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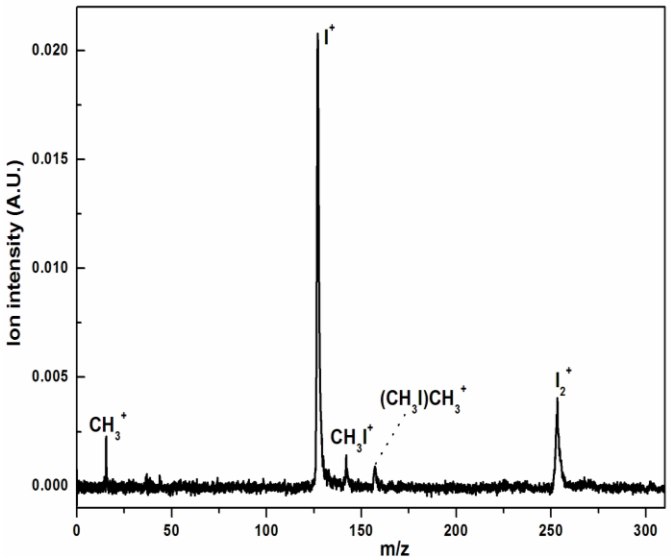
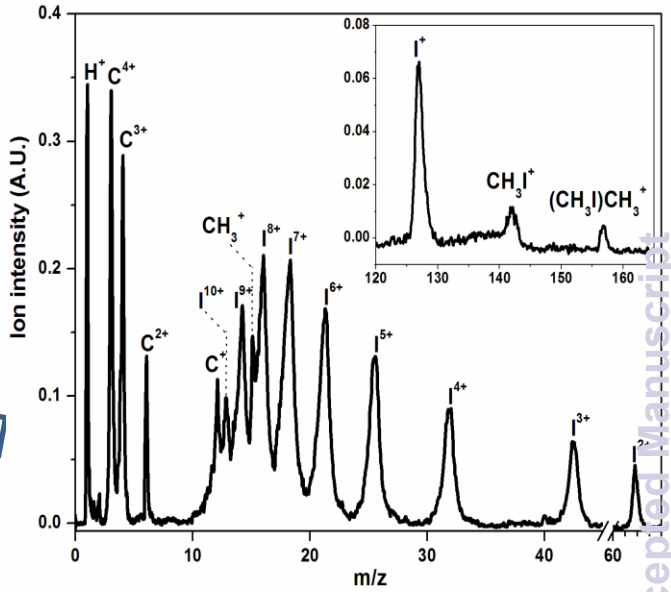
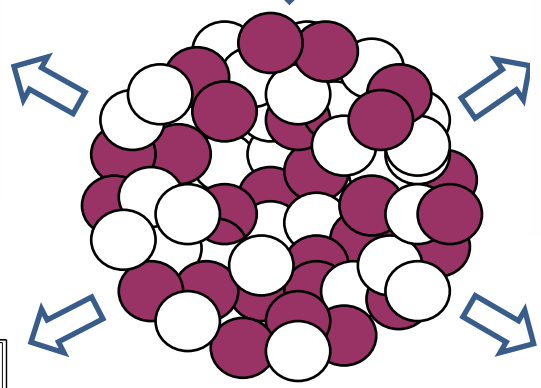
Singly charged positive ions



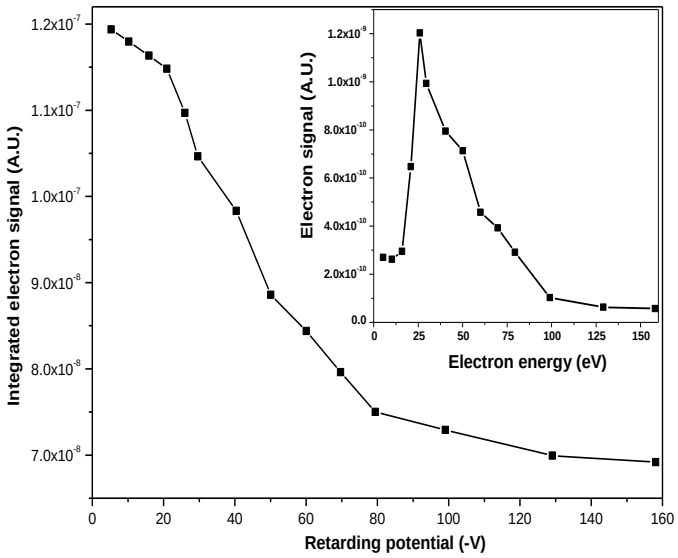
Multiply charged positive ions



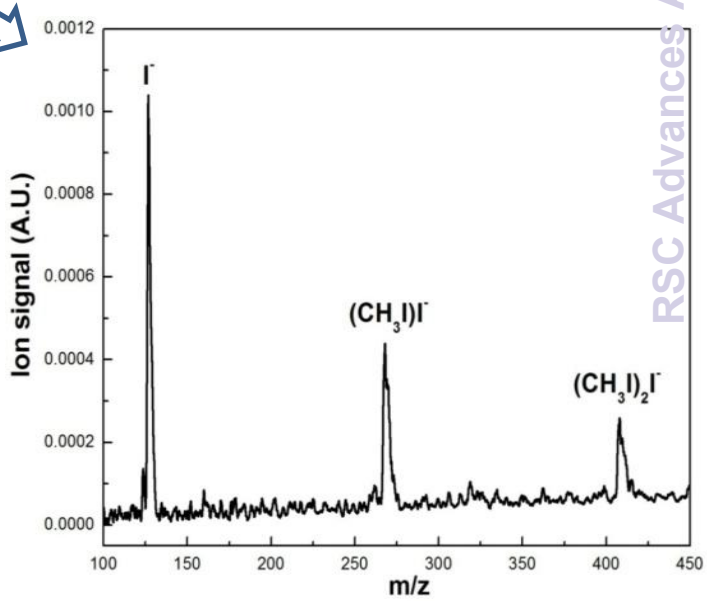
Laser light
I ~ 10^9 W/cm^2



CH_3I clusters



Energetic electrons



Singly charged negative ions

Ionisation of methyl iodide clusters using nanosecond laser pulses: Detection of multiply charged positive ions, negative ions and energetic electrons

