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Ionization/dissociation processes in some alkyl iodides induced by strong picosecond laser beam

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Abstract

The interaction of 1-, 2-iodopropane, 1-, 2-iodobutane and 1-iodopentane with strong (2×10^{15} W cm^{-2}) picosecond laser fields at 1064, 532, 355 and 266 nm is studied by means of time-of-flight (TOF) mass spectrometry. The experimental findings are compared with those reported, for the same molecules, from fs experiments at similar laser intensities.

The pertaining molecular ionization mechanism (multiphoton and/or field ionization) is found to depend on the laser wavelength, while the recorded multiply charged atomic ions are generated via field ionization processes in all cases. The identification of these ionization mechanisms has been based on the dependence of the signal intensity and the peak profiles on laser polarization.

The recorded mass spectra are analyzed vis-à-vis those reported for methyl iodide. The observed similarities and differences are discussed in detail.

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

1. Introduction

The multielectron dissociative ionization (MEDI) induced by ps lasers [1,2] and the influence of the laser pulse duration on parent ion production [3–6] has been the subject of many papers in the past.

In a recent publication [7] we have studied the interaction of CH_3I—which is the simplest alkyl iodide molecule—with strong picosecond laser field at 1064 and 532 nm. The experimental findings were compared to those reported from 50 fs experiments at similar laser intensities [8–10] and a mechanism describing the ionization/dissociation processes has been suggested. Multiply charged atomic ions (up to I^{6+}) have been observed in both sets of experiments (ps and fs), but their kinetic energies were found to be dramatically different which implies that the ionization/dissociation mechanism is different too. We have suggested that at high ps laser intensities—especially at 1064 nm—multiply charged unstable parent ions are generated which fragment through Coulomb explosion thus leading to I^{2+} ion production. The atomic fragments are further ionized via field ionization processes (at 1064 nm) resulting in higher multiply charged ion generation.

Recently, the interaction of some alkyl—iodocompounds with 60 fs laser pulses has been studied [11] in order to explore the influence of the alkyl chain size in the molecular coupling with the laser field and the role of resonance states in the ionization/dissociation processes at high laser intensities (5×10^{15} W cm^{-2}). The analysis of the recorded mass spectra at various laser intensities led to the interesting conclusion that multiphoton ionization (MPI) processes are involved in the ionization of these compounds, even for Keldysh parameter values $\gamma \sim 0.3$ ($\lambda = 800$ nm, $I = 10^{15}$ W cm^{-2}) (The Keldysh parameter γ is defined as $\gamma = (\mathrm{IE}/2U_\mathrm{p})^{1/2}$, where IE stands for the ionization energy and U_p for the ponderomotive energy of the free electron [12]). It is worth mentioning that a spectral feature used in the analysis of the fs mass spectra was the 'unexpected single peak' profile of some molecular fragment ions, at variance with the com-

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plex profile structure of the multiply charged atomic fragment ions.

This brings new insight in the subject and therefore, it is of interest to compare the above fs experimental data with those recorded using ps pulses at similar laser intensities.

In the present work, the interaction of some alkyl iodides (1-, 2- iodopropane, 1-, 2-iodobutane and 1-iodopentane) with strong 35 ps laser field is studied. The aim is to explore if the interaction mechanism proposed for the CH_3I case can be invoked for these molecules too and to check if it is also valid at shorter laser wavelengths. Thus, the molecular/35 ps laser interaction at λ = 266 and 355 nm has been also studied by means of a time-of-flight (TOF) spectrometer.

2. Experimental details

The Nd-YAG picosecond laser system (Quantel YG-901C) used in the present work produces 35 ps pulses at 1064, 532, 355 and 266 nm with pulse energy of 80, 40, 10 and 11 mJ respectively, at a repetition rate of 10 Hz.

A homemade TOF mass spectrometer based on the 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 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. Furthermore, in order to increase the angular and mass resolution of the spectrometer another 1 mm pinhole at a distance of 12 cm from the acceleration region has been added. The electronic signal was recorded with an Agilent 54830B (600 MHz, 4 Gs/s) digital oscilloscope. The mass resolution was typically 700 at 100 Da.

The background pressure of the system was below 10^{-7} Torr, while the molecular vapor was allowed to expand through a needle valve into the interaction region. The pressure in the chamber was kept below 3×10^{-7} Torr during the experiments in order to ensure that no space-charge effects were perturbing the mass spectrum measurements. The alkyl iodides, purchased from Fluka, had purity better than 99.5% and they were 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 controlled with a Brewster angle polarizer and was rotated by using half-wavelength plates at the particular wavelengths of interest. Furthermore, circular polarization was achieved by using quarter-wavelength plates. The intensities attained at the focus were also checked through comparison with the intensities needed to produce multiply charged Argon ions [13].

3. Results and discussion

In Figs. 1–4 the mass spectra of 1-iodopropane, 2-iodopropane, 1-iodobutane, 2-iodobutane and 1-iodopentane for 1064, 532, 355 and 266 nm recorded at $I = 2 \times 10^{15}$ W cm^{-2} are presented.

The first striking difference between these mass spectra and those recorded under 60 fs, 800 nm laser irradiation at the same laser intensity [11] is the absence of the parent ion (P^+) from some spectra. In particular, the P^+ has been clearly observed at 1064 nm only for the two iodopropane isomers and 2-iodobutane, at 532 nm only for the case of 2-iodopropane and for 355 nm only for the two iodopropane isomers.

It is assumed that the parent ions are produced via MPI processes, which are taking place, at least, at the temporal and spatial wings of the focused laser beam [14,15]. The MPI processes are sensitive to the existence (or not) of resonances with molecular states in the neutral and/or the ionic manifold. Thus, the ionization/dissociation proceeds through the well known 'ladder climbing' and 'ladder switching' mechanisms [16–18].

