

Molecular hydrogen ion elimination from alkyl iodides under strong laser beam irradiation

C. Kosmidis^{a,*}, S. Kaziannis^a, P. Siozos^a, A. Lyras^a, L. Robson^b,
K.W.D. Ledingham^{b,c}, P. McKenna^b, D.A. Jaroszynski^b

^a Department of Physics, University of Ioannina, 45110 Ioannina, Greece

^b Department of Physics and Applied Physics, University of Strathclyde, Glasgow G4 0NG, Scotland, UK

^c AWE Ltd., Aldermaston, Reading RG7 4PR, UK

Received 5 September 2005; received in revised form 12 October 2005; accepted 12 October 2005

Available online 16 November 2005

Abstract

The elimination of H_2^+ from alkyl iodides under strong (up to $5 \times 10^{15} \text{ W cm}^{-2}$) laser irradiation is studied by means of time-of-flight mass spectrometry. The study has been performed by using 60 fs ($\lambda = 800 \text{ nm}$) and 35 ps ($\lambda = 1064, 532, 355$ and 266 nm) laser pulses. It is concluded that the H_2^+ ions are ejected from ionic states via Coulomb explosion processes. The molecular rearrangement leading to H_2^+ formation is attributed to a tunneling process through a H transfer barrier. For the case of methyl iodide, about 10% of the doubly charged parent ions undergo molecular rearrangement. From a comparison of the H_2^+/H^+ ion yield ratio of the studied molecules, it turns out that the H_2^+ formation from H atoms bonded to a terminal carbon atom is more efficient than that arising from H atoms bonded to central C atoms of the molecular chain.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Mass spectrometry; Molecular hydrogen elimination; Strong laser field; Alkyl iodide

1. Introduction

The detection of molecular hydrogen ion (H_2^+) in the mass spectra of many organic compounds under strong laser irradiation has been reported on many occasions [1–7].

Recently, we have studied the ionization/dissociation processes of some alkyl iodides by means of time-of-flight (TOF) mass spectrometry under strong ($\sim 10^{16} \text{ W cm}^{-2}$) femtosecond [8] and picosecond [9,10] laser irradiation. In both cases, an intense ionic signal corresponding to atomic and molecular hydrogen ions has been recorded. The H_2^+ elimination process is a complicated one since, at least, the rupture of two bonds and the formation of a new one are needed. To the best of our knowledge, the appearance of the H_2^+ ion in the mass spectra of organic compounds induced by strong lasers has not been studied extensively in the past [7].

On the other hand, molecular hydrogen elimination, among the other dissociation channels, from small alkanes (methane,

ethane, propane, etc.) has been studied extensively [11,12]. The conclusions of these studies are of importance because the alkyl iodides are the products of the substitution of a hydrogen atom by an iodine one in the molecular skeleton. For the case of propane, Tonokura et al. [13] have shown that the atomic hydrogen elimination channel exhibits a site specificity. The hydrogen atoms are produced mostly by a C–H bond rupture from the terminal carbon atoms of the alkyl chain. On the other hand, other groups [14–16] have shown that for the case of small alkanes the vast majority of the released molecular hydrogen is formed from hydrogen atoms bonded to carbons in the middle of the alkyl chain. Molecular hydrogen formation from the other hydrogen atoms of the skeleton (i.e., from the terminal CH_3 groups) is also possible and it is found that they are released with higher kinetic energies ($\sim 3.3 \text{ eV}$) compared to those generated from the middle of the alkyl chain ($\sim 1.5 \text{ eV}$). It should be noted that these experiments on alkanes have been performed using a laser beam at $\lambda = 157 \text{ nm}$, i.e., below the ionization energy and for this case the efficiency of the channels leading to H_2 elimination is higher than that leading to atomic hydrogen formation.

In addition, H_2 elimination has also been reported from ionic species and for the case of C_2H_4^+ , using a photoelectron–

* Corresponding author. Fax: +30 26510 98695.

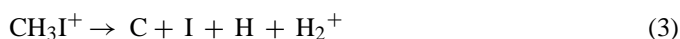
E-mail address: kkosmid@cc.uoi.gr (C. Kosmidis).

photoion coincidence technique, it has been proposed that the H₂ formation proceeds via tunneling of H atoms through a H-atom transfer barrier [17,18]. It was also found that the unimolecular reaction leading to H₂ elimination takes place on the microsecond time scale.

For the case of alkyl iodides, the H₂ and H₂⁺ elimination channels have been studied by a comprehensive work on methyl iodide (CH₃I) by Olney et al. [19]. At least two channels leading to H₂ have been identified:



with appearance energies (AE) of 15 and 20 eV, respectively. Furthermore, a channel resulting in H₂⁺ elimination has been clearly identified



with an AE equal to 41 eV. According to the authors, the H₂⁺ elimination process it “likely arises from direct valence shell double photoionization or from a VUV Auger process”. From the reported data (Table 4 of Ref. [19]) it can be concluded that the ratio of H₂⁺/H⁺ production efficiency decreases with the photon excitation energy in the range of 41–59.5 eV, while the ratio is always smaller than 1. This study distinguishes the dissociation from ionic and neutral molecular states.

As mentioned above, H₂⁺ ions have been observed in the mass spectra of alkyl iodides [8,9,19,20] under strong femtosecond and picosecond laser irradiation but the mechanism involved remains largely unexplained. For instance, it has been suggested that when fluorobenzene is subjected to strong laser fields, the H atoms are ejected from the molecular skeleton very rapidly (within ~7 fs) [21]. If this is also the case for the alkyl iodides, then the question arises, how and when the H₂⁺ is formed? Moreover, some related questions are:

- What is the precursor of H₂⁺? Is this ion formed by further excitation of H₂ (liberated from neutral and/or ionic states) or is it ejected from a multiply charged ion via a Coulomb explosion process? If the latter is the case, when does this ejection take place (during or after the end of the laser pulse)?
- Is the site specificity in H₂ formation preserved in strong fields too?