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Abstract

Methyl iodide clusters has been ionised using laser pulses of intensity ~ 10^9 W/cm^2 at 266, 355, 532 and 1064 nm and the ions produced in laser-cluster interaction were analysed with time-of-flight mass spectrometer. Multiply charged atomic ions of carbon and iodine have been observed at 355, 532 and 1064 nm. Charge state of multiply charged atomic ions was found to enhance at longer laser wavelength with highest charge state of I^{10+} observed at 1064 nm. Charge density produced upon interaction with clusters was also measured at different laser wavelengths. Charge density was found to increase with laser wavelength which complements the time-of-flight mass spectra results. Generation of negative ions like I^-, $(CH_3I)I^-$, $(CH_3I)_2I^-$ were also observed in the mass spectra. In order to understand the ionisation mechanism of methyl iodide clusters at gigawatt intense laser field, kinetic energy of electrons produced upon laser-cluster interaction was measured at different laser wavelengths. At 266 and 355 nm, electron signal could not be observed because of low yield. However, at 532 and 1064 nm, electrons with kinetic energy up to ~50 & ~100 eV were observed having mean electron energy ~ 5 & ~25 eV respectively. Based on electron energy measurement, generation of multiply charged atomic ions can be explained using electron heating mechanism at gigawatt laser field.

Keywords: Methyl iodide clusters, multiply charged atomic ions, time-of-flight mass spectra.

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1. Introduction

Ionisation and fragmentation of methyl iodide clusters have been extensively studied using various techniques such as mass spectrometry[1], photofragment imaging spectroscopy[2], absorption spectroscopy[3] where D_2 or Xe lamp was used as ionisation source. In these studies, only singly charged fragment and cluster ions were observed. However, multiply charged atomic ions have been observed in methyl iodide clusters using laser pulses ranging from femtosecond to nanosecond time regime. Castleman and co-workers studied photoionisation of methyl iodide clusters using femtosecond laser pulses as a function of laser fluence and wavelength for different size clusters produced using different carrier gas.[4-6] Longer laser wavelength (795 nm) was found to interact more efficiently leading to higher charge state of carbon (up to C^{4+}) and iodine (I^{15+}) where laser fluence plays an important role.[4] At shorter wavelength (397 nm), the highest observed charge state was I^{7+} and C^{4+} where laser fluence has moderate dependence.[5] Moreover, heavier carrier gas was found to produce larger clusters which facilitate higher charge state formation for given experimental conditions.[4] These experimental observations were supported by molecular dynamics simulation which predicts the temporal evolution of a cluster system after the ionisation event.[7] The salient observations of methyl iodide clusters in femtosecond laser pulses were explained based on two ionisation models i.e. ionisation ignition model and coherent electron motion model.[4] Using picoseconds laser pulses of intensity ~10^{12}-10^{13} W/cm^2, Kosmidis and co-workers studied photoionisation of methyl iodide clusters at 266 nm, 532 nm and 1064 nm.[8,9] Multiply charged ions of iodine and carbon were observed at 532 nm and 1064 nm and charge state of these atomic ions was found to increase with wavelength.[8] The explosion of the multiply charged cluster ions is found to be isotropic, while an asymmetric charge distribution prior to their fragmentation is observed.[9] These authors suggested that clusters are initially singly ionized by multiphoton absorption and an internal electric field is created within the cluster. The electric field results in a higher distortion of the internal barriers and an increased ionisation of the cluster which finally explodes leading to energetic multiply charged ion production.[8] In nanosecond regime, methyl iodide clusters were ionised with laser pulses of intensity ~10^{9}-10^{11} W/cm^2 as a function of laser wavelength, intensity and polarization. Multiply charged atomic ions of carbon and iodine were observed in the mass spectrometer. Extent of charge state was found to increase with laser wavelength.[10,11] With increase in laser intensity, charge state of atomic ions remains unchanged however an increase in the kinetic energy of multiply charged ions was observed.[12] Moreover, charge

state and kinetic energy of multiply charged ions were studied as a function of laser polarization. Multiply charged ions were found to disintegrate isotropially with laser polarization and charge state and kinetic energy remains unaffected by the laser polarization.[13] In order to explain these observations, combination of multiphoton ionization and electron impact ionization has been considered.[14]

In the present work, methyl iodide clusters have been ionised using nanosecond laser pulses of intensity ~ 10^9 W/cm^2 and experiments have been carried out at 266, 355, 532 and 1064 nm. Singly charged fragment ions were observed at 266 nm while multiply charged atomic ions of iodine and carbon were observed in the mass spectra of methyl iodide clusters at 355, 532 and 1064 nm. In order to determine the total number of ions produced as a result of ionisation process under particular set of experimental conditions, charge density has been measured as a function of laser wavelength. In addition to positive ions, negative ions were also detected by changing the detector bias in the mass spectrometer. In order to understand the ionisation mechanism leading to multiply charged atomic ions, kinetic energy of electrons produced in laser-cluster interaction has been measured as a function of laser wavelength. In our earlier work, electron energy has been measured for 532 nm laser pulses[11], while in the present study, variation of electron energy as a function of laser wavelength has been demonstrated for methyl iodide clusters which is decisive for understanding the mechanism of generation of multiply charged ions under our experimental conditions. Moreover, role of screening effect due to ions and electrons within the cluster has been discussed in lowering the ionisation energy of multiply charged atomic ions which is relevant in ionisation process of methyl iodide clusters at gigawatt laser field.