In the present case, irradiation of the molecules at 1064, 532 and 266 nm excites them (after 4-, 2- and 1-photon absorption, respectively) to the dissociative A state which lies in the region around 4.7 eV (38500 cm^{-1}) [19]. The dissociation proceed via the cleavage of the C–I bond and the dissociation lifetime is of the order of few hundreds fs [20], i.e., much shorter than the laser pulse duration. At this electronic state the excited molecules can either relax (ultimately fragment) or ionize by further photon absorption. Thus, the observed variation of the P^+ abundance at the different wavelengths can be ascribed to the competition between the relaxation and the 'pumping up' (ionization) processes. The ionization at 1064 nm is probably facilitated by a resonance with a higher excited state after seven-photon absorption (excited states in the region 8.2 eV (∼66.000 cm^{-1})) which is not involved when 532 nm laser is used. This difference in the ionization rate between excitation with 1064 and 532 nm could account for the observed difference of the parent ion abundance in the mass spectra of iodopropane isomers and 2-iodobutane.

For the interpretation of the parent ion absence from the spectra recorded at 266 nm it should also be taken into account that three-photon absorption (=13.98 eV) is sufficient for excitation to ionic states above the energy thresholds of some fragmentation channels. For instance, it is known that the Appearance Energy (AE) of $C_3H_7^+$ is 9.84 and 9.77 eV while the AE for $C_3H_5^+$ is 11.23 and 11.67 eV for the case of 1- and 2-iodopropane, respectively [21].

When a laser beam at 355 nm was used, molecular ionization was achieved via a three-photon absorption process (=10.47 eV) and the electronic state A is not involved in this ionization scheme. However, resonances with higher excited electronic states (assigned as C and D) cannot be excluded, facilitating in this way molecular ionization. From the absorption spectra it is clear that, at least for the iodopropane

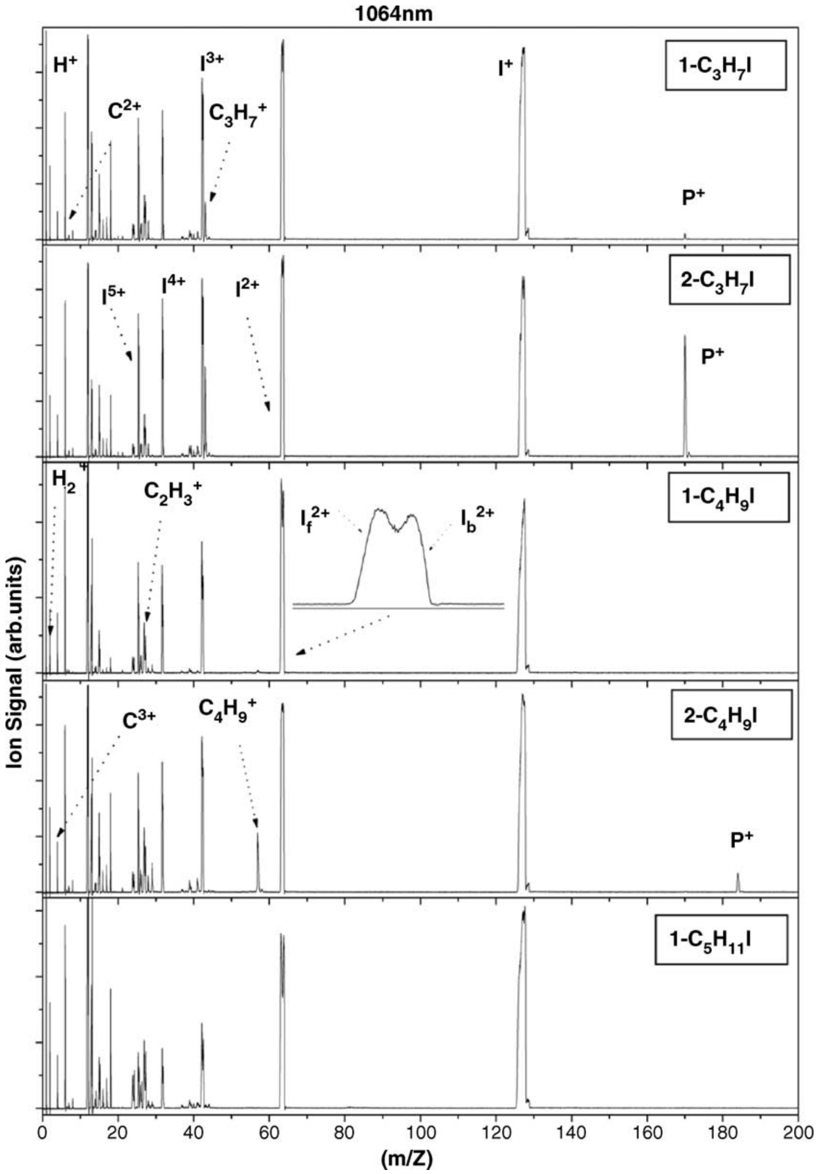

Fig. 1. The mass spectra of alkyl iodide molecules recorded at 1064 nm ($I = 3.0 \times 10^{15}$ W/cm^2). The inset spectra recorded at 1064 nm also shows the complex peak profiles of I^{2+} ions. The $I_f{}^{2+}$ and $I_b{}^{2+}$ symbolize the forward and backward component of the I^{2+} ion peak, respectively.

isomers, the bandwidth of the absorption bands corresponding to transitions to these states are narrower than that of the A band [21]. Thus, the dissociation rate from neutral excited electronic states is expected to be relatively smaller at 355 nm. Therefore, the absence of parent ions must be a result of fragmentation from ionic states. The AE of the fragmentation channels which result in $[P–I]^+$ production are smaller than the three-photon (355 nm) absorption energy. For 1- and 2-iodobutane the AE for $C_4H_9{}^+$ production (i.e., cleavage of the C–I bond in an ionic state) is 9.75 [22] and 9.54 eV [21], respectively, which are lower than that of iodopropane isomers.

To the best of our knowledge, there are no available experimental data about the AE values for the case of 1-iodopentane, but it is reasonable to assume that they are close to those of the rest of the molecules and smaller than 10.47 eV (=three-photon absorption energy at 355 nm). For this molecule, parent ions have not been observed in the mass spectra recorded at all laser wavelengths used. This implies that the dissociation rate of the intermediate states should be higher compared to that of the rest of the molecules.