To address these questions, the aim of the present work is to explore the molecular hydrogen ion elimination processes when certain alkyl iodides are subjected to strong laser fields. The alkyl iodides studied are: methyl iodide, ethyl iodide, 1-, 2-iodopropane and 1-, 2-iodobutane.

2. Experimental details

The picosecond laser experiments were performed at the Central Laser Facility of the University of Ioannina. The Nd-YAG picosecond laser system (Quantel YG-901C) used produces 35 ps pulses at 1064, 532, 355 and 266 nm with pulse energies of 80, 40, 10 and 11 mJ, respectively, at a repetition rate of 10 Hz.

A custom built time-of-flight 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 120 mm from the acceleration region has been added. The electronic signal was recorded with an Agilent 54830B (600 MHz, 4 Gs s⁻¹) digital oscilloscope. The mass resolution was typically 700 at 100 Da.

The laser light was focused with a 35 mm focal length spherical mirror at about 10 mm from the repeller electrode. Optimum spatial conditions were achieved using a *xyz* vernier-controlled mechanism attached to the focusing mirror. Moreover, experiments using an *f*=250 mm lens were performed especially for the lower laser intensity range. The polarization of the laser light was controlled by a Brewster angle polarizer and was rotated by using half-wavelength plates at the particular wavelengths of interest.

The femtosecond experiments were performed using the Strathclyde Terahertz to Optical Pulse Source (TOPS) femtosecond laser system [22]. To produce the seed pulse for the system a Ti:sapphire Femtosource F220 laser was employed, pumped by a VERDI CW laser (532 nm, 5 W). The repetition rate of the oscillator was 76 MHz with an average power output of 500 mW, generating pulses of 7 nJ with a pulse length of 20 fs. The low energy, ultrashort pulses are then stretched to 200 ps before being amplified in a 10 Hz, 10 ns, Nd:YAG pumped regenerative Ti:sapphire amplifier. Two further multipass amplifiers generate the pulse of required energy: first a pre amplifier, pumped by the same YAG as the regenerative amplifier, secondly a main amplifier pumped by two 10 Hz, 8 W SAGA YAGs. The amplified pulses are re-compressed using a grating. This set-up delivered linearly polarized pulses of 250 mJ, and temporal pulse widths (FWHM) of 60 fs (as measured by an autocorrelator) at 800 nm. The laser light was focused with a 250 mm focal length lens and the polarization was rotated by using a half-wavelength plate at 800 nm.

The reflectron time-of-flight mass spectrometer used for the femtosecond experiments has been described in detail previously [23]. The ion optics arrangement is based on Wiley McLaren principles. The ions pass through the ion optics from a slit with 1 mm diameter and are accelerated into the reflectron electrostatic mirror before detection by the MCP (Galileo). A digital oscilloscope (Tektronix TDS7104) is used for averaged data collection and is connected to a PC.

The laser intensities attained at the focus were determined after a comparison with the intensities needed to produce multiply charged argon ions [24].

The background pressure for both experimental arrangements was below 1.3 × 10⁻⁶ Pa, while the molecular vapor was allowed to expand through a needle valve into the interaction region. The pressure in the chambers was kept below 4 × 10⁻⁵ Pa (=3 × 10⁻⁷ Torr) during the experiments in order to ensure that no space-charge effects perturbed the mass spectrum

measurements. The alkyl iodides, purchased from Fluka, with a purity > 99.5%, were used after several freeze–thaw–degassing cycles under vacuum.

3. Results and discussion

In Fig. 1 the TOF mass spectra of 2-iodopropane and the enlarged regions showing the H_2^+ ions recorded under strong laser irradiation ($I = 2 \times 10^{15} \text{ W cm}^{-2}$) using 60 fs and 35 ps laser pulses are presented. The laser polarization vector was parallel to the TOF axis. For the 60 fs ($\lambda = 800 \text{ nm}$) and the 35 ps ($\lambda = 1064 \text{ nm}$) mass spectra, the H^+ and H_2^+ ions exhibit a complex structure composed from at least two peak components. These components correspond to ions ejected towards or away from the ion detector. From their time separation, the recoil energies of the ions can be estimated [25] and the calculated values are presented in Table 1. This kind of peak shapes is typical in strong-field laser mass spectrometry and reflects the result of a Coulomb explosion process taking place within a multiply charged precursor. This is not always the case since molecular dissociation from neutral states is also possible resulting in fragment production with considerable recoil energies and if the dissociation rate is faster than the rotational period, complex ion peak profiles appear in the mass spectra. As mentioned in Section 1, the dissociation of small alkanes from highly excited neutral states results in H_2 formation with almost 3 eV recoil energy. Therefore, the recorded complex peak shape of the ions in Fig. 1 does not a priori imply that their origin is a Coulomb explosion process.

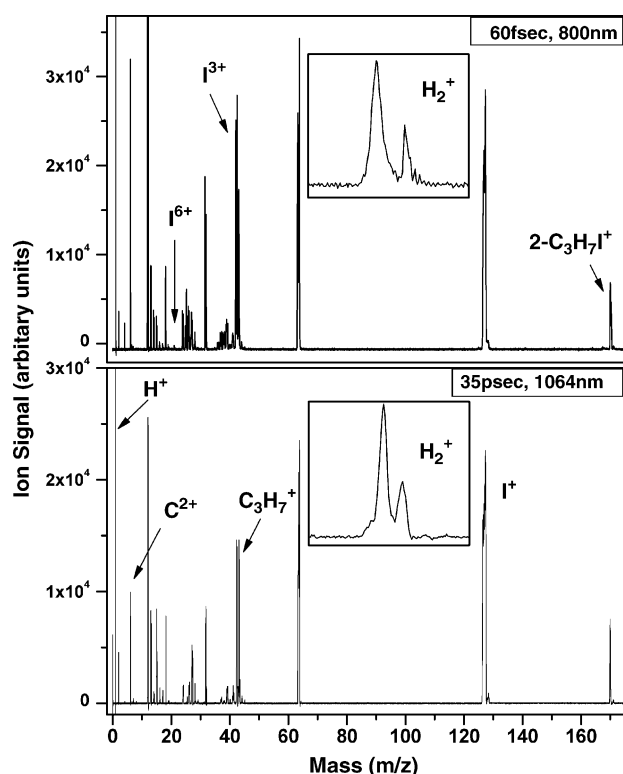


Fig. 1. Mass spectra of 2-iodopropane induced by 60 fs (800 nm) and 35 ps (1064 nm) at the intensity of $2 \times 10^{15} \text{ W cm}^{-2}$.