2. Experimental details

Details of the experimental setup have been described in our earlier publications [15-17] and only a brief description relevant to this work is given here. Neutral methyl iodide clusters were generated via supersonic expansion of CH_3I vapors seeded in argon at a pressure of 3 bar using a pulse valve (0.8 mm nozzle diameter and 300 μs pulse duration). The supersonic jet so produced was skimmed at a distance of 5 cm from the pulsed nozzle. The distance between the skimmer and the ionization region is 17 cm. Ionization was carried out using fundamental (1064 nm) as well as different harmonics (second (532nm), third (355 nm) and fourth (266 nm)) of a pulsed Nd:YAG nanosecond laser (Quanta System, Italy; 10 ns pulse width, GIANT G790-10). The positive and negative ions so formed were accelerated and guided into a 100 cm field free region using a home built Wiley–McLaren assembly and

detected using a channel electron multiplier (CEM) detector (Dr. Sjuts Optotechnik GmbH, Germany). Typical voltages applied to the repeller and extractor grids were ± 2700 and ± 2000V, respectively and polarity of the applied voltage was changed according to the polarity of the ions. The ion signal from the CEM detector was recorded on a digital storage oscilloscope and averaged for 500 shots. The averaged signal was finally transferred to a computer for further processing. The mass resolution of the instrument is ~300.

For total charge density measurements, the time-of-flight mass spectrometer was modified by replacing the repeller and accelerator grids by solid thin metal plates (anode and cathode) for collecting the total charge produced in the laser-cluster interaction zone. A sufficiently high positive voltage (3000 V) was applied to the anode in order to repel the ions towards the cathode (collector) and the ion current was measured across a suitable resistance (10 kΩ) connected to the collector plate[18].

For kinetic energy measurement of electrons produced in photoionisation of methyl iodide clusters, an electron energy analyzer setup was designed and mounted at a distance of ~ 8 cm from the laser-cluster interaction zone. Electron energy analyser is based on retarding field method and was fixed orthogonally to the direction of laser and cluster beam. The analyzer consists of three stainless steel grids in 0-V-0 configuration (1 cm away from each other) for energy filtering and is coupled with a CEM detector. The CEM detector has been suitably configured for detection of electrons.

3. Results and Discussions

3.1 Time-of-flight mass spectra of methyl iodide clusters at 266, 355, 532 and 1064 nm

Figure 1(a) represents time-of-flight mass spectrum of methyl iodide clusters at 266 nm having laser intensity of ~ 10^9 W/cm^2. The major ion peaks was due to I^+ at m/z 127 along with weak peaks of CH_3^+, CH_3I^+, $(CH_3I)CH_3^+$. The mass spectrum is in agreement with the earlier observed results of Choi *et al.*[1] Further, molecular iodine (I_2^+) was observed in the mass spectra at m/z 254. Formation of I_2^+ can be attributed due to direct concerted elimination from the ionised cluster[19, 20].

Figure 1 (b) depicts the time-of-flight mass spectrum of methyl iodide clusters at 355 nm under laser intensity of ~ 10^9 W/cm^2. The mass spectra consists of singly charged ion fragments H^+, C^+, CH_3^+, I^+, CH_3I^+ and $(CH_3I)CH_3^+$ due to multiphoton ionisation of methyl iodide clusters. Apart from these, doubly charged carbon (C^{2+}) and iodine (I^{2+}) ions were also observed in the mass spectrum at m/z 6 and 63.5 respectively. This observation is different to

the earlier observed mass spectra of methyl iodide clusters at 355 nm which consists of only singly charged fragment ions [1, 14].

Figure 1 (c) represents the time-of-flight mass spectrum of methyl iodide clusters at 532 nm having laser intensity of ~ 10^9 W/cm^2. Multiply charged atomic ions of carbon and iodine were observed up to +4 charge state. Thus, increase in the laser wavelength enhances the charge state of atomic ions under similar experimental conditions. Based on our earlier results and by Li and co-workers, the highest observed charge state of carbon and iodine at 532 nm was up to +3. [10 - 13] This enhancement in the charge state in the present study can be explained based on the cluster size effect. In earlier studies, mass spectra were recorded for clusters produced with 0.5/ 0.6 mm nozzle diameter however the present mass spectrum was recorded with 0.8 mm nozzle diameter. Larger nozzle diameter will produce larger average cluster size based on the Hagena's empirical formula. Dimensionless Hagena's parameter (Γ^*) is expressed as [21] -

$$\Gamma^* = k\frac{(d/\tan\alpha)^{0.85}}{T_0^{2.29}}P_0 \qquad \text{(Eq .1)}$$

where d is the nozzle diameter (μm), α the expansion half angle (α=45° for sonic nozzles, α<45° for supersonic nozzles), P_0 the stagnation pressure (mbar), T_0 the pre-expansion temperature (Kelvin) and k a constant related to the bond formation. Thus, larger cluster size helps to induce higher multiple charge state formation in methyl iodide cluster. Equation 1 qualitatively explains the enhancement in charge state of multiply charged atomic ions, due to increase in nozzle diameter. Here we would like to mention that Equation 1 has been widely used for estimation of average size distribution of clusters produced via supersonic expansion of pure gases. However under our experimental condition, which involves cluster generation by bubbling inert carrier gas through a liquid methyl iodide sample, estimation of cluster size distribution of methyl iodide clusters on the basis of above equation is inappropriate.[22] Under our experimental conditions, which involves excessive ionization/fragmentation of methyl iodide clusters upon interaction with laser pulses cluster fragment ions up to $(CH_3I)_{5\text{-}6}CH_3^+$ are typically observed,[11] though the actual cluster size distribution of neutral methyl iodide clusters is expected to be much higher than those observed in the mass spectra.

Figure 1 (d) shows the time-of-flight mass spectrum of methyl iodide clusters at 1064 nm having laser intensity of ~ 10^9 W/cm^2. Apart from singly charged fragments (H^+, C^+, CH_3^+, I^+, CI^+, CH_3I^+ and $(CH_3I)CH_3^+$) multiply charged ions of carbon and iodine were

observed. The highest charge state of iodine was found to be +10. Thus, our results clearly indicate that longer wavelength leads to higher charge state formation as a result of interaction with methyl iodide clusters. Here it is worth mentioning that the threshold laser intensity required to form multiply charged ions is higher at 1064 nm compared to 355 or 532 nm. Typically, the threshold laser intensity for observation of Coulomb explosion at 532 nm was found to be ~ 2 x 10^9 W/cm^2 however for 1064 nm the value is about 2.5 times more (~ 5 x 10^9 W/cm^2). This is due to higher multiphoton ionisation cross-section of methyl iodide clusters at shorter wavelength compared to longer wavelength.

