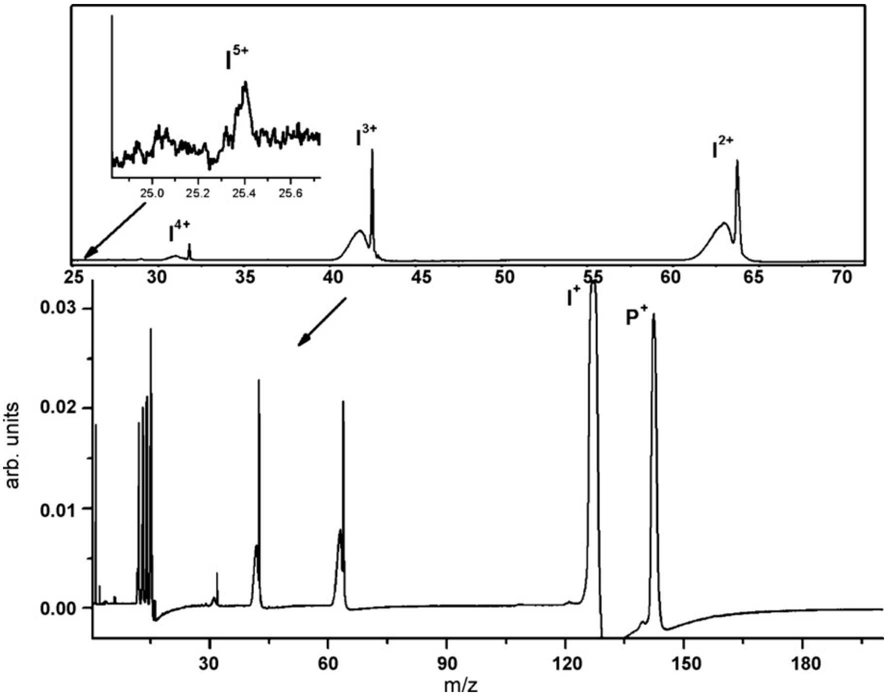

Fig. 2. Mass spectra of (CH_3I) clusters recorded at 532 nm ($I = 5 \times 10^{12}$ W/cm^2) under the expansion conditions for which the 266 nm excitation gives maximum cluster ion signal.

the spectrometer lower I_{th} values are expected) and they should be thought of as an upper limit for the true intensity thresholds.

Nevertheless they are of importance, since they can be compared to those determined for the case of the interaction of CH_3I monomers with 35 ps laser pulses using the same experimental set up [26]. These determined I_{th} values for the various atomic ions are presented in Table 1.

From the values presented in Table 1 it is obvious that the cluster I_{th} values are about three orders of magnitude smaller from those in the monomer experiments. The same trend for the laser intensity threshold values of atomic iodine ions has been observed for the interaction of CH_3I clusters and monomers with strong fs laser irradiation ~10^{15} W/cm^2, according to Refs. [5] and [27].

Some interesting points arise from the comparison of the presented mass spectra at 532 nm with ps and those reported for ns laser pulses. Specifically, atomic fragments I^{n+} with $n > 3$ have not been recorded in the ns spectra, while carbon ions up to C^{3+} have been observed. In the ps mass spectra I^{5+} ions have been identified, while the maximum charge multiplicity for carbon ions is $n = 2$ (C^{2+}). Also the I_{th} values for I^{n+} ($n = 1–3$) are determined to be about 30 times smaller in the ns experiments compared to those found in the present work [11].

As far as the kinetic energies of the ejected multiple charged atomic ions are concerned their calculation is based on the time separation between the back and the forward component of each peak (insert in Fig. 2) by using the equation [3]:

$$E_{\text{kin}}(\text{eV}) = 9.65 \times 10^{-7} \cdot \frac{\Delta t^2(\text{ns}) \cdot z^2 \cdot E_o{}^2(\text{V/cm}^2)}{8 \cdot m(\text{au})}$$

We have used the same method and TOF system in the past for the determination of the E_{kin} of the ejected fragment ions from CH_3I monomers, thus the comparison with the estimated E_{kin} values for the released ions from CH_3I clusters is straightforward. Contrary to that reported for the interaction of CH_3I monomers with 35 ps laser pulses, in the present case the kinetic energy of the ejected atomic ions increases with their charged state. Specifically, in the monomer experiments the highly charged ions were generated by further ionization of the I^{2+} ions released from the dissociation – via Coulomb explosion – of the doubly (and/or triply) charged parent ion molecule. Therefore the I^{n+} ions with $n > 2$ were detected to have essentially the same kinetic energy with that of I^{2+}. In the present case the parallel increase of the charge and the kinetic energy of the atomic fragment ions (I^{n+}, C^{m+}) indicates that these ions are direct products of Coulomb explosion taking place within the clusters. Thus, it is reasonable to conclude that the clusters are reaching higher multiple charged states prior to their fragmentation and at lower laser intensity compared to the monomer case.