It could be argued that the observed H_2^+ ions are generated by ionization, within the pulse duration, of neutral H_2 fragments released from dissociation of neutral and/or singly charged parent molecules. This could be possible if the formation and the ejection of H_2 from the molecular skeleton could be completed on a time scale shorter than the pulse duration (60 fs). Thus, once again the question about the time scale of fragmentation in femtosecond ionization experiments is emerging, especially as far as the elimination of such light fragments is concerned [26,27]. As mentioned previously, from experimental work in similar molecular systems it is known that the H_2 formation takes place on a microsecond time scale [17]. Moreover, the calculated kinetic energies (Table 1) are found to be much higher than those reported for small alkanes. Furthermore, the kinetic energy values exhibit a dependence on laser intensity. This observation cannot be explained if the H_2^+ ions were the ionization products of neutral H_2 fragments. Alternatively, this implies that H_2^+ ions are generated with higher kinetic energy as the charged state of the precursors increases which is achieved by increasing the laser intensity. Therefore, the recorded H_2^+ ions in the femtosecond experiments should be considered as direct products of dissociation processes within multiply charged precursors. This is in agreement with the conclusions drawn for the case of linear alcohols under strong femtosecond laser irradiation [7]. It should be noted that, as presented in a following paragraph, this conclusion is clearly also evident in the 35 ps experiments.

In Fig. 2 the ratio of H_2^+ versus the ‘total ion signal’ and the H^+ ion yield as a function of the laser intensity (60 fs) are presented for the case of 2-iodobutane. Similar dependence on the laser intensity is also found for the other molecules studied. From this figure it is clear that the relative abundance of H_2^+ decreases with increasing laser intensity and for the range of intensities used, both ratios always have values smaller than 1. This observation is different from that reported for small alkanes when irradiated by a 157 nm laser beam and the H_2 formation is a reaction channel in the neutral manifold.

The dependence of these ratios on laser intensity (Fig. 2) can be understood if:

- (a) the ejection of the H_2^+ from the charged precursor takes place within the pulse duration and subsequently interacts with the laser field and finally fragments to H^+ and H atom and/or

Table 1
Estimated kinetic energy values (eV) of ejected H_2^+ ions

	$2 \times 10^{14} \text{ W cm}^{-2a}$		$2 \times 10^{15} \text{ W cm}^{-2a}$	
	60 fs ^b	35 ps ^b	60 fs ^b	35 ps ^b
1-Iodobutane	6.0 ± 0.8	1.7 ± 0.3	8 ± 1	2.0 ± 0.3
2-Iodobutane	8 ± 1	1.8 ± 0.3	12 ± 1	1.8 ± 0.3
1-Iodopropane	4.2 ± 0.9	1.6 ± 0.3	9 ± 1	1.9 ± 0.3
2-Iodopropane	5.8 ± 0.8	1.9 ± 0.3	12 ± 1	2.1 ± 0.3
Iodoethane	–	1.7 ± 0.3	–	1.8 ± 0.3
Methyl iodide	–	1.7 ± 0.3	–	1.9 ± 0.3

^a Laser intensity.

^b Pulse duration.

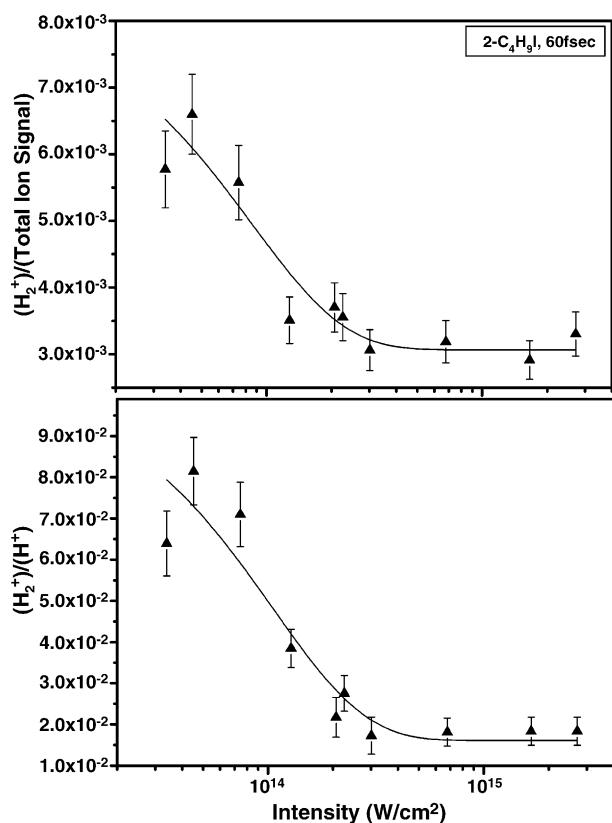


Fig. 2. The ratio of H_2^+ vs. the “total ion signal” and the H^+ ion yield produced by the interaction of 2-iodobutane with 60 fs, (800 nm) laser pulses as a function of the laser intensity.

(b) the H_2^+ formation is not facilitated in highly charged species, which are a consequence of the laser intensity increase.