3.2 Charge density measurement of methyl iodide clusters at different laser wavelength

Mass spectrum of methyl iodide clusters shows enhancement in charge state of carbon and iodine with increasing laser wavelength which is contrary to common perception, as photon energy decreases with increase in laser wavelength. However, simply based on the charge state observed in the mass spectra, it is difficult to comment on the efficiency of laser-cluster interaction at different wavelengths. It is possible that the total yield of ions (including multiply charged ions) generated in the ionization volume at longer wavelength might be less than the total yield of singly charged ions generated at shorter wavelength. To throw more light on the interaction of lasers with clusters at different wavelengths, charge density of ions generated upon the ionization of methyl iodide clusters at 266, 355, 532 and 1064 nm was quantified using the parallel plate method.

In order to determine charge density at different wavelengths, ion optics of the time-of-flight mass spectrometer was modified as described in experimental section. The charge density at different wavelength is plotted in figure 2 as a function of extraction voltage. For a particular wavelength, with increase in extraction voltage, charge density was found to increase and finally saturate at higher voltage. Thus, at higher voltage, saturation of the charge density value indicates complete collection of the ions in the interaction zone. Thus, the saturated charge density value will represent the charge density of interaction zone at the respective wavelength. The charge density of interaction zone was found to be 4 x 10^9, 2 x 10^{10}, 2 x 10^{11} and 9 x 10^{11} charges/cc at 266, 355, 532 and 1064 nm respectively. Since experiments have been carried under similar expansion conditions, neutral molecule density in the interaction zone is expected to be similar. However, more than two orders of magnitude enhancement in the charge density has been observed from 266 to 1064 nm. Thus, based on the charge density of the interaction zone at different wavelengths and the charge state of the multiply charged ions it can be concluded unambiguously that efficiency of laser-cluster interaction increases with laser wavelength.

3.3 Detection of negative ions in methyl iodide clusters

Negative ion formation depends on the electron affinity of neutral atom/molecule and the amount of energy released due to addition of an electron to the neutral atom/molecule is the measure of electron affinity. Halogen atoms have very high electron affinity since addition of one electron leads to stable electronic configuration. Therefore, we tried to explore possibility of negative ion formation in methyl iodide clusters which contains iodine atom having high electron affinity of ~ 3.05 eV [23]. Negative ions were detected by suitably modifying the ion optics of mass spectrometer and detector system. Figure 3 represents the time-of-flight mass spectrum of negative ions when methyl iodide clusters were irradiated with 532 nm laser pulses. The mass spectrum consists of I^- as the major ion peak along with cluster ion signal $(CH_3I)I^-$ and $(CH_3I)_2I^-$. Similar mass spectra have been observed when methyl iodide clusters were interacted with other wavelengths. Based on the ion intensity of the negative ions, it can be concluded that the yield is much less compared to positive ions.

Most of the earlier reports of negative ion formation in methyl iodide monomer and cluster deal with low energy electron attachment method.[24, 25] Using picoseconds laser pulses, Kosmidis and co-workers showed negative ions like H^-, I^- $C_xH_y^-$ (x = 1, 2; y = 1, 2) in methyl iodide clusters at laser intensity ~10^{12}-10^{13} W/cm^2.[26] In the present study nanosecond laser pulses of intensity ~ 10^9 W/cm^2 has been used for methyl iodide clusters to detect negative ions. Previously, negative ions were observed in CF_2Br_2 clusters at laser intensity ~10^9 W/cm^2.[27] Generation of negative ion formation has been explained based on dissociative electron attachment process. In the present study, formation of negative ions in methyl iodide clusters can also be explained using similar mechanism.

Observed negative ion signals in methyl iodide clusters are I^-, $(CH_3I)I^-$, $(CH_3I)_2I^-$ which can be explained based on the mechanism (R1 and R2 channel) shown below [25]-

$$CH_3I + e^- \rightarrow \quad CH_3I^{*-} \rightarrow CH_3 + I^- \qquad (R1)$$

$$(CH_3I)_n + e^- \rightarrow CH_3 + I^-(CH_3I)_{n-1} \qquad (R2)$$

For dissociative electron attachment, electron energy plays a crucial role in determining the electron attachment cross-section to a particular atom or molecule. In case of methyl iodide molecule, highest electron attachment cross-section for I^- was 5.8 x 10^{-15} cm^2 at resonance electron energy of 0.17 eV which decreases to 9.3 x 10^{-21} cm^2 at 8.6 eV. Moreover, an electron attachment cross-section of ~ 3.2 x 10^{-19} cm^2 was reported at electron energy of 16.5 eV in the polar dissociation continuum of CH_3I.[28] Under our experimental conditions, electron energy is found to be much more than thermal electron (See section 3.5), thus electron attachment cross-section is expected to be low. As a result, yield of negative

ions was found to be less and constitutes a minor channel in laser-cluster interaction at gigawatt laser field.