The determined kinetic energies for the atomic ions, for laser polarization parallel to the time-of-flight axis, are presented in Table 2. These values could be slightly overestimated due to space charge effects. Nevertheless, they lie in between those reported by ns experiments although they are closer to the ones presented by Sharma et al. [8]. The observed differences should be attributed to the higher charged states reached by the unstable precursors in the present experiments, as indicated by the appearance of I^{n+} ($n = 4$, 5) ions which are absent in the ns mass spectra.

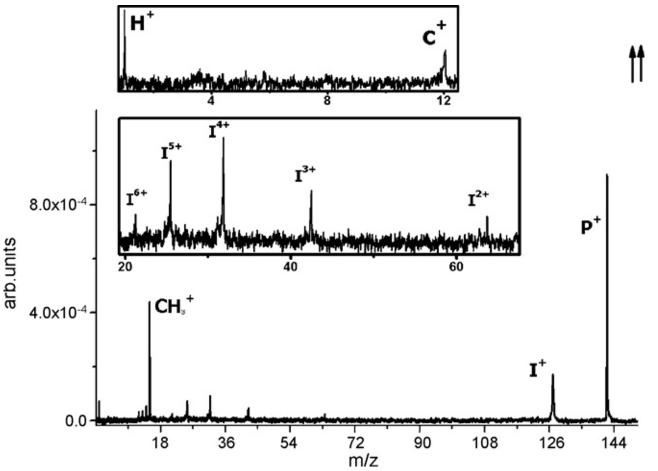

Fig. 3. TOF mass spectra of methyl iodide clusters induced at 1064 nm ($I = 3.3 \times 10^{12}$ W/cm^2). From the insets charge asymmetric distribution prior to cluster fragmentation is implied. Laser polarization is parallel to the TOF axis.

In order to gain more insight for the mechanism involved in the ionization/dissociation processes of the clusters the dependence on laser polarization has been studied by changing the polarization axis of the linearly polarized laser beam with respect to the TOF axis. Despite the small orifice on the first ion optic and the high kinetic energies of the ejected ions no variation in the mass spectra has been observed in contrast to the ejection anisotropy observed for the case of CH_3I monomer at comparable conditions of irradiation [38]. This implies an isotropic explosion of the multiple charged cluster ions. Furthermore, we performed experiments with a circularly polarized beam at various laser intensities. An increase of the I_{th} values has been observed in this case but this is smaller than that reported for the monomer case, where an (optical) field ionization mechanism (Barrier Suppression Ionization (BSI) and tunneling) was involved in the highly charged ion generation. The I_{th} values for the circularly polarized laser beam are presented in Table 1.

The mass spectra recorded at 1064 nm, under the same expansion conditions, are depicted in Figs. 3 and 4. As in the 532 nm case, no cluster ion peaks have been detected. The charge multiplicity for the iodine ions is higher (I^{7+}), but no signal corresponding to C^{3+} has been recorded. It should be noted that the ionization energy for the I^{7+} is 92.35 eV while for C^{3+} is 47.89 eV. Thus it seems that an anisotropic charge distribution exists prior to cluster dissociation. One remarkable difference with the 532 nm experiments is that it was impossible to determine the I_{th} values for the various atomic

Table 1
Intensity thresholds for multiple charged atomic fragments.

Wavelength	Polarization	I^{2+}	I^{3+}	I^{4+}	I^{5+}	C^{2+}
Clusters						
1064 nm	Linear	<3.3 ± 0.1	<3.3 ± 0.1	<3.3 ± 0.1	<3.3 ± 0.1	4.3 ± 0.1
	Circular	<4.4 ± 0.3	<4.4 ± 0.3	<4.4 ± 0.3	<4.4 ± 0.3	6.7 ± 0.4
532 nm	Linear	1.6 ± 0.3	1.7 ± 0.3	2.9 ± 0.3	4.1 ± 0.3	2.3 ± 0.3
	Circular	1.9 ± 0.3	2.1 ± 0.3	3.2 ± 0.3	5.3 ± 0.3	2.7 ± 0.3
Monomers						
1064 nm(26)	Linear	<0.1 ± 0.01	1.7 ± 0.1	3.7 ± 0.1	9.9 ± 0.3	<0.1 ± 0.01
	Circular	1.9 ± 0.1	2.8 ± 0.1	5.5 ± 0.4	11.7 ± 0.4	10 ± 0.4
532 nm(26)	Linear	<0.76 ± 0.02	1.7 ± 0.3	6.3 ± 0.4	15 ± 1	7.8 ± 0.
	Circular	2.5 ± 0.3	5.9 ± 0.3	15.3 ± 0.8	32.7 ± 0.8	14 ± 0.8

For the cluster ions produced at 532 and 1064 nm the units are ×10^{12} W/cm^2 and for the monomers they are ×10^{14} W/cm^2.

Table 2
KER (eV) of multiple charged fragment ions.