Another interesting spectral feature appearing in Fig. 1 is the complex structure of some ion peaks, while such profiles have not been observed in the mass spectra recorded at 355 and 266 nm (Figs. 3 and 4). The complex peak profiles are common features in mass spectra induced by strong laser fields. They are attributed to the recoil energy of the ejected multiply charged species in directions away and towards the ion detector (Coulomb explosion). Nevertheless, ‘double peak profiles’ have been also reported by studies at

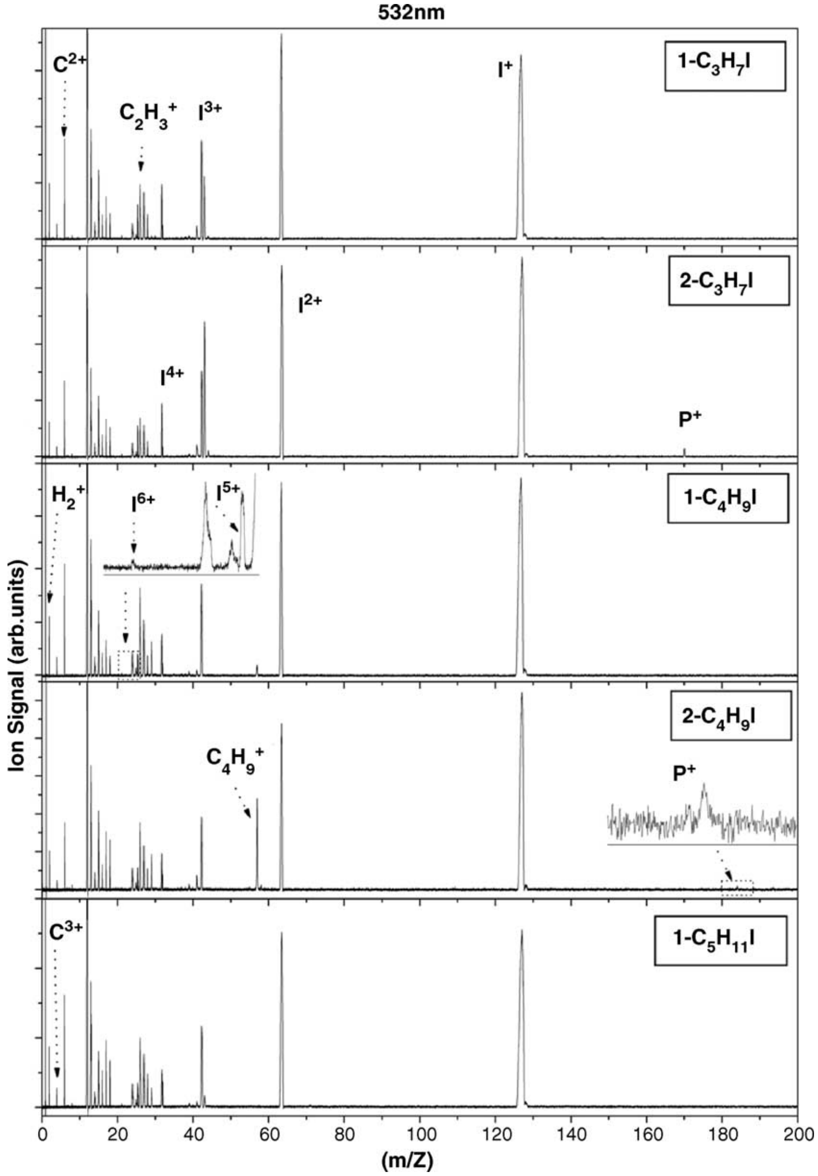

Fig. 2. The Mass spectra of alkyl iodide molecules recorded at 532 nm ($I = 4.0 \times 10^{15}$ W/cm^2).

much lower laser intensities on molecules with fragmentation time shorter than their rotational period. For the molecules studied in the present work it is known that the dissociation time is shorter than their rotational period, especially for those with the longer alkyl chain. Thus, the fact that the spectra of Figs. 1 and 2 have been recorded at high laser intensities does not a priori implies that the origin of this complex structure is the Coulomb explosion mechanism which is taking place within a multiply charged precursor.

On the other hand, the absence of these complex profiles from the mass spectra at 355 and 266 nm, rules out the production of multiply charged parent ions at these wavelengths even at the higher laser intensities used ($\sim 3 \times 10^{15}$ W cm^{-2}) in the present work. This is opposite to the results reported for methyl iodide (CH_3I) where complex profiles for the ion peaks have been clearly observed even at 355 and 266 nm. In the CH_3I case, it was possible to distinguish the contribution to the fragment ion peak components from the different multiply charged unstable parent ions [7]. Moreover, methyl iodide was found to be dynamically aligned even when 266 nm was used, although the degree of alignment with the laser polarization vector was higher at longer (1064 nm) wavelengths [23]. Thus, the comparison implies that there is a clear difference in the coupling mechanism with the laser field between the molecules under study and the CH_3I. The origin of this difference could be related to the difficulty in achieving dynamic alignment for the heavier alkyl iodides at 355 and 266 nm. The lack of molecular alignment with the laser polarization vector results in weaker molecule/laser field coupling and therefore the possibility of multiply charged unstable parent ion production decreases.