3.4 Probable mechanism of multiply charge atomic ion formation at gigawatt intensity laser field

Observation of multiply charged atomic ions in CH_3I cluster photo ionization can be explained qualitatively by the three-stage cluster ionization mechanism, [29,30] which suggests that upon multi-photon ionization of the cluster, some of the liberated electrons (i.e. inner ionized electrons) are caged within the cluster. These confined electrons, which are under the influence of Coulomb field inside the cluster, keep extracting energy from the laser pulse via inverse Bremsstrahlung (IBS) process during electron-ion and electron-neutral collisions. Once the electron energy exceeds the ionization energy, further ionization can occur via electron impact ionization, resulting in augmentation of the charged state on the cluster. This sequence of events continues until a stage comes when Coulomb repulsion overcomes the total cohesive energy of the cluster and the multiply charged cluster explodes resulting in formation of multiply charged atomic ions with large kinetic energy. The rate of energy extraction by the electron via IBS process from the laser pulse is given by equation (2) [31]:

$$\frac{dE}{dt} = U_p \text{x } \nu \qquad \text{(Eq. 2)}$$

Here **ν** is the collision frequency of the inner ionized electrons and of the order of ~ 10^{14}-10^{15} Hz [32] and U_p is ponderomotive energy of electrons given by equation (3) -

$$U_p(\text{eV}) = 9.33 \text{ x } 10^{-14} I(W/cm^2)\lambda^2(\mu m^2) \qquad \text{(Eq.3)}$$

where I, λ are laser intensity and wavelength respectively. From equation 3, it is clear that as wavelength (λ) increases, ponderomotive energy (U_p) of electrons increases quadratically for a given laser intensity. As a result, net energy extraction by the electron from the optical field is higher at longer wavelength. Thus, higher level of ionization and charging is expected at longer wavelength, which is qualitatively in agreement with the mass spectrometer and charge density results.

In order to understand the role of electron impact ionisation for generation of multiply charged ions and validate the three stage cluster ionisation mechanism under our experimental conditions, it is necessary to determine energy of the electrons produced as a result of laser-cluster interaction. Thus, electron energy distribution has been measured for methyl iodide clusters at different wavelengths and presented in the subsequent section.

3.5 Determination of kinetic energy of electrons in methyl iodide clusters at different wavelengths

Kinetic energy of electrons produced as a result of interaction of methyl iodide clusters with different laser wavelength has been measured using retarding field analyser. At 266 and 355 nm, no electron signal was detected. This could be because of lower charge state and charge density associated with these two wavelengths due to less efficient laser-cluster interaction. Figure 4 and 5 represents the electron energy distribution of methyl iodide clusters at 532 and 1064 nm respectively. At 532 nm, the mean electron energy lies ~ 5-10 eV with cut-off up to 50 eV. On the contrary, at 1064 nm, mean electron energy lies in the range of 25-50 eV with cut-off up to ~ 100 eV. Previously, electron energy was measured for methyl iodide clusters at 532 nm which shows similar trend with the present result.[11, 33] In the present experiment, electron energy of methyl iodide clusters has also been measured at 1064 nm and compared with 532 nm results.

Considering the ionisation energy of methyl iodide and photon energy of 532 and 1064 nm, one can calculate the electron energy ($nh\gamma$ – I.E.) after initial multiphoton ionisation process. Based on this consideration, electron energy is expected to be ~ 2 eV, 0.9 eV for 532 and 1064 nm respectively. However, experimental result demonstrates that the highest electron energy extends up to ~ 50 eV, 100 eV at these two wavelengths. Thus, energisation of electrons at these two wavelengths in the laser field has been observed after initial multiphoton ionisation which was proposed in three stage cluster ionisation model. Moreover, energisation of electrons was expected to be more at longer wavelength based on the inverse bremsstrahling absorption mechanism and experimentally observed electron energy at different laser wavelength follows the trend. Therefore, electron energy measurement validates the three stage cluster ionisation mechanism to generate multiply charged ions under gigawatt laser intensity conditions.

Based on electron energy measurement, generation of multiply charge atomic ions at different laser wavelength can be explained using electron impact ionisation. However, if we compare the ionisation energy of the highest observed charge state and the maximum observed electron energy at a particular wavelength, there is an inconsistency. At 532 nm, highest observed charge state was C^{4+} having ionisation energy of 64.49 eV though the maximum electron energy was found to be ~ 50 eV. Similarly, at 1064 nm, highest observed charge state of iodine was +10 having ionisation energy 202.8 eV but maximum electron energy limits to ~ 100 eV. To explain the discrepancy, screening effect in the ionised cluster has been evoked.

3.6 Screening effect in the cluster for lowering of ionisation energy of multiply charged ions

Screening effect arises within the ionised cluster because of presence of ion and electrons produced as a result of ionisation of the cluster constituents. Presence of each positive ion produces an internal electric field equivalent to ~ 10^9 V/m on the neighbouring atom within the cluster. [26] However, the effective electric field produced within the cluster is difficult to calculate due to presence of large number of ions and electrons. The high electric field produced due to positive ions is expected to lower the Coulombic barrier of neutral atoms/ ions present in the vicinity. Thus, ionisation energy of multiply charged ions decreases thereby facilitating higher charge state formation. Moreover, inner ionised quasi free electrons also assist the ionisation process by decreasing the ionisation energy of the charged species. Trajectories of the quasi free electrons are bent towards the ion due to Coulombic interaction. This result the increase of the average electron density on the ion compared to the average electron density of the cluster. Consequently, quasi free electrons will screen the nucleus more efficiently thereby decreasing the binding energy of the electrons of singly or multiply charged ions within the ionised cluster. Thus, ionisation energy of cluster constituents is expected to be lower than isolated atom/ion due to both ions and electrons which in turn facilitates generation of multiply charged atomic ions.

The extent of screening effect in the ionised cluster can be calculated based on equation (4) [34] –

$$E_{I.E.} = \frac{Z_{eff}^2}{2n^2} - \frac{Z_{eff}}{R} + \frac{[3n^2 - l(l-1)]}{4R^2} - \frac{n^2[5n^2 + 1 - 3l(l+1)]}{12 Z_{eff} R^3} \quad \text{(Eq. 4)}$$

where, $E_{I.E.}$ = ionisation energy of atomic ions after considering screening effects, Z_{eff} = effective charge of the atomic core = $n\sqrt{2E_i}$, E_i = ionisation energy of isolated atomic ion, n = principal quantum number, l = azimuthal quantum number, R = Debye radius = $\sqrt{\frac{T_e}{4\pi n_e}}$, T_e = electron energy, n_e = electron density = $Q(n_a \Sigma Z_i m_i)$, Q = fraction of molecules that are ionized in cluster medium, n_a = number density of molecules in clusters, Z_i = charge state of atomic ions, m_i = number of particular element in a molecule. Cluster density is considered as the liquid density of methyl iodide (2.28 g/cm^3), corresponding to n_a = 0.00143 a.u. Calculations are performed for different charge state atomic ions of carbon and iodine, at varying electron energy, assuming 1% ionization (Q = 0.01) in cluster medium. Figure 6 represents the lowering of ionisation energy of multiply charged carbon and iodine as a function of electron energy due to screening effect. From the figure, it is very clear that,

screening effect is more dominant at lower electron energies which eventually lead to lowering of the ionisation energy of different charge state of carbon and iodine. Thus, based on screening effect generation of multiply charged species can be explained even with low energy electron impact ionisation within the ionised cluster.