Wavelength (nm)	Intensity (W/cm^2)	I^{2+}	I^{3+}	I^{4+}	I^{5+}	I^{6+}	C^{2+}
1064	4×10^{12}	7.5 ± 0.2	82.2 ± 4.3	210 ± 25	420 ± 80	723 ± 230	110 ± 18
532	3.5×10^{12}	6.1 ± 0.1	48.7 ± 2.1	150 ± 15			103 ± 17
532[a]	10^{11}	9.5	27				55.5
532[b]	5.1×10^{9}	114 ± 12	376 ± 25				115 ± 30

[a,b] From experiments with (CH_3I) clusters using ns laser pulses [8,11].

fragment ions because all the multiple charged ions were generated at the same laser intensity. At a laser intensity of 2.5×10^{12} W/cm^2 the mass spectra consisted of only two ion peaks, those corresponding to $(CH_3)^+$ and $(CH_3I)^+$ ions. As the laser intensity increased to 3.3×10^{12} W/cm^2 multiple charged species (up to I^{7+} and to C^{2+}) started to appear in the mass spectra with the peak intensity distribution of the I^{n+} fragment ions at $n = 5$. The dependence of the mass spectra features on the laser intensity and the delay between the valve opening and the laser beam was the same as that reported previously for the monomer case (i.e., well resolved I_{th} values for the various multiple charged ions).

Moreover, we found that the I_{th} exhibits a dependence on laser polarization (Fig. 4). For circularly polarized beam the I_{th} for this abrupt multiple ionization of clusters is increased to 4.4×10^{12} W/cm^2 and the maximum of the ion peak distribution is slightly shifted to a lower charged state (I^{4+}). It should be noted that, in order to observe the I^{7+} ion with circular polarization the laser intensity had to be increased up to 5×10^{12} W/cm^2.

The kinetic energy of the fragment ions released at 1064 nm experiments are presented in Table 2. The kinetic energy values reported from other experiments are also included for comparison reasons.

In summary, the interaction of 532 and 1064 nm, 35 ps laser pulses at 1×10^{12}–3×10^{13} W/cm^2 with CH_3I clusters leads to the production of multiple charged fragment ions:

- with higher kinetic energies compared to those estimated from the mass spectra of the CH_3I monomers, while the corresponding I_{th} values are much lower;
- the explosion of the cluster ions is isotropic and abrupt (1064 nm);
- there is an asymmetric charge distribution prior to cluster fragmentation;
- there is a deviation in the kinetic energies of the fragment ions and the charge distribution within clusters prior to their fragmentation from the corresponding values of ns laser experiments.

Multiple charged ion fragments are typically the product of strong laser beam (>10^{14} W/cm^2) interaction with matter, they have been reported for the monomer [27] and the CH_3I clusters [5,6] and they have been attributed to (optical) field ionization, i.e., processes like tunneling and BSI, which require a laser electric field comparable to the internal molecular (atomic) field. A commonly used criterion then is that of the adiabatic Keldysh parameter γ: $\gamma < 1$ ($\gamma = (I_p/2U_p)^{1/2}$, where I_p is the molecular ionization energy and U_p is the ponderomotive energy ($U_p = 9.33 \times 10^{-14} \times I$ (W/cm^2) $\times \lambda^2$ (μm)). This approach cannot be strictly applied to the molecular case [39]. The γ value for the present experiments at 532 nm is estimated to be $\gamma \sim 5$, while at 1064 nm and for the intensity where the abrupt explosion is taking place with linear polarization, is $\gamma \sim 3$. These γ values do not exclude *a priori* the involvement of field ionization processes, especially for extended systems like clusters. Nevertheless, the estimated laser intensity for the production by BSI for instance of I^{6+} ions, seen at both wavelengths used, is about 4×10^{14} W/cm^2, i.e., two orders of magnitude greater than the intensities used in the present work. Although it is known that BSI model predictions are overestimated for atomic multiple charged ions production released from molecular fragmentation, the difference of two orders of magnitude in the laser intensity is too large to be ignored. Thus, although the field ionization mechanism cannot be excluded, it is clear that this is not the only mechanism involved.

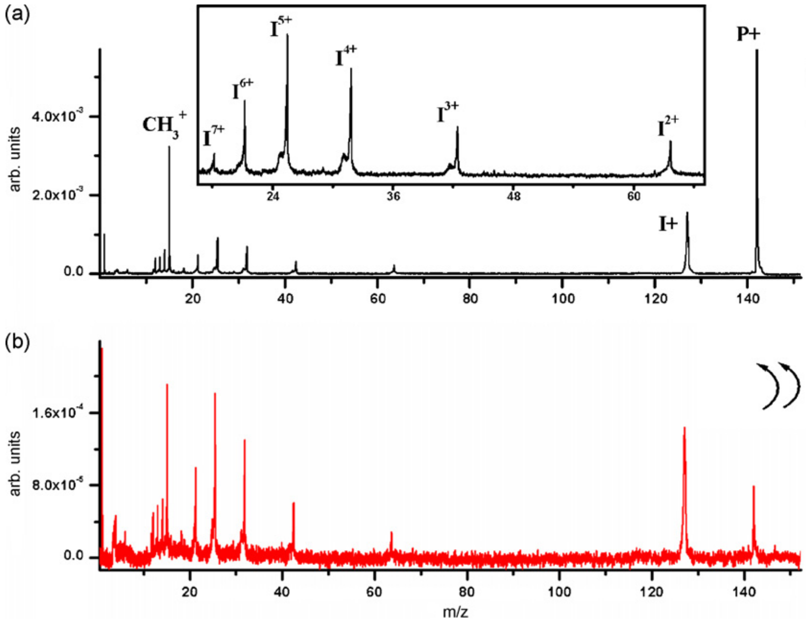

Fig. 4. TOF mass spectra of methyl iodide clusters induced at 1064 nm ($I = 5 \times 10^{12}$ W/cm^2). (a) Laser polarization parallel to the TOF axis and (b) circular laser polarization.