It should be clarified that the ejection of the H_2^+ varies from that of neutral H_2 discussed earlier. As the charge state of the precursor increases with the laser intensity, the recoil energy of the H_2^+ ions also increases. For laser intensity about $2 \times 10^{15} \text{ W cm}^{-2}$ the kinetic energy of the H_2^+ ions is about $\sim 10 \text{ eV}$ (Table 1), which means that the velocity of the released H_2^+ is $\sim 0.3 \text{ \AA fs}^{-1}$. Thus, if the H_2^+ formation is a very fast process the fragmentation of H_2^+ by the same laser pulse is possible. The H_2^+ formation could be very fast if the H transfer barrier is strongly suppressed by the laser field and the whole process could be completed within few femtoseconds. A typical value for a C–H stretch vibration is about 2900 cm^{-1} which means that the vibration time is about 11 fs. The barrier suppression due to the external electrical field lasts for half of the optical cycle of the laser used ($\sim 1.3 \text{ fs}$) and therefore the effectiveness of the H_2^+ formation depends on the ‘height’ and the ‘length’ of the suppressed barrier. Thus, at high laser intensities there is strong barrier suppression and higher charge multiplicity for the precursor, which results in H_2^+ ejection with high kinetic energy. Therefore, the first process (a) cannot be excluded since the excitation from the ground state of H_2^+ into the $2p\sigma_u$ repulsive state leads to rapid dissociation into neutral H and H^+ and this process

is dipole allowed which means that it can take place even in the wings of the laser pulse.

On the other hand, the process (b) acts in the opposite direction. It implies that after the multiple ionization of the precursor, the rearrangement leading to H_2^+ formation becomes more difficult as the Coulombic repulsion increases. In other words, if the H_2^+ formation is a tunneling process – as it has been proposed [17] – the stronger Coulombic repulsion implies an increase of the barrier through which the tunneling should take place and therefore smaller probability for H_2^+ production.

Therefore, the H_2^+ elimination from the organic compounds under strong laser irradiation should be thought of as a dynamic effect where both these processes (a and b) could be in operation in a competitive way. It is inadvisable to draw further conclusions based on the available femtosecond data. Nevertheless, some insight on the H_2^+ elimination process can be gained from the analysis of the picosecond experimental data.

In Fig. 3 the ratios of H_2^+/H^+ and $\text{H}_2^+/\text{total ion signal}$ versus the 35 ps laser intensity at 1064 nm are presented. The difference from the femtosecond experiments is obvious. In the picosecond experiments the ratio H_2^+/H^+ increases with laser intensity and it reaches an almost constant value for intensity higher than $\sim 2 \times 10^{14} \text{ W cm}^{-2}$.

The increase of the ratio H_2^+/H^+ for intensity up to $2 \times 10^{14} \text{ W cm}^{-2}$ reflects the fact that the H_2^+ ion generation process has an intensity threshold. The determined intensity

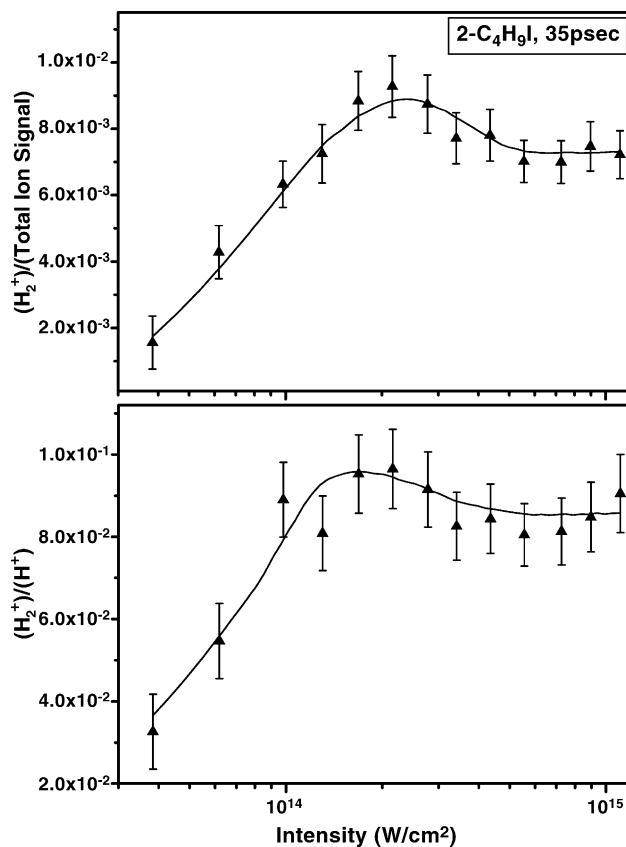


Fig. 3. The ratio of H_2^+ vs. the “total ion signal” and the H^+ ion yield produced by the interaction of 2-iodobutane with 35 ps, (1064 nm) laser pulses as a function of the laser intensity.

Table 2
Intensity thresholds ($\times 10^{14} \text{ W cm}^{-2}$) for H_2^+ production by picosecond laser pulses

λ (nm)	CH_3I	$1\text{-C}_3\text{H}_7\text{I}$	$2\text{-C}_3\text{H}_7\text{I}$	$1\text{-C}_4\text{H}_9\text{I}$	$2\text{-C}_4\text{H}_9\text{I}$
1064	1.0	0.46	0.45	<0.34	0.38
532	1.3	0.7	1.0	<0.7	1.3
355	2.5	0.9	1.0	1.1	0.7
266	4.2	6.1	4.6	7.2	3.6

thresholds for H_2^+ observation in the mass spectra for the laser wavelengths used are presented in Table 2. However, these experimental values should be considered as upper intensity limits, while lower ones could have been achieved, for instance, if a larger diameter hole had been used in the first ion optic. From these values it is evident that the intensity threshold increases as the wavelength decreases. This observation excludes that there is a contribution to the recorded H_2^+ signal from neutral H_2 molecular fragments, which are ejected and subsequently being ionized, by multiphoton processes, within the pulse duration. If the later was the case, then the H_2^+ intensity thresholds should be lower at the shorter laser wavelengths used, where the multiphoton ionization probability is higher. Furthermore, the trend of the intensity thresholds implies that if there is ejection of H_2 from neutral fragments these are generated after the pulse end, i.e., in a time scale longer than 35 ps. Thus, the recorded H_2^+ are ejected as ions, obviously, from the dissociation of charged precursors.