4. Conclusions

Methyl iodide clusters were photoionised with nanosecond laser pulses of intensity ~ 10^9 W/cm^2 at 266, 355, 532 and 1064 nm and the ions have been probed using time-of-flight mass spectrometer. Multiply charged atomic ions of carbon and iodine have been observed at 355, 532 and 1064 nm. Charge state of multiply charged ions was found to increase with increasing laser wavelength and the highest charge state was I^{10+} observed at 1064 nm. The charge density of interaction zone was found to be 4 x 10^9, 2 x 10^{10}, 2 x 10^{11} and 9 x 10^{11} charges/cc at 266, 355, 532 and 1064 nm respectively. Thus, charge density results complement the observation of time-of-flight mass spectrometer. In addition to positive ions, negative ions like I^-, $(CH_3I)I^-$, $(CH_3I)_2I^-$ were also observed in the mass spectra. Observation of negative ions can be explained based on dissociative electron attachment to the neutral molecule. In order to understand the mechanism of formation of multiply charged positive ions, electron energy has been measured as a function of laser wavelength. Based on the electron energy measurement, energisation of electrons in the laser field has been observed and electron energy found to increase with laser wavelength. Thus, energised electron plays an important role in producing multiply charged ions at gigawatt intense laser field. Moreover, role of screening effect was also considered which helps to decrease the ionisation energy of multiply charged atomic ions within the cluster. As a result, electrons having comparatively lower energy are able to cause higher charge state within the ionised cluster. Therefore, these results help in understanding of the ionisation mechanism of methyl iodide clusters comprehensively at gigawatt laser intensity.

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Figure Caption

Figure 1: Time-of-flight mass spectrum of methyl iodide clusters at (a) 266 (b) 355 (c) 532 and (d) 1064 nm under laser intensity of ~ 10^9 W/cm^2. Please note that the mass scales are different for all the reported spectra, for clarity.

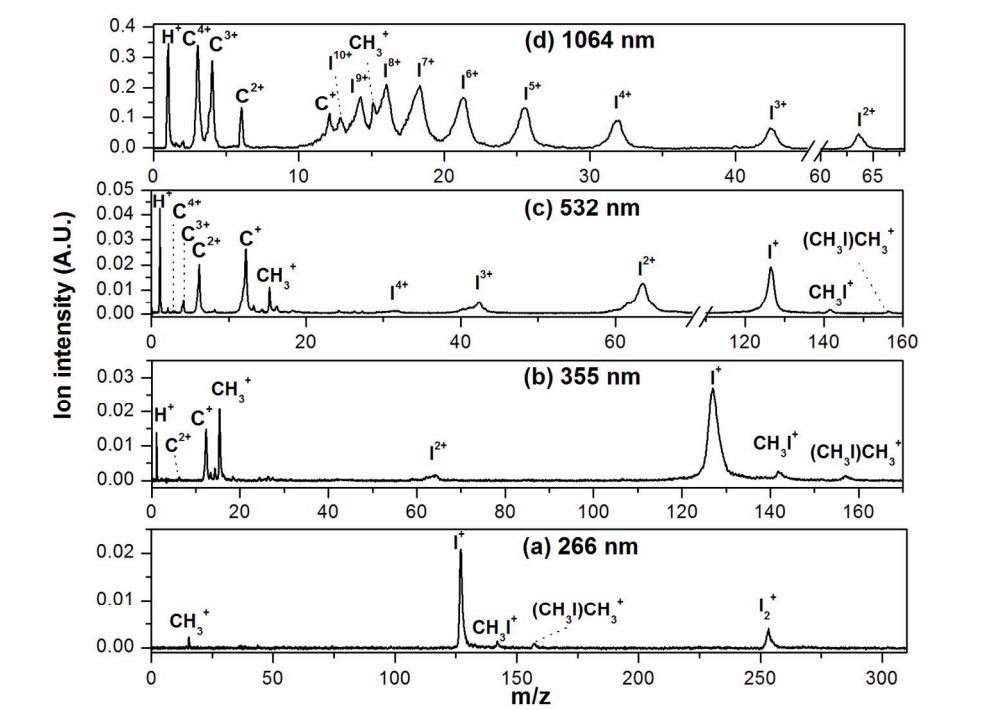
Figure 2: Charge density of methyl iodide cluster as a function of applied voltage between parallel plates at 266, 355, 532, and 1064nm.

Figure 3: Negative ion time-of-flight mass spectra of CH_3I clusters at 532 nm under a laser intensity of ~ 10^9 W/cm^2.

Figure 4: The integrated electron intensity as functions of retarding potential obtained upon irradiation of methyl iodide clusters with 532 nm laser pulses. The inset shows the area normalised electron energy distribution generated from the integrated data.

Figure 5: The integrated electron intensity as functions of retarding potential obtained upon irradiation of methyl iodide clusters with 1064 nm laser pulses. The inset shows the area normalised electron energy distribution generated from the integrated data.

Figure 6: Calculated $E_{I.E.}$ of I^{n+}(n = 2–10) and C^{n+}(n = 2–4) as a function of electron energy.