For the interpretation of the multiple charged ion generation from molecular clusters, at relatively low laser intensity, two other mechanisms have been proposed.

Initially, the MEDI of clusters by ns laser pulses was attributed to the IBS mechanism [10]. Recently, Sharma et al. [8] have shown in a comprehensive manner, that for the interpretation of the ns laser experimental findings the IBS model is inadequate. At least the required atom densities in the clusters are far from those available in these experiments. These authors have attributed the MEDI to an ‘energy pooling’ mechanism [24]. Moreover, by changing the wavelength of the ns laser they observed an increase of MEDI, when resonant excitation to the C state was involved in the multiphoton ionization process.

At this point we would like to comment on the way the laser-cluster interaction is described. Frequently, this interaction is methodologically approached by assuming that at first the light couples to the monomers as if they were isolated, i.e., the cluster environment does not have an effect. This interaction leads to monomer excitation and/or ionization and the created ions result in cluster expansion [19]. We believe that this approach cannot have a universal applicability, especially when long (ps and ns) laser pulses are used. For instance, it is worth to be discussed the case of the $(CH_3I)_n$ clusters interaction with a laser beam at 266 nm. In the mass spectra presented in (Fig. 1) the appearance of the $(CH_3I)_n^+$ ion peaks is evident. The ionization of $(CH_3I)_n$ $(n = 2–4)$ at 266 nm can be induced by a two photon absorption since their I_p are 9.19 ± 0.05, 9.07 ± 0.1 and 9.38 ± 0.15 eV, respectively [40]. At the same time, the monomer ionization is impossible to take place by two photon absorption ($I_p = 9.54$ eV). This difference could be of importance since the three photon monomer ionization requires higher laser intensity and during the rise time of the laser pulse towards this intensity the clusters have already been ionized which obviously affects the whole process.

For reasons of completeness it is mentioned that the one photon absorption at 266 nm by the clusters lying within the valence A band which origin is the $n \rightarrow \sigma^*$ transition of the monomer and it is expected to be slightly shifted in energy position due to the van der Waals interactions in clusters. This band is known to be dissociative but under ps excitation at these laser intensities, it is believed that dissociation is ‘suppressed’ while the ‘pumping up’ rate to ionization increases in comparison to that reported from ns laser experiments. This reason could also account for the differences between the mass spectra at 532 nm reported by Sharma et al. [8] and those presented in this work.

The single cluster ionization seems to trigger the whole MEDI process. In all models proposed for the cluster’s multiple ionization it is assumed that the released electrons remain within the cluster (caged). The question arising at this point is related to the role of the iodine atoms which exist in the molecular skeleton of the monomers. Snyder et al. [2] in their work on the multiple charged krypton ions production from clusters reported that these species were observed ‘only when a trace amount’ of HI was present in the interaction region of the laser and the atomic cluster beam. More recently, Sharma and Vatsa [41] found that iodine containing molecules show an increase of the multiple charged ion production. It seems reasonable to relate this ‘contribution’ of I atoms to its high electron affinity (295 kJ/mole). Thus, we performed experiments under the same experimental conditions in order to explore the probability (if any) of negative ion production during the laser–cluster interaction. In Fig. 5 the recorded mass spectra at 1064 nm are presented at various delays between the laser pulse and the valve opening. The respective mass spectra at 266 and 532 nm are very similar. It is clear that the abundance of the recorded negative ions, as the delay varies, is following a similar trend to that of clusters. From the analysis of the mass spectra the main peaks are attributed to H^- and I^- negative ions. Smaller peaks corresponding to $C_xH_y^-$ $(x = 1, 2$ and $y = 1, 2)$ have also been recorded. Similar peaks have been reported by Krishnakumar and Nagesha in the negative ion mass spectra of CH_3I [42]. A detailed analysis of the negative ion mass spectra will be presented in a forthcoming paper. For the present work their formation in the laser–cluster interaction is very helpful for the understanding of the cluster ion stability. As stated above, the experimental findings about the kinetic energy of the atomic multiple charged fragment ions are indicating that these ions are the direct product of Coulomb explosion taking place within the clusters. Thus, the detection of negative ions and the implicit attractive electrostatic forces with the positive charged ions offer a reasonable explanation for the stability of the multiple charged clusters, especially for the abrupt explosion recorded at 1064 nm.