In the 35 ps laser experiments, it is probable that molecular fragments produced even from neutral molecular states can be ionized (or multiply ionized) by the same laser pulse. It is known that for alkyl iodides the rupture of the C–I bond, when the molecule is excited to the A state, is very fast and takes place in a time scale of ~ 100 fs [28,29]. The [P–I] fragments (and/or the

[P–I]⁺ if the dissociation takes place in the ionic manifold, where P stands for the parent ion) can absorb further photons and after rearrangement in their ionic states dissociate to H_2^+ . It should be mentioned that the above process is expected to contribute to the H_2^+ signal only from ionic states (the contribution from neutral hydrogen molecules has been excluded above). It is worth noting that the dissociation to [P–I] fragments has been identified even for the case of the femtosecond experiments [8].

The contribution of [P–I] fragments to the H_2^+ signal when picosecond pulses are used is expected to be more significant and can account for the different dependence of the ratio $\text{H}_2^+/\text{total ion signal}$ on laser intensity (Fig. 3) as compared to that of femtosecond experiments. This is due to the fact that the increase of laser intensity results in higher probability for [P–I] ionization and subsequently for H_2^+ ion formation. The peak profile of the H_2^+ signal provides evidence for this process. The peak component denoted by an asterisk (Fig. 4), which is well above the signal noise, corresponds to H_2^+ ions released with higher (~ 6 eV) kinetic energies and its dependence on laser polarization varies from the rest peak components. The intensity of this component is dramatically reduced when the polarization vector of the laser beam is vertical to the TOF axis. It is believed that H_2^+ ions are liberated from lighter (with respect to the parent ion) precursors which have been aligned with the polarization vector (this accounts for the stronger dependence on laser polarization) and they have higher charge multiplicity (higher recoil energies). It should be mentioned that, as it has been proposed earlier, the higher charged state of the parent ions for alkyl iodides at these laser intensities is P^{n+} with $n \leq 3$ and it is much lower compared to that achieved in femtosecond experiments performed at the same laser intensity [9,30].

In Fig. 5 the dependence of the ratio of $\text{H}_2^+/\text{total ion signal}$ on the laser intensity at different wavelengths for the case of 1-iodopropane is presented. From this figure it is evident that

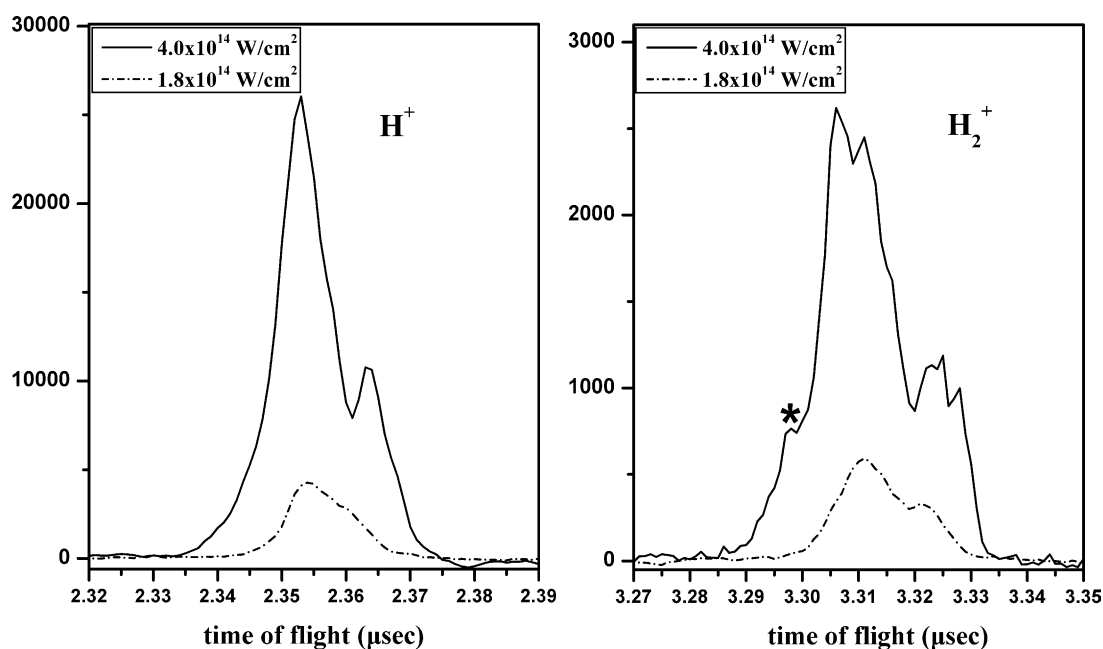


Fig. 4. The peak profiles of the H_2^+ and H^+ fragments of methyl iodide induced by 35 ps (1064 nm) laser pulses at different laser intensities.