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297x209mm (150 x 150 DPI)

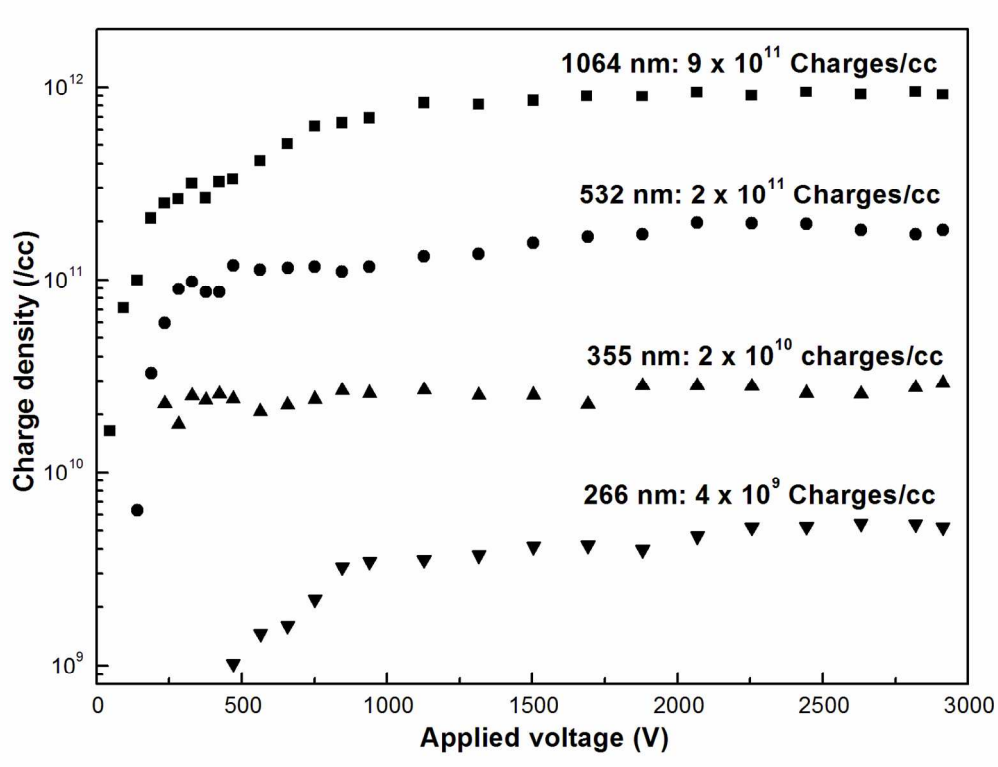
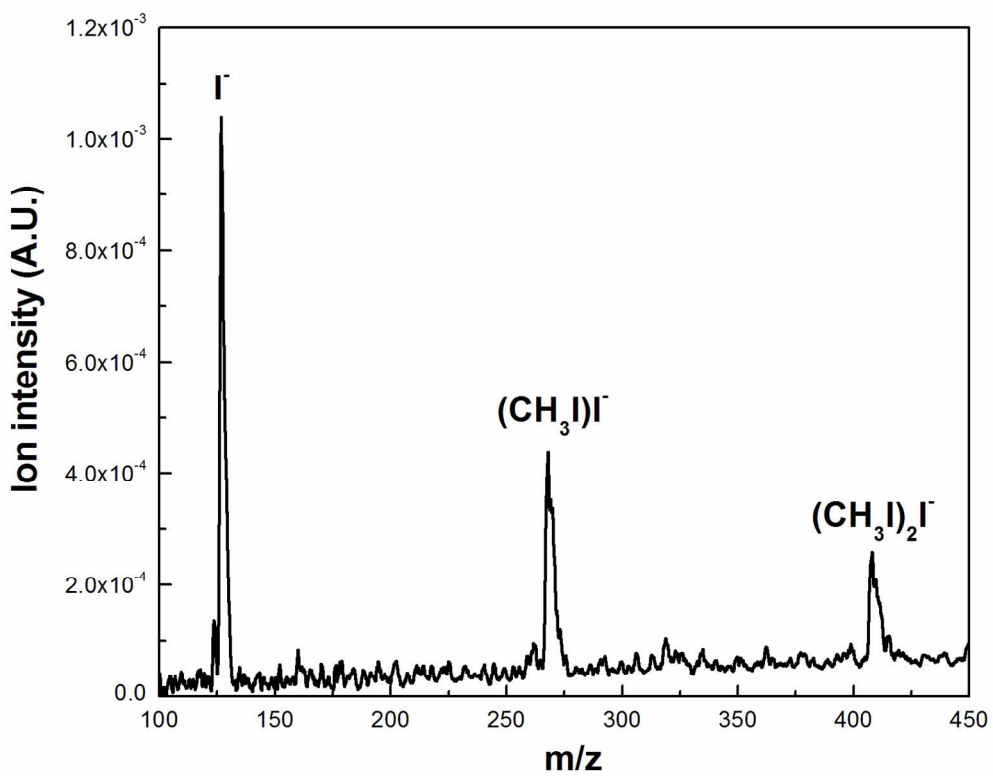


Figure 2: Charge density of methyl iodide cluster as a function of applied voltage between parallel plates at 266, 355, 532, and 1064nm.
279x215mm (150 x 150 DPI)