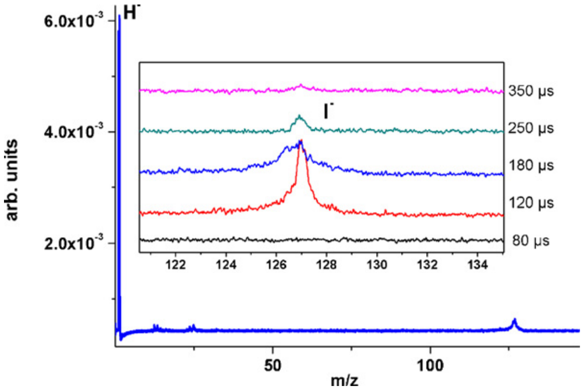

Fig. 5. Negative ion TOF mass spectra of (CH_3I) clusters induced at 1064 nm ($I = 1.6 \times 10^{13}$ W/cm^2). The inset presents the dependence of iodide anion to the delay between the laser pulse and the valve opening.

The distribution of the formed negatively charged moieties within the clusters is not obvious. It has been proposed, for the case of iodine containing molecular cluster that the negative ion is more probable to be on the surface of the cluster [43]. Moreover, for the case of CH_3I clusters, it has been proposed that the arrangement of the monomers within the cluster ionic states is a Head to Head (HH) geometry, while in the ground state of the neutral cluster the Head to Tail (HT) configuration seems to be energetically favored [44]. The time scale for this rearrangement is estimated to be about 1 ps. Therefore the description of charge distribution within clusters is not, by any means, trivial.

In order to unroll Ariadni’s thread, the single charged cluster ionization should be considered first. At 532 nm this ionization is achieved by a four photon absorption, which is supported well enough by the slope of 3.3 ± 0.1 the parent ion signal (CH_3I^+) versus the laser intensity (Fig. 6). The electron ejection from the cluster

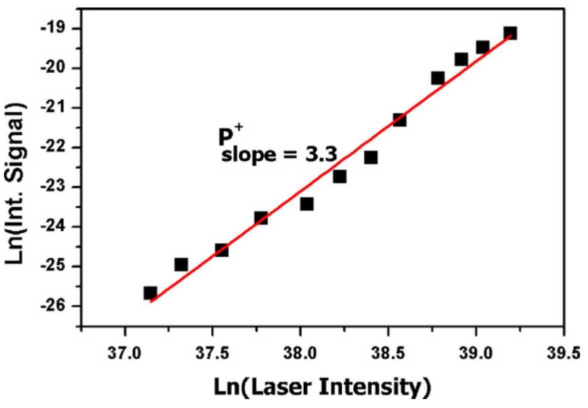

Fig. 6. Laser intensity dependence of the P^+ ion at 532 nm.

creates an excess of one positive charge and the emergence of an internal field which as pointed out by Last and Jortner [17,18] is of crucial significance. This internal field affects the potential barriers within the cluster. Ito et al. [45] have estimated the distances between monomers in a $(CH_3I)_4$ tetramer to be between 4.19 and 4.41 Å. At these distances the electric field created by a positive charge is about 8×10^9 V/m. This is quite a strong field and the corresponding laser intensity for the creation of an equivalent electric field can be estimated by the expression:

$$E\,(\mathrm{V/cm}) = 27.4\sqrt{I\,(\mathrm{W/cm^2})}$$

which gives $I \sim 8.5 \times 10^{12}$ W/cm^2. Clearly this laser intensity is higher than that used in the present experiments (the I_{thr} for the I^{5+}, which was the ion with the highest charge multiplicity, was found to be less than half this value). Obviously, the existence of this internal field diversifies cluster ionization from that of monomers in gas phase.

The strength of this internal field seems insufficient to lead to further ionization of the cluster by BSI. The laser intensity threshold for single ionization of a monomer by BSI is estimated to be slightly higher than 3×10^{13} W/cm^2. It can be argued that the I_{thr} is overestimated by the BSI model. Nevertheless, it is found experimentally that, in order to record multiple charged atomic ion fragments, the laser intensity should be increased, which implies that the role of the laser beam does not expire with the creation of the singly charged cluster ion. On the contrary, it seems that the MEDI of the cluster is a result of the created internal field and the applied laser beam.

After its single ionization, the cluster starts to expand and at the same time the internal potential barriers are distorted due to the existence of the internal field. Although the laser intensity is not strong enough for BSI, ionization can be induced by the laser beam through tunneling processes. The probability for tunneling ionization is increased due to the distortion of the barriers within the cluster. This approach is reasonable and compatible with the observation that the determined I_{thr} for the circularly polarized laser beam experiments were found to be higher than those with linear polarization. The fact that the I_{thr} for the circularly polarized beam are not twice those determined for linear polarization – as expected by the theory – is attributed to the involvement of the internal field, i.e., it is not the case of a purely tunneling ionization process.

The liberated electron via tunneling is expected to be released with negligible kinetic energy. Thus, the probability for electron attachment increases. It is known that the electron attachment of CH_3I is dissociative [46] and leads to the cleavage of the C–I bond

$$CH_3I + e^- \rightarrow CH_3 + I^-$$

Similarly, for the case of the methyl iodide clusters, the reaction expected to take place is:

$$(CH_3I)_n + e^- \rightarrow CH_3 + I^-(CH_3I)_{n-1}$$

The above reactions could explain the experimental findings of Fig. 5.