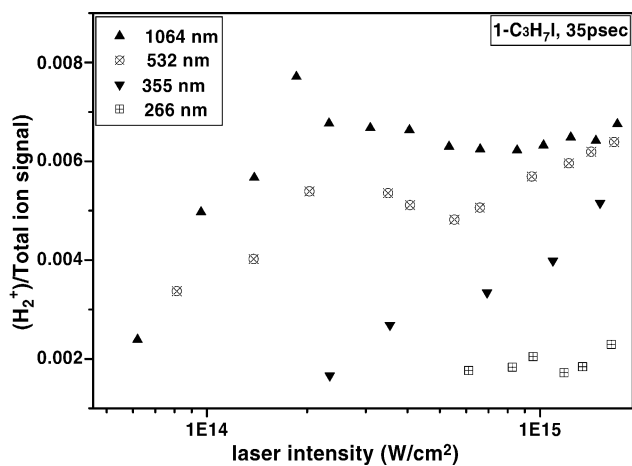


Fig. 5. The ratio of H_2^+ vs. the “total ion signal” produced by the interaction of 1-iodopropane with 35 ps (1064 nm) laser pulses as a function of the laser intensity.

the H_2^+ / “total ion signal” ratio decreases at shorter wavelengths and it seems that the longer optical cycle of a long-wavelength laser field facilitates the H_2^+ formation. This is conceivable in a model where the H_2^+ formation is attributed to a tunneling process with the reasonable consequence that the rearrangement leading to H_2^+ takes place within the pulse duration.

The analysis of our CH_3I data offers some additional information. This molecule is the simplest alkyl iodide molecule and the signal that corresponds to $[P-I]^+$ fragment exhibits a complex structure, which has been analyzed recently [30]. In Fig. 6a the enlarged TOF mass spectra region of CH_3^+ shows that there are three pairs of back and forward components. These components correspond to CH_3^+ ions ejected from differently charged states of the parent ion. The outer pair of peak components has been attributed to dissociation channels within triply charged parent ions $[P^{3+}]$ [30]. In the same figure (Fig. 6b) the relative ion yields of the H_2^+ and that of each of the three CH_3^+ pairs of components are shown as a function of laser intensity at 1064 nm. It is evident that the laser intensity thresholds for CH_3^+ ions generated from doubly charged parent ions $[P^{2+}]$ and that of H_2^+ are practically identical. This observation can be interpreted as an indication that H_2^+ ions are produced from the dissociation of $[P^{2+}]$ ions following molecular rearrangement. From the relative ion yields it can be deduced that about 10% of the $[P^{2+}]$ ions undergoes rearrangement and then fragments to molecular hydrogen, CH and iodine. At the same time, from the plot of the ratio H_2^+/H^+ versus laser intensity (Fig. 6c) it is clear that this ratio decreases for laser intensities higher than $\sim 2 \times 10^{14} \text{ W cm}^{-2}$. This value is very close to the intensity threshold of the CH_3^+ pair components that are produced by Coulomb explosion within $[P^{3+}]$ ions (Fig. 6b).

Once again the emerging question is what causes the decrease of the ratio at this laser intensity? As stated above, the molecular rearrangement leading to H_2^+ formation is taking place within the pulse duration and thus if these ions are released rapidly their fragmentation by the incident beam could account for the decrease of the ratio. Of course, the recoil energy, compared to that found in femtosecond experiments, is much lower ($\sim 1.7 \text{ eV}$)

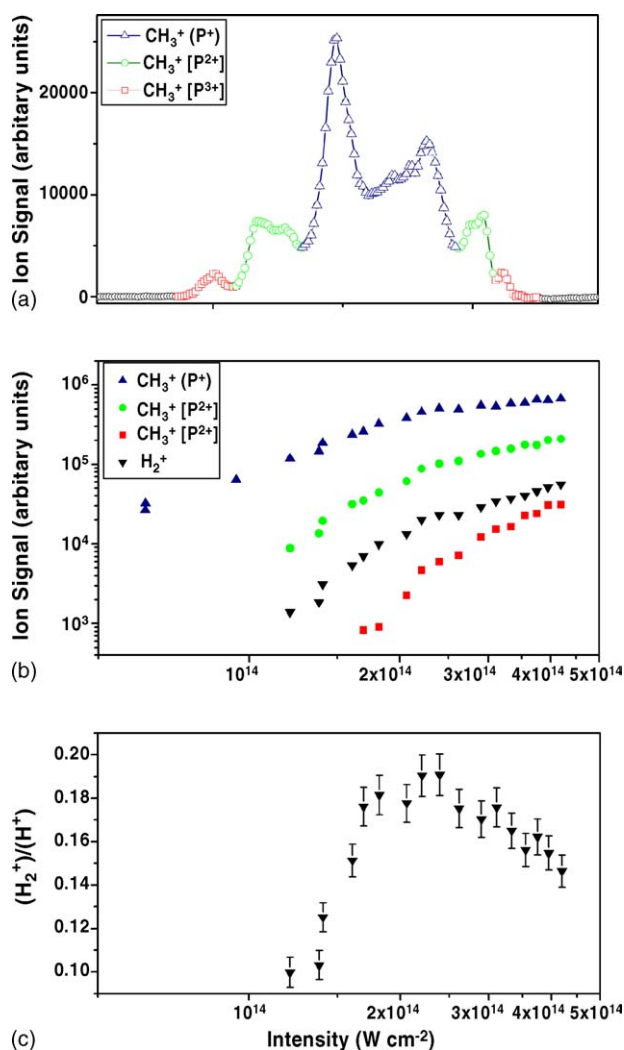


Fig. 6. (a) The peak profile of the CH_3^+ ion produced by the fragmentation of methyl iodide by 35 ps (1064 nm) laser pulses at the intensity of $10^{15} \text{ W cm}^{-2}$. The colors are used to discriminate ions coming from the dissociation of simply charged parent ions or the Coulomb explosion of multiply charged unstable ones $[P^{2+}]$, $[P^{3+}]$. (b) The variation of H_2^+ and CH_3^+ ions yields with laser intensity. The symbols “ \blacktriangle ”, “ \bullet ” and “ \blacksquare ” are used for the CH_3^+ ions produced by the fragmentation of P^+ , $[P^{2+}]$ and $[P^{3+}]$, respectively. (c) The ratio of the H_2^+ signal to that of H^+ as a function of laser intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

but this is compensated by the longer pulse duration. If this process is in operation then it is expected that the fragments (H and H^+) will share equally the available recoil energy of the H_2^+ ions. The estimated kinetic energy for the vast majority of the H^+ fragment ions at $4 \times 10^{14} \text{ W cm}^{-2}$ was found to be also $\sim 1.7 \text{ eV}$ and no peak component corresponding to H^+ ions with $\sim 0.8 \text{ eV}$ has been clearly recorded and maybe it is overshadowed by the higher kinetic energy species. In any case, this implies that the fragmentation of H_2^+ is not the main channel leading to H^+ ion production.