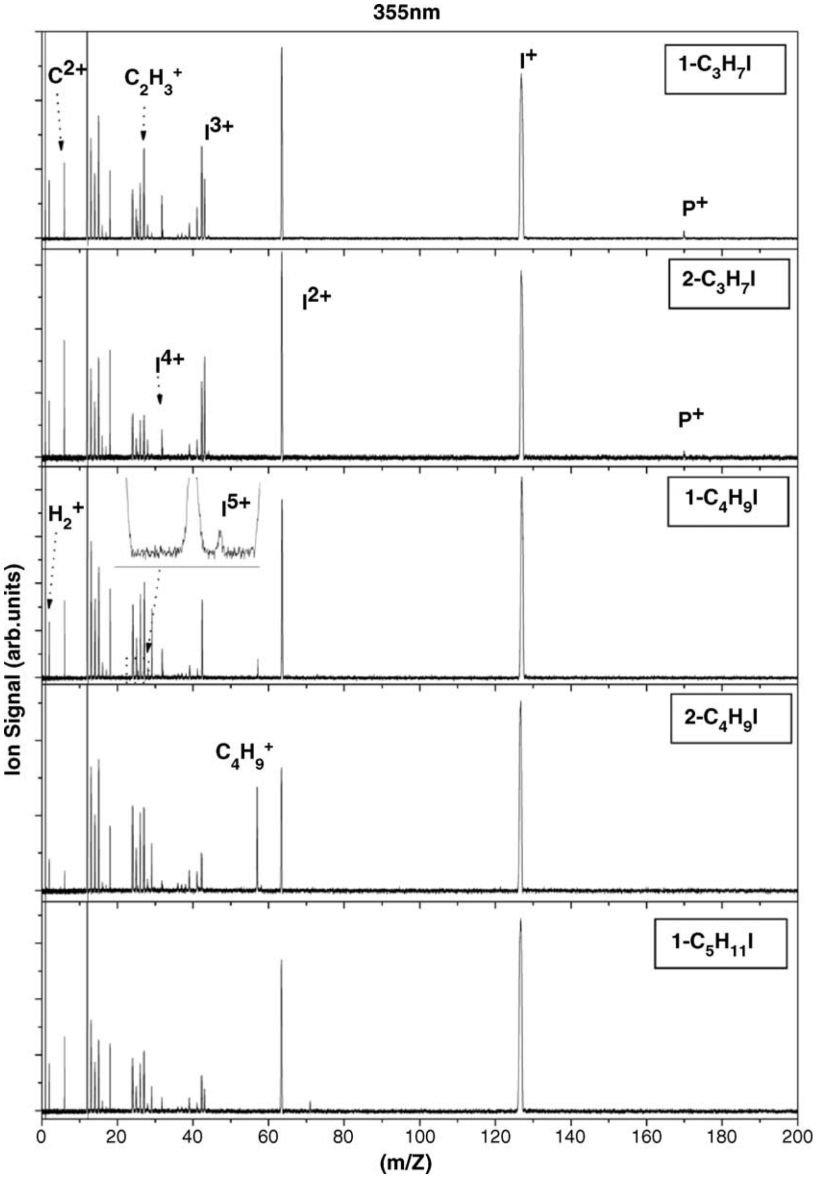

Fig. 3. The Mass spectra of alkyl iodide molecules recorded at 355 nm ($I = 2.0 \times 10^{15}$ W/cm^2).

On the other hand, at 1064 and 532 nm the peak profiles of the fragment ions exhibit a complex structure. Each peak component corresponds to ions generated from different precursors because the fragment ions are liberated with different kinetic energies (E_{kin}) from the various dissociation channels. If the ejection away and towards the detector is also considered then the appearance of pair of components (backward and forward) is expected. The TOF separation between the backward and forward components of an ion peak can be used to estimate the kinetic energies of the fragment ions in accordance to the following relation:

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

where Δt (in ns) stands for the time difference between the forward and the backward component, F (in V/cm) is the electric field applied in the acceleration region of the TOF system, z is the charge and m (in amu) the mass of the fragment ion.

The estimated E_{kin} values for some of the fragment ions are presented in Table 1.

The E_{kin} values appearing in this table offer some insight into the origin of the complex ion peak profiles discussed above. Thus, the E_{kin} values of $[\text{P–I}]^+$ at 1064 nm which are found to be 2.3–3 eV, are conceivable only if a Coulomb explosion mechanism within a multiply charged unstable parent ion is assumed. Although at this stage it remains unclear how these multiply charged species are produced (i.e., via MPI or field ionization (FI) processes), their generation is beyond any doubt. This conclusion is also supported by the E_{kin} values of C^{2+} ions. As far as the E_{kin} values of the I^+ and I^{2+} ions are concerned, it is obvious that these species

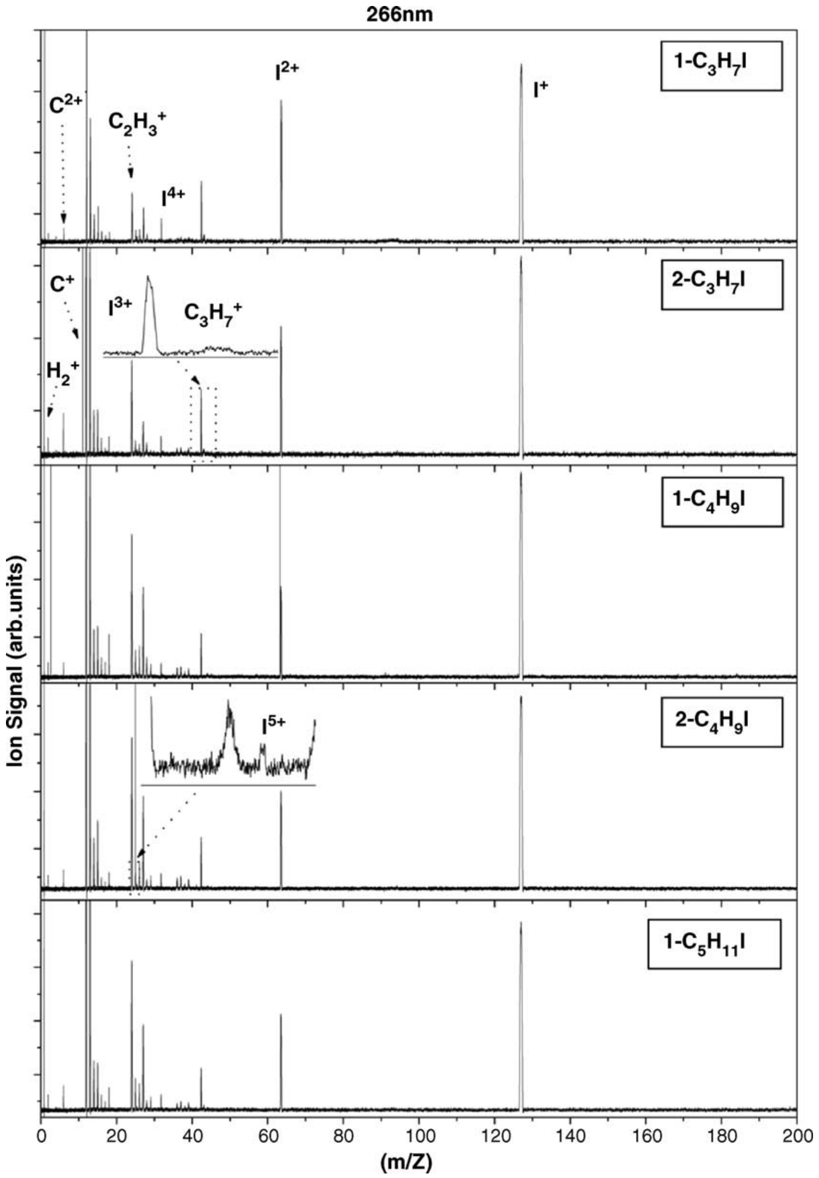

Fig. 4. The Mass spectra of alkyl iodide molecules recorded at 266 nm ($I = 2.0 \times 10^{15}$ W/cm^2).