The appearance of negatively charged moieties within the clusters prevents their expansion and somehow temporally stabilizes the charged cluster ions. This is of importance because in a doubly charged cluster ion the repulsive forces are strong enough causing an elongation of the cluster and thus a decrease of the internal field. In the present experiments especially, assuming a Gaussian temporal distribution for the 35 ps laser pulses used, the time interval between the intensity needed for single cluster ionization and the peak laser intensity (where the multiple charged fragment ions have been recorded) is estimated to be more than 6 ps. Within this time interval, if the presence of negative ions is ignored, significant elongation of the cluster configuration could take place, minimizing thus the contribution of the internal field.

The resultant new charge distribution, after the ejection of two electrons, modifies even more drastically the potential barriers within the cluster. Therefore, the multiple ionization is facilitated and it is achieved at much lower laser intensity than those typically reported from experiments in gas phase. As a consequence of the multiple ionization, the repulsion between the positive charges increases and dominates over the attractive forces, resulting thus in the cluster fragmentation (Coulomb explosion).

At 1064 nm the multiphoton ionization of clusters is a higher order process (8 photons). Therefore, single ionization, in the case of a non-resonant process, is expected to take place at a higher laser intensity compared to that at 532 nm. The significance of the involvement of a real state resonance in the ionization process of CH_3I clusters has been discussed by Sharma et al. [8]. In their ns mass spectra recorded at 640 nm the MEDI features were clearly observed in contrast to that at 532 nm. We referred to the 640 nm case, because the three photon excitation at this wavelength coincides though with the five photon excitation at 1064 nm and thus the resonance MPI at 1064 nm cannot be excluded. But, because of the already mentioned abrupt explosive fragmentation at 1064 nm, it is impossible to plot the signal abundance versus the laser intensity for the determination of the slope and the participation (or not) of a resonant state in the multiphoton ionization process is unresolved. In any case, single ionization at 1064 nm is observed at laser intensity similar to that at 532 nm. By slightly increasing the laser intensity to $\sim 3.3 \times 10^{12}$ W/cm^2 the abrupt explosion of the cluster takes place and multiple charged atomic fragment ions (up to I^{6+}) have been recorded.

The intensity threshold for the observation of the above process with circularly polarized beam was found to be higher ($\sim 4.2 \times 10^{12}$ W/cm^2). This is in agreement with the proposed participation of the tunneling process in the cluster MEDI. Moreover, the fact that the I_{thr} for I^{5+} in 532 nm experiments with linear polarized beam was found to be higher ($\sim 4.1 \times 10^{12}$ W/cm^2), is, once again, indicative of the participation of an internal tunneling ionization mechanism in MEDI of clusters, since the duration of the optical field is longer at 1064 nm facilitating thus the electron penetration through the distorted (by the internal field) potential barriers.

The above approach also accounts for the observed higher KER of the atomic ion fragments, given in Table 2, at 1064 nm as compared to those determined at 532 nm experiments, since higher charged states for the unstable precursors can be reached at the former wavelength.

As far as the asymmetric charge distribution (CAD) of the atomic fragment ions is concerned we would like to mention that such results have been also reported previously in experiments under strong laser field irradiation and for the case of I_2 and alkyl halides among others [47,48]. The possibility for multi-electron excitation has been described by Mulliken [49]. In the case of molecular interaction with strong laser fields this observation has been attributed to the relation between the pulse duration, the time needed for the molecular bond elongation (towards the critical distance (R_{cr}) where enhanced ionization is taking place) and the dissociation lifetime [50].

In the present experiments the pulse duration is long but, as explained above, the elongation is not a prerequisite for the MEDI of the clusters.

Furthermore, especially for the methyl iodide case, the efficient multiple ejection of electrons from the atomic iodine could well be conceptualized by taking into account the asymmetric structure of the Highest Occupied Molecular Orbital (HOMO) of CH_3I. It has been shown by *ab initio* calculations that the HOMO is a strongly asymmetric π-MO with the larger part of its wave function covering the I-atom side. Ohmura et al. [48] have shown that, when an asymmetric laser field is used, the electrons are more likely to be removed from the large-amplitude part of the HOMO. In the present experiments no such asymmetric laser field has been used, but the internal field within the cluster ions could be asymmetric. Of course, the observation of CAD in molecules like the I_2 indicates that the existence of an asymmetric HOMO is not a prerequisite for CAD. The contribution, if any, of the asymmetric π-MO to the recorded CAD could be checked by measuring, under the same experimental conditions, the TOF mass spectra of similar molecules like CH_3Cl and CH_3Br, where the HOMO presents smaller anisotropy.

4. Conclusions

The interaction of $(CH_3I)_n$ clusters with moderate intensity (10^{12}–3×10^{13} W/cm^2) 35 ps laser pulses is reported. These clusters are formed in a supersonic molecular beam and their formation, up to tetramers, is confirmed by spectral features in the 266 nm mass spectra. MEDI of $(CH_3I)_n$ clusters has been observed at 532 and 1064 nm, under the same expansion conditions. To the best of our knowledge, MEDI of $(CH_3I)_n$ clusters induced by ps laser pulses in this intensity region is reported for the first time.

