Coulomb explosion phenomenon using gigawatt intensity laser fields: an exotic realm of laser–cluster interaction

S. Das, P. M. Badani, P. Sharma and R. K. Vatsa*

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 094, India

Flanked between isolated atoms/molecules and bulk materials at the two extremes, there exists a unique class of matter known as clusters, which consist of a few to thousands of atoms or molecules held together. Upon irradiation with lasers, these clusters exhibit diverse photochemical behaviours which are altogether different from those of their individual constituents. Coulomb explosion phenomenon is one such facet of laser–cluster photochemistry, which results in the generation of multiply charged atomic ions and electrons with large kinetic energy. Observation of Coulomb explosion at laser intensities of 10^{14} W/cm^2 and higher, achieved using femtosecond lasers is reasonably well understood. Such cluster-explosion studies have obvious implications for the development of tabletop accelerators. In contrast to the high-intensity studies, the present article summarizes various experiments carried out using nanosecond laser pulses with intensities as small as 10^9 W/cm^2 in our laboratory, that establish the occurrence of Coulomb explosion in molecular clusters. Our present finding regarding utilization of low-cost, rugged and easy to use solid-state nanosecond Nd : YAG laser at comparatively lower laser intensity, for generation of multiply charged atomic ions would provide impetus to laser–cluster interaction studies.

Keywords: Clusters, Coulomb explosion, laser fields, multiphoton ionization.

THERE is an ever-increasing demand to develop advanced materials with novel and exotic properties for various technological applications. In this quest, researchers have focused their attention towards nanoparticles[1,2] and clusters[3]. Nanoparticles exhibit size-dependent variation in magnetic, electrical and optical properties, which is altogether different from their bulk counterparts. In order to engineer the properties of materials for specific applications, the potential of the interdisciplinary field of cluster science cannot be overlooked, since clusters are considered to be a bridge in understanding the properties of materials as they evolve from atomic/molecular level to bulk (solid/liquid phase) level[4–6]. In layman's term, clusters can be defined as an aggregate of atoms/molecules held by interactions ranging from weak van der Waals to strong ionic forces[7]. In these clusters, nearly all the constituents (i.e. atoms/molecules) are on or near the surface, which is distinct from the liquids or solids. Due to this surface effect, properties of a cluster can be significantly altered with the loss or addition of a single atom/molecule. This results in size-dependent alteration in electrical, magnetic, optical, chemical and catalytic properties. For small clusters, the variation in properties is considerable and is not a linear function of size. For larger clusters, the dependence on size gradually weakens and there is smooth convergence of properties towards those of its corresponding bulk phase (Figure 1). These larger clusters have dimensions in the nanometre range, which qualifies them to be called as small nanoparticles. This size dependence of chemical and physical properties of clusters has provided a convenient handle to researchers for tuning the cluster properties to any desired value, thus leading to advancement in nanotechnology[8].

Clusters have also been the subject of basic research for many years, as their physical nature and reactivity provide valuable information in many fields. For instance, clusters lead to the formation of aerosols in the atmosphere and cosmic dust[9,10]. A study of clusters also gives useful insight into many condensed phase phenomena, as they provide bulk-like density in gas phase unperturbed by external influences. Due to this ability, clusters have

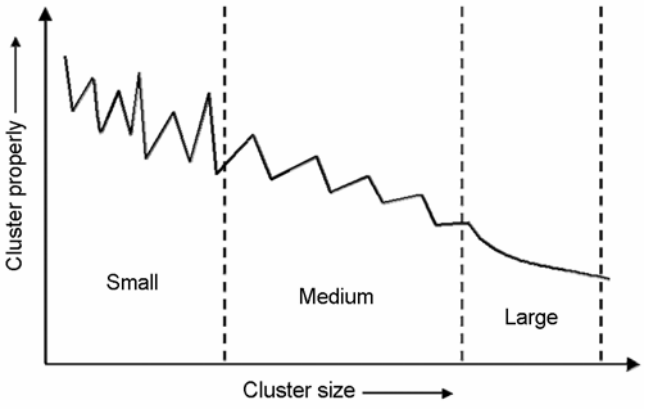

Figure 1. Representative graph depicting variation in properties of clusters as a function of size.