are generated from different precursors. In other words, the I^{2+} are not produced by further ionization of singly charged iodine ions (because they have different E_{kin}) and therefore their precursor should be higher charged molecular ions in accordance with what is stated above. However, the fact that the E_{kin} values of the I^{n+}, $n > 2$, ions are similar to those of I^{2+} could imply that these species are generated from further ionization of I^{2+} ions. This approach is in agreement with the proposed mechanism for the interpretation of the ionization/dissociation processes in the case of CH_3I under the same experimental conditions (at $\lambda = 1064$, 532 nm and $I = 2 \times 10^{15}$ W cm^{-2}) [7].

Table 1
Estimated kinetic energy values (eV) of the fragment ions at $I = 3 \times 10^{15}$ W/cm^2

	λ (nm)	I^+	I^{2+}	I^{3+}	I^{4+}	I^{5+}	C^+	C^{2+}
1-Iodopropane	1064	0.71 ± 0.08	1.3 ± 0.2	1.2 ± 0.2			2.9 ± 0.4	7.9 ± 1.2
2-Iodopropane	1064	0.80 ± 0.07	1.3 ± 0.2	1.2 ± 0.2	1.1 ± 0.2		1.9 ± 0.3	5.2 ± 1.0
1-Iodobutane	1064	0.93 ± 0.07	1.4 ± 0.2	1.2 ± 0.2	1.3 ± 0.3	1.6 ± 0.3	2.0 ± 0.3	4.0 ± 1.0
2-Iodobutane	1064	0.76 ± 0.06	1.06 ± 0.15	1.0 ± 0.2	1.1 ± 0.2		1.5 ± 0.3	4.0 ± 1.0
1-Iodopentane	1064	1.10 ± 0.08	2.0 ± 0.2	1.5 ± 0.2	1.8 ± 0.4		1.9 ± 0.3	4.6 ± 1.0
2-Iodopropane	532		0.2 ± 0.06	0.4 ± 0.09	0.6 ± 0.10		1.0 ± 0.18	1.6 ± 0.2

Table 2
The intensity threshold values predicted by the BSI model and those determined by the present work with linear laser polarization at 1064, 532, 355, 266 nm

λ (nm)	Intensity thresholds according to the BSI model (10^{14} W/cm^2)	I^{2+}	I^{3+}	I^{4+}	I^{5+}	I^{6+}	C^{+}	C^{2+}	C^{3+}	C^{4+}
		2.1	4.6	9.4	15	43	0.6	3.5	23	43
1064	1-Iodopropane	<0.4	0.79	2.7	4.7	11.3	<0.4	1.2	9.4	–
	1-Iodobutane	<0.4	0.79	3.0	6.8	11.3	<0.4	0.81	8.8	–
	2-Iodopropane	<0.4	0.81	2.6	5.1	12.0	<0.4	0.81	6.6	30
	2-Iodobutane	<0.4	0.81	2.5	4.7	10.0	<0.4	0.81	8.1	30
	1-Iodopentane	<0.4	0.79	3.0	7.0	14	<0.4	1.07	9.0	30
532	1-Iodopropane	<0.6	1.5	4.4	9.3	27	<0.6	1.5	15.5	42
	1-Iodobutane	<0.6	1.5	3.5	9.6	27	<0.6	1.5	16.3	40
	2-Iodopropane	<0.6	1.7	5.0	10.5	31	<0.6	1.7	17.1	45
	2-Iodobutane	0.7	1.3	3.2	10.5	34	<0.4	2.4	18.7	–
	1-Iodopentane	<1.4	2.5	5.4	12.1	26	<1.4	2.5	12.6	46
355	1-Iodopropane	0.8	3.6	7.0	13.9	23	<0.6	4.5	17	–
	1-Iodobutane	1.1	3.2	5.3	13.2	24	<0.6	5.3	22	–
	2-Iodopropane	1.0	3.1	7.5	15.1	–	<0.7	4.9	22	–
	2-Iodobutane	0.5	2.3	4.7	15.3	–	<0.8	2.3	25	–
	1-Iodopentane	1.1	3.8	5.3	15.1	27	<0.7	3.8	19	–
266	1-Iodopropane	1.6	4.2	7.4	21	–	<1.0	10.7	25	–
	1-Iodobutane	2.0	5.1	15	24	–	<0.7	15	–	–
	2-Iodopropane	2.0	4.6	13.4	23	–	<1.3	10.7	28	–
	2-Iodobutane	2.1	4.8	15	21	–	<0.7	15	26	–
	1-Iodopentane	1.7	4.0	9.6	19	–	<0.9	10.3	26	–

In Table 1 the estimated E_{kin} values for the fragment ions at 532 nm are given only for the case of 2-iodopropane because the temporal splitting between the backward and forward components is even smaller for the rest of the molecules and the accuracy in the E_{kin} values is reduced. The E_{kin} values were found to be less than 1 eV, i.e., smaller than the values determined from the experiments at 1064 nm. Thus, the involvement of a Coulomb explosion mechanism is uncertain at this wavelength and this will be further discussed in a following paragraph.