MEDI results in multiple charged fragment ion production (up to I^{7+} and C^{2+}) with high kinetic energy. The comparison with the ps experiments on methyl iodide monomers reveals that the intensity thresholds for the observation of the multiple charged atomic fragment ions is about three orders of magnitude lower in the case of ps cluster experiments, while their kinetic energy is found to be about two orders of magnitude higher. Clearly, different mechanisms are involved in the MEDI processes for monomers and clusters.

In the present work, the I_{th} for the fragment atomic ions is found to be higher for experiments performed with circularly polarized laser light than those determined from experiments under linearly polarized laser irradiation. This is an indication that an optical field ionization process is involved. The increase in the I_{th} values for the circularly polarized laser experiments is not that expected by the theory (factor of two) for the case of a purely optical field ionization process (BSI, tunnelling). These is reasonable, because it is known that for the purely field ionization it is required a laser intensity orders of magnitude higher than that used in the present work. Therefore, another process has to be involved, which is in cooperation with the optical field ionization. It is proposed that this process is related to the internal electrical field created within the cluster after its single ionization. Initially, the clusters are ionized by multiphoton absorption (four photons at 532 nm and eight photons at 1064 nm) since their dissociation from the intermediate the neutral manifold (A band) is relatively small, compared to that in ns experiments, because the shorter laser pulse used for the excitation increases the 'pumping up' rate.

After the single ionization, an internal field is created within the clusters which is strong enough ($\sim 8 \times 10^9$ V/m) to distort the internal potential barriers. This distortion increases the probability for electron tunnelling even at the relatively low laser intensities used. The electrons liberated by tunnelling are expected to have small kinetic energy which facilitates the formation of negative moieties within the clusters. The formation of negative ions has been verified experimentally. The co-existence of positive and negative charges within the cluster prevents its elongation. This is of importance for the resumption of the laser induced tunneling process. This procedure results in higher distortion of internal barriers and finally the multiple ionization of clusters. Due to the increased repulsive forces, the created multiple charged clusters fragment, leading to multiple charged atomic fragment ion production. The ejected fragments are expected to be released with high kinetic energy, because of the strong repulsion within clusters ions (high charge and small cluster elongation).

The charge distribution within cluster prior to the fragmentation, is found to be asymmetric because the recorded I^{7+} ion has an ionization energy (IE) of 92.35 eV while C^{3+} and C^{4+}, which are absent from the mass spectra, have an IE of 47.89 and 64.49 eV, respectively. Similar observations have been reported previously and they have been attributed to the relation between the pulse duration, the time needed for the molecular bond elongation and the dissociation lifetime.

The observed CAD in the present experiments seems to be significant and the influence (or not) on CAD of the spatial distribution of the molecular wave function could be explored by performing experiments with clusters consisting of monomers with no such extended anisotropy.