Alternatively, the reduction of the ratio H_2^+/H^+ versus laser intensity could be interpreted by assuming that for laser intensities $> 2 \times 10^{14} \text{ W cm}^{-2}$ the dissociation channels leading to atomic hydrogen ion production have higher efficiency com-

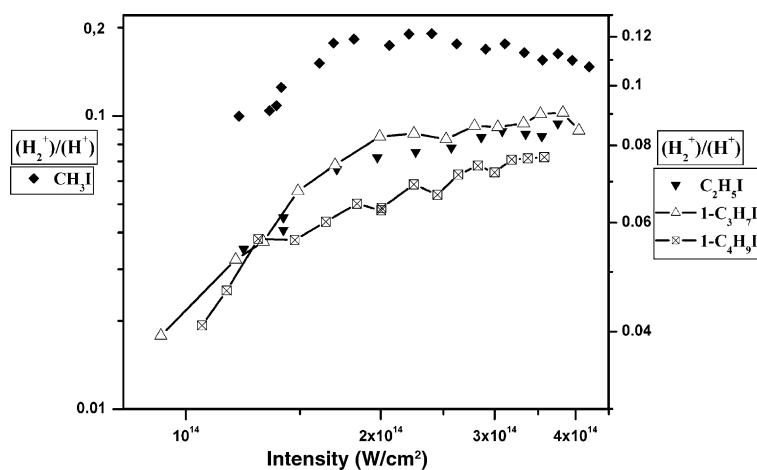


Fig. 7. The dependence on the laser intensity (35 ps, $\lambda = 1064$ nm) of the ratio H_2^+/H^+ for the studied alkyl iodides.

pared to those resulting in H_2^+ elimination. In other words that, at least for the case of methyl iodide, the H_2^+ ion formation channel is less efficient in parent ions $[P^{n+}]$ with $n > 3$. Of course, the generalization of the above interpretation for all alkyl iodides is not obvious since more dissociation channels are available and the corresponding processes are expected to be more complicated.

Although the minimum time needed for H_2^+ ejection cannot be defined precisely, the experimental data provide a way to estimate the maximum time interval within which the H_2^+ is liberated from the molecular skeleton. The shape of the ion peak that corresponds to the H_2^+ ions (well-recorded back and forward components) allows us to conclude that the ejection of these ions is taking place while the precursors were in the acceleration region of the TOF mass spectrometers used. This can be utilized for a rough estimation of the time scale needed for H_2^+ liberation. This type of calculations depends on the charged state and the molecular weight of the precursor. Thus, for the singly charged methyl iodide parent as precursor, the time is estimated to be more than 1 μ s, while for the doubly charged parent about 900 ns. If the singly charged $[P-I]$ ion ($m/z = 15$) is assumed as the precursor of H_2^+ then the estimated time is about 450 ns. Obviously, for the higher charged precursors the time is even less.

As far as the site specificity in H_2^+ formation is concerned it is possible to draw some conclusions based on Fig. 7 where the dependence of the H_2^+/H^+ ratio on laser intensity for different alkyl iodides is depicted. The laser wavelength was chosen to be 1064 nm because for this wavelength the H_2^+ signal is stronger and the statistical variation of the ratio smaller.

Wu et al. [14] have shown that at $\lambda = 157$ nm, the H_2^+ formation increases as the size of the molecular chain of small alkanes increases and that the H_2 fragments mostly come from central carbon atoms. Moreover, the same group has shown that for branched alkanes the H_2^+ formation becomes less efficient. From Fig. 7 it can be seen that as the number of the hydrogen atoms in the molecular skeleton increases the ratio H_2^+/H^+ remains almost constant, with the exception of the methyl iodide case.

The latter manifests the ability for H_2^+ formation from the $-CH_3$ group of the alkyl compounds. The almost constant ratio value for the larger molecules implies that there is contribution to H_2^+ formation from H atoms bonded to central carbon atoms of the molecular skeleton and the yield of this process is independent on the size of the alkyl chain. The fact that the ratio takes higher values in CH_3I could be interpreted as an indication that the H_2^+ formation is more efficient for the terminal CH_3 group, as compared to that from H atoms bonded to the rest carbons of the molecular chain. Otherwise, the ratio H_2^+/H^+ should have the same value for all molecules studied.

Thus, it could be argued that the suppression of the H transfer barriers is more efficient in the case of H atoms bonded to a terminal carbon atom.

4. Conclusions

From the femtosecond and picosecond experiments we conclude that the H_2^+ formation process when alkyl iodides are subjected to strong laser fields ($>10^{14}$ W cm^{-2}) varies from that reported for the case of alkanes at 157 nm.

Under strong laser irradiation, the recorded H_2^+ ions in the mass spectra are generated through Coulomb explosion within charged precursor following a molecular rearrangement. For the femtosecond experiments the charged precursors are mostly parent ions, while lighter fragment ions are also expected to act as precursors for H_2^+ when picosecond laser pulses are used.

From the picosecond experiments it is concluded that, for the case of methyl iodide, the H_2^+ is generated from the dissociation of $[P^{2+}]$ ions following rearrangement while it is possible that this mechanism becomes less efficient in higher charged precursors.

The wavelength dependence of H_2^+ implies that the mechanism involved in the H_2^+ generation is a tunneling process. This process, in the case of methyl iodide, leads to rearrangement for about 10% of the produced $[P^{2+}]$ ions.