In order to elucidate the ionization mechanisms involved in multiply charged ion production, the intensity thresholds for the appearance (I_{thr}) of the fragment ions have been determined. These values are presented at Table 2. In the same Table the intensity thresholds predicted by the Barrier Suppression Ionization (BSI) model [24,25] are also depicted. The latter intensity thresholds can be calculated using the expression:

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

where E_{I} is the ionization energy (eV) of the atom (ion) and z is the charge of the ionic state.

The BSI model is applicable in the field ionization regime and the predicted I_{thr} values are presented because the values of the Keldysh parameter γ for the laser intensities used are $\gamma < 1$ ($\gamma \approx 0.15$ at 1064 nm and $\gamma \approx 0.6$ at 266 nm).

The experimental I_{thr} values presented in Table 2 should be considered as upper intensity limits. Lower values could have been found if, for instance, a larger diameter hole had been used in the first ion optic. However, all the experimentally determined I_{thr} values are lower that those predicted by the BSI model. This is in accordance to results reported previously [7,11] and it implies that simple quasistatic models are inadequate. Moreover, while the BSI model predicts no wavelength dependence for the I_{thr}, from the Table 2 it is clear that this is at variance with our experimental values since the I_{thr} values for I^{n+} and C^{n+}, with $n \geq 2$, are increasing as the laser wavelength decreases. The trend of the I_{thr} values reveals that the multiply charged atomic ions are not generated by MPI processes, because at shorter wavelengths the multiple ionization can be achieved by lower order multiphoton processes which have higher cross section and therefore a decrease of the I_{thr} values should be observed.

The I_{thr} values determined when a circularly polarized laser beam was used are shown in Table 3. It is clear that the I_{thr} values are increasing as the laser wavelength decreases for all multiply charged atomic ions. The comparison of the I_{thr} values appearing in Tables 2 and 3 indicates that the I_{thr} increases when a circularly polarized laser is used.

In Fig. 5 the peak profiles of some ions recorded with linear and circular polarization at different wavelengths are presented. The influence of laser polarization on the ion signal varies at the different wavelengths used. For instance, the signal variation of the molecular fragments ions ($C_xH_y{}^{+}$, $x = 1$–3, $y = 0$–7) is significant at 1064 nm while no change was observed for these species at 355 nm. In contrast, the multiply charged iodine ion signal is dramatically reduced in the spectra recorded with a circularly polarized laser and this observation is valid for all wavelengths used. Therefore, also from this point of view, the multiply charged atomic ion production should be attributed to a common mechanism for

Table 3
The intensity threshold values predicted by the BSI model and those determined by the present work with circular laser polarization at 1064, 532, 355 nm

λ (nm)	Intensity thresholds according to the BSI model (10^{14} W/cm^2)	I^{2+}	I^{3+}	I^{4+}	I^{5+}	I^{6+}	C^{+}	C^{2+}	C^{3+}
		2.1	4.6	9.4	15	43	0.6	3.5	23
1064	1-Iodopropane	0.5	3.6	9.4	16	–	<0.4	2.7	24
	1-Iodobutane	0.5	4.1	8.8	17	–	<0.4	2.3	20
	2-Iodopropane	0.5	3.2	7.9	18	–	<0.4	2.5	20
	2-Iodobutane	0.5	3.6	10.0	17	–	<0.4	2.5	22
	1-Iodopentane	0.6	3.1	12	19	–	<0.4	2.4	22
532	1-Iodopropane	1.1	4.4	11.8	23	–	<0.8	2.2	27
	1-Iodobutane	1.1	5.3	12.4	27	–	<0.8	5.3	30
	2-Iodopropane	1.6	6.9	16.3	27	–	<0.6	6.9	39
	2-Iodobutane	2.0	6.8	13.0	25	–	<0.8	6.8	39
	1-Iodopentane	1.4	4.2	15.8	26	–	<0.8	3.7	40
355	1-Iodopropane	0.8	6.2	19	–	–	<0.52	6.6	–
	1-Iodobutane	1.1	8.3	23	–	–	<0.64	8.3	–
	2-Iodopropane	1.6	7.2	21	–	–	<0.68	7.2	–
	2-Iodobutane	2.1	9	24	–	–	<0.40	7.9	–
	1-Iodopentane	1.2	7.9	19	–	–	<0.72	5.4	–

all wavelengths and this mechanism appears to have a strong dependence on laser polarization, which is a characteristic of FI processes.

For the molecules studied in the present work no polarization dependence in the multiphoton ionization is excepted because of the low molecular symmetry. Therefore, the absence of polarization dependence for the molecular fragment ions ($C_xH_y{}^+$) in the spectra recorded at 355 nm indicates that molecular ionization at this wavelength is taking place within the MPI regime. At the same time, the dependence of the same molecular fragment ions at 1064 nm on the laser polarization implies that at this wavelength another mechanism contributes to the molecular ionization, i.e., a FI mechanism. It is known that FI processes such as the electron tunneling, barrier suppression [24], and electron re-scattering processes, are dependent on laser polarization [26,27].

Some further discussion is needed to explain the dependence on laser polarization of $C_3H_7{}^+$ as seen in the spectra recorded at 532 nm. At this wavelength, the signal intensities of the molecular fragment ions are found to be slightly weaker when a circularly polarized laser beam is used. This is reasonable because the contribution of FI processes is expected to be smaller at 1064 nm (shorter optical cycle and smaller pondermotive energy). Nevertheless, the back and forward components of the $C_3H_7{}^+$ peak appear to gain intensity in the spectra recorded with circularly polarized laser at 532 nm. Obviously, the ions contributing to the formation of these peak components are not generated via FI processes. The dependence of the $[P–I]^+$ ions peak components on laser polarization has been clearly observed in the mass spectra of 1-iodopropane while for the rest of the molecules (due to the fact that the peak splitting is somewhat smaller, as commented previously) this behavior is not so pronounced. The TOF splitting between these two peak components reveals that the corresponding ions were ejected with a kinetic energy of about 0.6 eV. In a recent publication on CH_3I, we found that the precursor of $[P–I]^+$ ions (ejected with E_{kin} of about 1 eV) were excited parent ions and the contribution of the corresponding back and forward peak components became dominant at shorter wavelengths [23]. The same argument can be used for the present case too. We suggest that after the absorption of six-photon at 532 nm (=13.98 eV) the molecules were excited to an ionic electronic state [28], and the observed recoil energy is due to the available excess energy after molecular dissociation. Undoubtedly, this approach lies within an MPI excitation scheme and its contribution becomes more prominent when the contribution of FI to the total ion signal is reduced, which is the case when circular polarization is used. In other words, the dependence of the $[P–I]^+$ ion peak components on laser polarization manifests the involvement of MPI processes at 532 nm in parallel with FI.