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References

[1] J. Purnell, E.M. Snyder, S. Wei, A.W. Castleman Jr., Chem. Phys. Lett. 229 (1994) 333.
[2] E.M. Snyder, S.A. Buzza, A.W. Castleman Jr., Phys. Rev. Lett. 77 (1996) 3347.
[3] E.M. Snyder, S. Wei, J. Purnell, S.A. Buzza, A.W. Castleman Jr., Chem. Phys. Lett. 248 (1996) 1.
[4] A.W. Castleman Jr., K.H. Bowen Jr., J. Phys. Chem. 100 (1996) 12911.
[5] J.V. Ford, Q. Zhong, L. Poth, A.W. Castleman Jr., J. Chem. Phys. 110 (1999) 6257.
[6] J.V. Ford, L. Poth, Q. Zhong, A.W. Castleman Jr., Int. J. Mass. Spectrom. 192 (1999) 327.
[7] I.V. Hertel, W. Radloff, Rep. Prog. Phys. 69 (2006) 1897–2003.
[8] P. Sharma, R.K. Vatsa, S.K. Kulshreshtha, J. Jha, D. Mathur, M. Krishnamurthy, J. Chem. Phys. 125 (2006) 034304.
[9] P. Sharma, R.K. Vatsa, Rapid Commun. Mass Spectrom. 21 (2007) 2663.
[10] X.L. Kong, X.L. Luo, D.M. Niu, H.Y. Li, Chem. Phys. Lett. 388 (2004) 139.
[11] X. Luo, D. Niu, X. Kong, L. Wen, F. Liang, K. Pei, B. Wang, H. Li, Chem. Phys. 310 (2005) 17.
[12] C. Rose-Petruck, K.J. Schafer, Barty C.P.J., in: M.C. Richardson, G.A. Kyrala (Eds.), Applications of Laser Plasma Radiation II, 2523, SPIE, Bellingham, 1995, p. 272.
[13] C. Rose-Petruck, K.J. Schafer, C.P.J. Barty, Phys. Rev. A 55 (1997) 1182.
[14] A. McPherson, B.D. Thompson, A.B. Borisov, K. Boyer, C.K. Rhodes, Nature (London) 370 (1994) 631.
[15] A.B. Borisov, J.W. Longworth, A. McPherson, K. Boyer, C.K. Rhodes, J. Phys. B 29 (1996) 247.
[16] T. Ditmire, T. Donnelly, A.M. Rubenchik, R.W. Falcone, M.D. Perry, Phys. Rev. A 53 (1996) 3379.
[17] I. Last, J. Jortner, Phys. Rev. A 58 (1998) 3826.
[18] I. Last, J. Jortner, Phys. Rev. A 60 (1999) 2215.
[19] U. Saalmann, C. Siedschlag, J.M. Rost, J. Phys. B 39 (2006) R39.
[20] U. Saalmann, J.M. Rost, Phys. Rev. Lett. 91 (2003) 223401.
[21] D. Niu, H. Li, F. Liang, L. Wen, X. Luo, B. Wang, H. Qu, J. Chem. Phys. 122 (2005) 151103.
[22] W. Wang, H. Li, D. Niu, L. Wen, N. Zhang, Chem. Phys. 352 (2008) 111.
[23] R. Zenobi, R. Knochenmuss, Mass Spectrom. Rev. 17 (1999) 337.
[24] S.J. Arnold, N. Finlayson, E.A. Ogryzlo, J. Chem. Phys. 44 (1966) 2529.
[25] C.T.J. Scott, C. Kosmidis, W.J. Jia, K.W.D. Ledingham, R.P. Singhal, Rapid Commun. Mass Spectrom. 8 (1994) 829.
[26] P. Siozos, S. Kaziannis, C. Kosmidis, Int. J. Mass. Spectrom. 225 (2003) 249.
[27] P. Graham, K.W.D. Ledingham, R.P. Singhai, S.M. Hankin, T. Mccanny, X. Fang, C. Kosmidis, P. Tzallas, P.F. Taday, A.J. Langley, J. Phys. B: Atom. Mol. Opt. Phys. 34 (2001) 4015.
[28] Y. Tanaka, M. Kawasaki, Y. Matsumi, Bull. Chem. Soc. 71 (1998) 2539.
[29] S.P. Sapers, V. Vaida, R. Naaman, J. Chem. Phys. 88 (1988) 3638.
[30] D.M. Szaflarski, M.A. Elsayed, J. Phys. Chem. 92 (1988) 2234.
[31] J. Steadman, J.A. Syage, J. Phys. Chem. 92 (1990) 4630.
[32] S. August, D. Meyerhofer, D. Strickland, S.L. Chin, J. Opt. Soc. Am. B 8 (1991) p858.
[33] K.V. Vidma, A.V. Baklanov, Y. Zhang, D.H. Parker, J. Chem. Phys. 125 (2006) 133303.
[34] K.V. Vidma, A.V. Baklanov, E.B. Khvorostov, V.N. Ishchenko, S.A. Kochubei, A.T.J.B. Eppink, D.A. Chestakov, D.H. Parker, J. Chem. Phys. 122 (2005) 204301.
[35] J. Steadman, E.W. Fournier, J.A. Syage, Appl. Opt. 29 (1990) 4962.
[36] O.F. Hagena, W. Obert, J. Chem. Phys. 56 (1972) 1793.
[37] P. Sharma, R.K. Vatsa, Europhys. Lett. 84 (2008) 43003.
[38] S. Kaziannis, P. Siozos, C. Kosmidis, Chem. Phys. Lett. 401 (2005) 115.
[39] C. Kosmidis, P. Siozos, S. Kaziannis, L. Robson, K.W.D. Ledingham, P. McKenna, D.A. Jaroszynski, J. Phys. Chem. A 109 (2005) 1279.
[40] J. Chen, L. Pei, J. Shu, C. Chen, X. Ma, L. Shen, Y.W. Zhang, Chem. Phys. Lett. 345 (2001) 57.
[41] P. Sharma, R.K. Vatsa, Curr. Appl. Phys. 9 (2009) 140.

[42] E. Krishnakumar, K. Nagesha, Rapid Commun. Mass Spectrom. 9 (1995) 336.
[43] C.E.H. Dessent, J. Kim, M.A. Johnson, Acc. Chem. Res. 31 (1998) 527.
[44] G.A. Bogdanchikov, A.V. Baklanov, D.H. Parker, Chem. Phys. Lett. 376 (2003) 395.
[45] F. Ito, T. Nakanaga, Y. Futami, M. Nakata, Chem. Phys. 286 (2003) 337.
[46] F. Ito, T. Nakanaga, J. Chem. Phys. 119 (2003) 5527.
[47] D.T. Strickland, Y. Beaudoin, P. Dietrich, P.B. Corkum, Phys. Rev. Lett. 68 (1992) 2755.
[48] H. Ohmura, F. Ito, M. Tachiya, Phys. Rev. A 74 (2006) 043410.
[49] R.S. Mulliken, J. Chem. Phys. 7 (1939) 20.
[50] C. Guo, M. Li, G.N. Gibson, Phys. Rev. Lett. 82 (1999) 2492.