Finally, our experimental data indicate that under strong laser irradiation the H_2^+ elimination process is more efficient for hydrogen atoms bonded to the terminal carbon of the alkyl chain.

The latter should be checked by further experiments with deuterated compounds in selective positions of the molecular skeleton.

Acknowledgements

We would like to express our thanks to the staff and administration of the TOPS Laboratory of the Strathclyde University and the Central Laser Facility of the University of Ioannina for their facilities and their assistance. This research was funded by the program “Heraklitos” of the Operational Program for Education and Initial Vocational Training of the Hellenic Ministry of Education under the 3rd Community Support Framework and the European Social Fund.

References

- [1] C. Cornaggia, *Phys. Rev. A* 52 (1995) 4328.
- [2] S. Shimizu, J. Kou, S. Kawato, K. Shimizu, N. Nakashima, *Chem. Phys. Lett.* 317 (2000) 609.
- [3] D.A. Card, E.S. Wisniewski, D.E. Folmer, A.W. Castleman Jr., *Int. J. Mass Spectrom.* 12270 (2002) 1.
- [4] D.A. Card, E.S. Wisniewski, D.E. Folmer, A.W. Castleman Jr., *J. Chem. Phys.* 116 (2002) 3554.
- [5] J. Chen, R. Ma, X. Li, H. Ren, H. Yang, Q. Gong, *J. Phys. B: At. Mol. Opt. Phys.* 37 (2004) 2501.
- [6] S. Wang, X. Tang, L. Gao, M.E. Elshakre, F. Kong, *J. Phys. Chem. A* 107 (2003) 6123.
- [7] M. Krishnamurthy, F.A. Rajgara, D. Mathur, *J. Chem. Phys.* 121 (2004) 9765.
- [8] C. Kosmidis, P. Siozos, S. Kaziannis, L. Robson, K.W.D. Ledingham, P. McKenna, D.A. Jaroszynski, *J. Phys. Chem. A* 109 (2005) 1279.
- [9] P. Siozos, S. Kaziannis, C. Kosmidis, *Int. J. Mass Spectrom.* 225 (2003) 249.
- [10] P. Siozos, S. Kaziannis, C. Kosmidis, A. Lyras, *Int. J. Mass Spectrom.* 243 (2005) 189.
- [11] S. Irle, K. Morokuma, *J. Chem. Phys.* 113 (2000) 6139.
- [12] S.H. Lee, Y.T. Lee, X. Yang, *J. Chem. Phys.* 120 (2004) 10983.
- [13] K. Tonokura, Y. Matsumi, M. Kawasaki, K. Kasatani, *J. Chem. Phys.* 95 (1991) 5065.
- [14] S.M. Wu, J.J. Lin, Y.T. Lee, X. Yang, *J. Chem. Phys.* 111 (1999) 1793.
- [15] J.J. Lin, S. Harich, D.W. Hwang, M.S. Wu, Y.T. Lee, X. Yang, *J. Chin. Chem. Soc.* 46 (1999) 3.
- [16] S.M. Wu, J.J. Lin, Y.T. Lee, X. Yang, *J. Phys. Chem. A* 104 (2000) 7189.
- [17] F. Güthe, M. Malow, K.M. Weitzel, H. Baumgärtel, *Int. J. Mass Spectrom.* 172 (1998) 47.
- [18] M. Malow, F. Güthe, K.M. Weitzel, *Phys. Chem. Chem. Phys.* 1 (1999) 1425.
- [19] T.N. Olney, G. Cooper, C.E. Brion, *Chem. Phys.* 232 (1998) 211.
- [20] P. Graham, K.W.D. Ledingham, R.P. Singhal, S.M. Hankin, T. McCanny, X. Fang, C. Kosmidis, P. Tzallas, P.F. Tadey, A.J. Langley, *J. Phys. B: At. Mol. Opt. Phys.* 34 (2001) 4015.
- [21] S. Shimizu, V. Zhakhovskii, F. Sato, S. Okihara, S. Sakabe, K. Nishihara, Y. Izawa, T. Yatsuhashi, N. Nakashima, *J. Chem. Phys.* 117 (2002) 3180.
- [22] D.A. Jaroszynski, B. Ersfeld, G. Giraud, S. Jamison, D.R. Jones, R.C. Isaac, B.M.W.C. Mcneil, A.D.R. Phelps, G.R.M. Robb, H. Sandison, G. Vieux, S.M. Wiggins, K. Wynne, *Nucl. Instrum. Methods Phys. Res. Sect. A* 445 (2000) 317.
- [23] A.D. Tasker, L. Robson, K.W.D. Ledingham, T. McCanny, S.M. Hankin, P. McKenna, C. Kosmidis, D.A. Jaroszynski, D.R. Jones, *J. Phys. Chem. A* 106 (2002) 4005.
- [24] S. Augst, P. Monot, L.A. Lompre, G. Mainfray, C. Manus, *J. Phys. B: At. Mol. Opt. Phys.* 25 (1992) 4181.
- [25] 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.
- [26] S.A. Trushin, W. Fuß, W.S. Schmid, *J. Phys. B: At. Mol. Opt. Phys.* 37 (2004) 3987.
- [27] T. Schlathölder, R. Hoekstra, S. Zamith, Y. Ni, H.G. Müller, M.J.J. Vrakking, *Phys. Rev. Lett.* 94 (2005) 233001.
- [28] D.P. Zhong, A.H. Zewail, *J. Phys. Chem. A* 102 (1998) 4031.
- [29] G. Knopp, P. Beaud, P. Radi, M. Tulej, T. Gerber, *Femtochemistry and Femtobiology, Ultrafast Dynamics in Molecular Science*, 2002, p. 117.
- [30] S. Kaziannis, P. Siozos, C. Kosmidis, *Chem. Phys. Lett.* 401 (2005) 115.