Hence, the above analysis can be summarized as follows:

- Molecular ionization at the shorter wavelengths (355 and 266 nm) is taking place mainly via MPI processes even at these high laser intensities ($\geq 10^{15}$ W cm^{-2}).
- At 1064 nm the multiple molecular ionization proceeds mainly through a FI mechanism. At 532 nm both MPI and FI have significant contribution. The contribution of FI processes is reduced when circularly polarized laser beam was used.
- Regardless of the mechanism involved in molecular ionization, the multiply charged iodine ions (I^{n+}, $n > 2$) are generated through FI processes at all the laser wavelengths used in the present work.

From the comparison of the presented data with those recently reported for the same molecules under strong fs laser irradiation [11] it is evident that:

- The recoil energies of the fragment ions is much lower when a ps laser was used and this is related to the fact that higher charged unstable parent ions were generated at

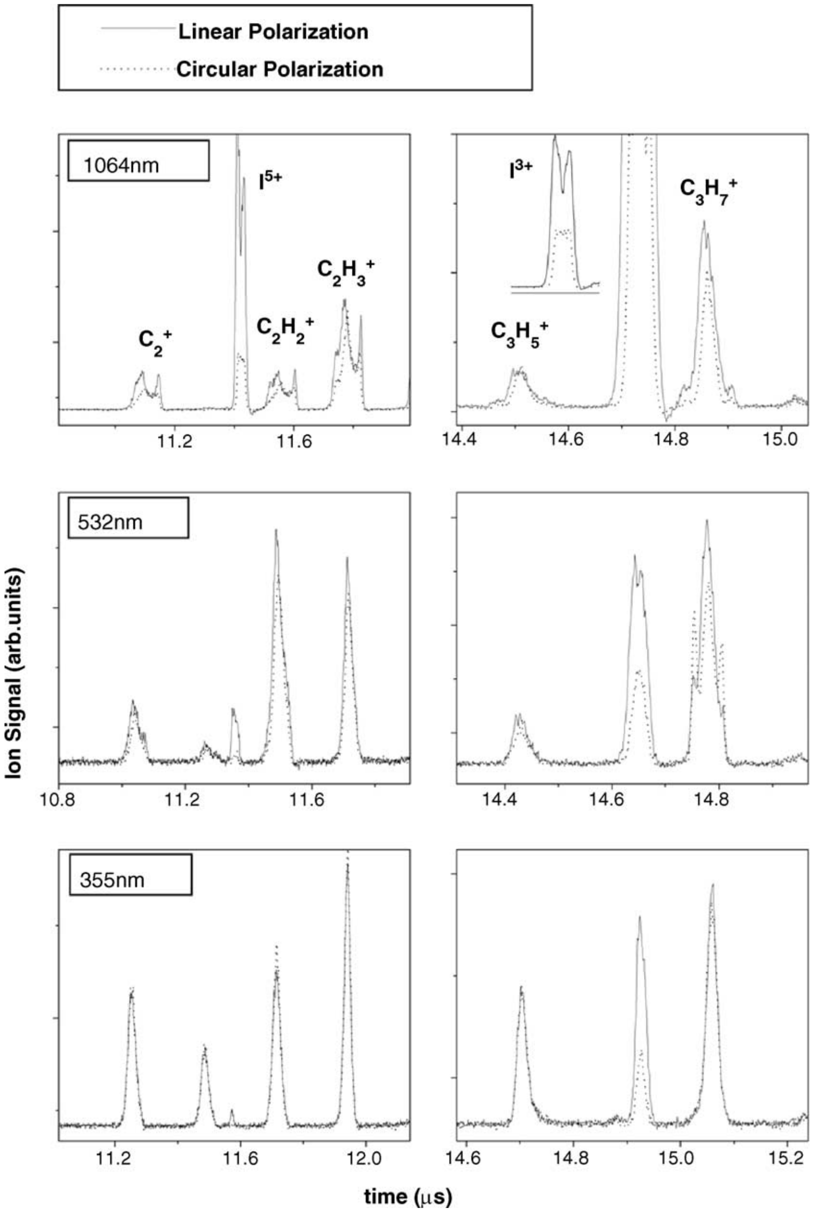

Fig. 5. The peak profiles of 1-C_3H_7I recorded at 1064, 532, 355 nm ($I = 2.0 \times 10^{15}$ W/cm^2) with linear (solid lines) and circular (dot lines) laser polarization.

fs experiments. Although the higher charged state of the recorded iodine ions is similar in both sets of experiments their production mechanisms are completely different. In fs experiments the I^{n+}, $n \leq 7$, ions are released from explosion within highly charged parent ions while in ps experiments these ions are generated via FI processes on I^{y+}, $y \leq 2$, ejected from unstable $[P]^{z+}$, $z \leq 3$.

- The charge distribution on the parent ion prior to Coulomb explosion is ascribed to be asymmetric in fs experiments. In the present ps work, the I_{thr} values for I^{n+} and C^{z+} ions are found to be in line with the trend of the ionization energy of these ions. This observation is reasonable because it is related to the fact that in the present experiments the pulse duration is much longer than the molecular dissociation time [29].
- In fs experiments the P^{2+} was clearly observed in the mass spectra of 2-iodobutane and its production was attributed to MPI processes. No such peak has been recorded in the present experiments. We suggest that this absence should be attributed to a ‘ladder switching’ mechanism, which is more probable to take place in ps experiments, compared to fs ones. The same argument is also valid for the observed parent ion abundance and it is in agreement with those reported in the past with respect to the efficient intact parent ion production by fs laser pulses [3,4,30].
- The intensity thresholds of the multiply charged I^{n+} ions, especially for $n \geq 3$, are found to decrease as the size of the alkyl chain increases in fs experiments. This was thought as evidence that the molecular coupling with the laser field

increases with the molecular length. In the present experiments no clear trend of the I^{n+} intensity thresholds has been determined. Obviously, this is related with the statement made above that the I^{n+} with $n \geq 3$, in the present experiments, are generated in a later step, i.e., after the molecular fragmentation. In the set of experiments at 1064 nm, where the FI processes have significant contribution in the molecular ionization, the variation in I_{thr} values for I^{n+} with $n \leq 2$ are within the experimental error and therefore no conclusion on the molecular coupling with the laser field can be drawn.