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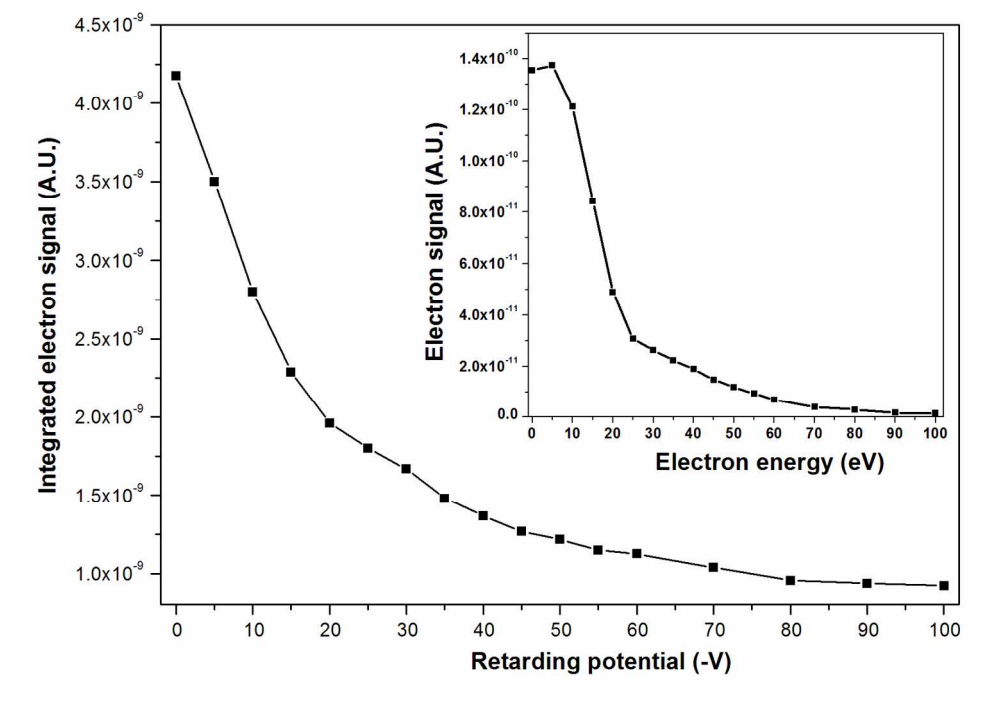
279x215mm (150 x 150 DPI)



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297x209mm (150 x 150 DPI)

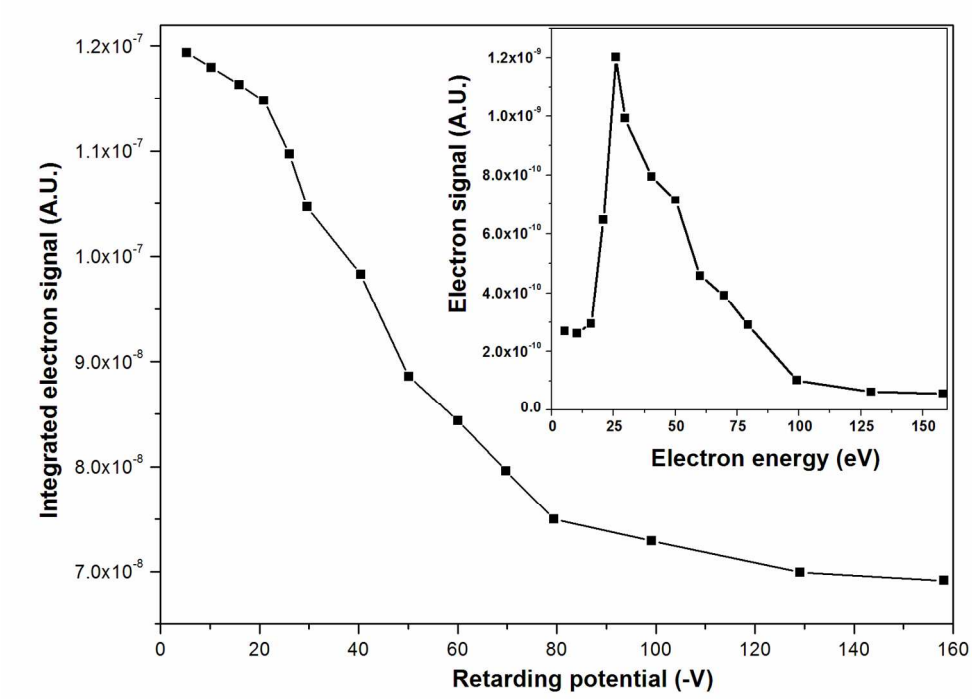

Figure 5: The integrated electron intensity as functions of retarding potential obtained upon irradiation of methyl iodide clusters with 1064 nm laser pulses. The inset shows the area normalised electron energy distribution generated from the integrated data.
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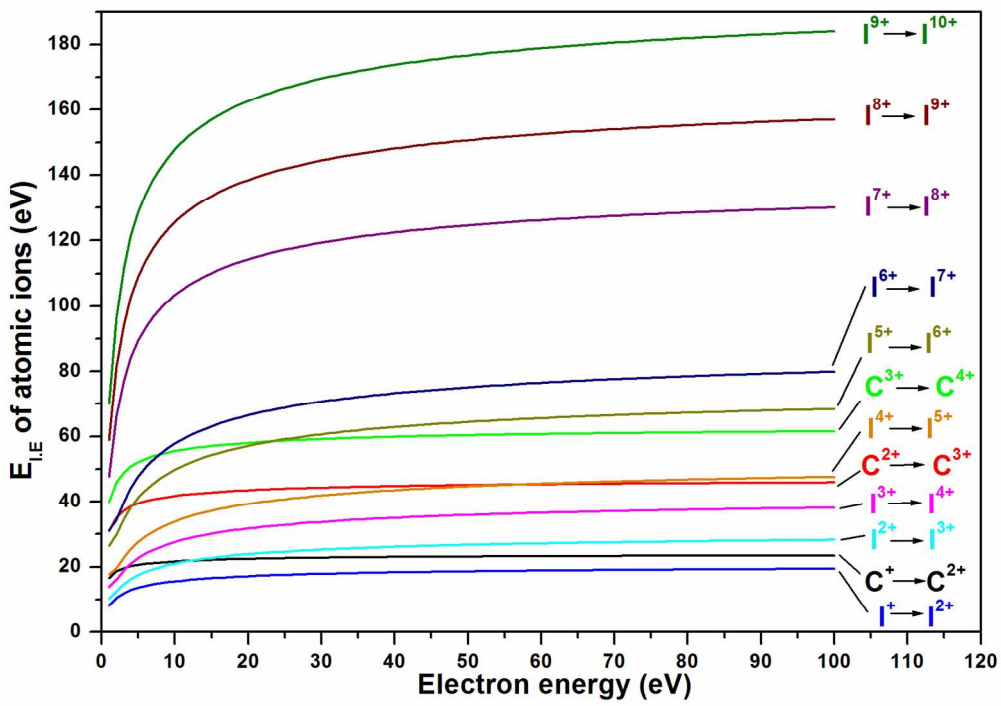

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