4. Conclusions

From the present work it is concluded that the proposed ionization/dissociation mechanism for the case of methyl iodide under strong ps laser irradiation at 1064 and 532 nm can be applied for the studied alkyl iodides too.

The contribution of FI processes in molecular ionization decreases, as the laser wavelength becomes shorter. This conclusion is based on the analysis of the dependence of the signal intensity and the peak profiles of the recorded ions on the laser polarization.

Thus, molecular ionization by ps lasers at 355 and 266 nm with intensity $2 \times 10^{15}\,\mathrm{W\,cm^{-2}}$ should be attributed to MPI processes and the contribution from FI—if any—is negligible. In the present work no evidence for multiply charged unstable parent ions was found for all molecules studied. This is at variance with that reported for CH_3I, where it has been suggested that multiply charged unstable parent ions are generated even at 266 nm. This difference could be attributed to the fact that the field can dynamically align CH_3I more efficiently thus resulting in stronger molecule/laser coupling.

As far as the multiply charged atomic ions are concerned their production is attributed to FI processes regardless of the laser wavelength and the way the molecular ionization is achieved.

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References

[1] V.R. Bhardwaj, K. Vijayalakshmi, D. Mathur, Phys. Rev. A 59 (1999) 1392.
[2] P.A. Hatherly, L.J. Frasinski, K. Codling, J.R.M. Barr, Chem. Phys. Lett. 149 (1988) 477.
[3] K.W.D. Ledingham, C. Kosmidis, S. Georgiou, S. Couris, R.P. Singhal, Chem. Phys. Lett. 247 (1995) 555.
[4] M.J. Dewitt, R.J. Levis, J. Chem. Phys. 102 (1995) 8670.
[5] R. Weinkauf, P. Aicher, G. Wesley, J. Grotemeyer, E.W. Schlag, J. Phys. Chem. 98 (1994) 8381.
[6] H.S. Kilic, K.W.D. Ledingham, C. Kosmidis, T. Mccanny, R.P. Singhal, S.L. Wang, D.J. Smith, A.J. Langley, W. Shaikh, J. Phys. Chem. A 101 (1997) 817.
[7] P. Siozos, S. Kaziannis, C. Kosmidis, Int. J. Mass Spectrom. 225 (2003) 249.
[8] 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: At., Mol. Opt. Phys. 34 (2001) 4015.
[9] J.V. Ford, Q. Zhong, L. Poth, A.W. Castleman, J. Chem. Phys. 110 (1999) 6257.
[10] J.V. Ford, L. Poth, Q. Zhong, A.W. Castleman, Int. J. Mass Spectrom. 192 (1999) 327.
[11] C. Kosmidis, P. Siozos, S. Kaziannis, L. Robson, K.W.D. Ledingham, P. McKenna, D.A. Jaroszynski, J. Phys. Chem. A 109 (2005) 1279.
[12] L.V. Keldysh, Sov. Phys. JEPT 20 (1965) 1307.
[13] T. Auguste, P. Monot, L.A. Lompre, G. Mainfray, C. Manus, J. Phys. B: At., Mol. Opt. Phys. 25 (1992) 4181.
[14] P. Tzallas, C. Kosmidis, K.W.D. Ledingham, R.P. Singhal, T. Mccanny, P. Graham, S.M. Hankin, P.F. Taday, A.J. Langley, J. Phys. Chem. A 105 (2001) 529.
[15] K.W.D. Ledingham, D.J. Smith, R.P. Singhal, T. Mccanny, P. Graham, H.S. Kilic, W.X. Peng, A.J. Langley, P.F. Taday, C. Kosmidis, J. Phys. Chem. A 103 (1999) 1952.
[16] U. Boesl, J. Phys. Chem. 95 (1991) 2949.
[17] A. Gedanken, M.B. Robin, N.A. Kuebler, J. Phys. Chem. 86 (1982) 4096.
[18] R.J. Levis, M.J. Dewitt, J. Phys. Chem. A 103 (1999) 6493.
[19] M.B. Robin, Higher Excited States of Polyatomic Molecules, vol. I, Academic Press, New York, London, 1974.
[20] D.P. Zhong, A.H. Zewail, J. Phys. Chem. A 102 (1998) 4031.
[21] NIST Chemistry WebBook [Web Page], available at NIST Chemistry WebBook: http://webbook.nist.gov/chemistry.
[22] S.T. Park, S.K. Kim, M.S. Kim, J. Chem. Phys. 115 (2001) 2492.
[23] S. Kaziannis, P. Siozos, C. Kosmidis, Chem. Phys. Lett. 401 (2005) 115.
[24] N.B. Delone, V.P. Krainov, Multiphoton Processes in Atoms, Springer-Verlag, Berlin Heidelberg, 1994.
[25] S. Augst, D.D. Meyerhofer, D. Strickland, S.L. Chin, J. Opt. Soc. Am. B: Opt. Phys. 8 (1991) 858.
[26] B. Walker, E. Mevel, B.R. Yang, P. Breger, J.P. Chambaret, A. Antonetti, L.F. Dimauro, P. Agostini, Phys. Rev. A 48 (1993) R894.
[27] P. Dietrich, N.H. Burnett, M. Ivanov, P.B. Corkum, Phys. Rev. A 50 (1994) R3585.
[28] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Molecules, Japan Scientific Society Press, Tokyo, 1981.
[29] J.H. Posthumus, A.J. Giles, M.R. Thompson, K. Codling, J. Phys. B: At., Mol. Opt. Phys. 29 (1996) 5811.
[30] M.J. Dewitt, D.W. Peters, R.J. Levis, Chem. Phys. 218 (1997) 211.