*For correspondence. (e-mail: rkvatsa@barc.gov.in)

been employed as isolated nano-laboratories for basic understanding of different physical, chemical and biological problems like energy dissipation, influence of solvation, interaction between biomolecules, etc.[11–13].

In the field of chemical physics, clusters have been used as model systems for understanding how the properties of a system change when solvation and/or degree of aggregation increases. In addition, these studies provide fundamental understanding of intermolecular interactions holding clusters and their structures. The stability, structure, reactivity and other properties of clusters are strongly dependent on the type of interactions, which hold the species within the cluster. At this point, it is relevant to distinguish between clusters and molecules, since in molecules also different atoms are held together by ionic and covalent interactions. Hence, it is necessary to know how clusters differ from the molecules. In brief, molecules are characterized by having definite composition and in most cases definite structure. On the other hand, clusters do not have definite composition and the number of atoms/molecules within the cluster can vary from two to several thousands. The structure and properties of the cluster in turn are also dependent on its size and with increase in size, the number of (locally) stable structures grows, unlike molecules which generally have unique structures[14].

The properties of a cluster could be altogether different when compared with isolated atoms/molecules and bulk matter. This is manifested most prominently in the interaction of clusters with intense laser fields. These studies have revolutionized our understanding of primary photophysical and photochemical processes of complex systems. It has been illustrated that cluster formation lowers the ionization threshold[15] as well as the electronic origins relative to those of the monomer, which in turn can introduce profound changes in the photolytic behaviour of molecules which form the cluster. For example, in water–ozone complex ($O_3 \cdot H_2O$), there is a red shift in the absorption of ozone and its absorption cross-section at 355 nm increases by about two orders of magnitude compared to that of the isolated ozone molecule[16]. Also, in certain cases, van der Waals clusters have been shown to exhibit different photochemistry, where new product channels open up which do not exist for the isolated molecule. For example, dimers of OCS and CS_2 generate S_2 as a photofragment, whereas O_2–O_2 complex gives rise to O_3 + O at excitation energies well below the dissociation threshold of their isolated counterparts[17]. Also for methyl iodide clusters excited at 266 nm, we observed ion signal corresponding to I_2 ions, which suggests that clusters of methyl iodide too exhibit concerted photochemistry similar to CS_2 and O_2 dimers (Figure 2). Similarly, upon multiphoton ionization, clusters have been found to exhibit intracluster ion–molecule reactions which depend on the degree of aggregation of the cluster[18,19].

Since molecular clusters exhibit diverse reaction channels as a function of wavelength and cluster size, we have performed wavelength-dependent multiphoton ionization studies on clusters of different molecular systems. These studies were carried out with the aim to understand the influence of the degree of aggregation in clusters on the electronic properties of the system, as well as its photochemical behaviour. During these studies, which were mostly carried out at 532 nm, clusters of several molecular systems were found to exhibit the phenomenon of Coulomb explosion at unusually low laser intensities of $\sim 10^9$ W/cm^2, resulting in the generation of energetic multiply charged atomic ions[20,21]. Historically, studies related with the generation of multiply charged species started long back, instigated by the development of picosecond and femtosecond lasers. However, these earlier studies were confined to rare-gas atoms and simple molecules[22–24]. Later on, use of atomic and molecular clusters as targets led to further advancement in the field of laser–matter interaction. These studies reported the generation of highly charged energetic atomic ions as a result of Coulomb explosion of clusters upon interaction with intense laser pulses having intensity of $\sim 10^{14}$–10^{20} W/cm^2 (refs. 25–29). The present study reports the generation of multiply charged, energetic atomic ions as a result of cluster Coulomb disintegration at gigawatt laser intensity. Observation of these multiply charged atomic ions at such a low laser intensity is rather uncommon. The intensity threshold for the appearance of these multiple charged ions assuming the simple Columbic barrier model can be estimated by the formula of Augst *et al.*[30]

$$I\ (\mathrm{W/cm^2}) = 4 \times 10^9\ (\mathrm{IE})^4/Z^2, \quad (1)$$

where IE is the ionization energy of the multiply charged ion (in eV) and Z is charge on the ion. The intensity threshold lies between 10^{14} and 10^{15} W/cm^2, which is at least four orders of magnitude higher than the intensity used in the present experiment. Below, we give a brief introduction to the phenomenon of Coulomb explosion.

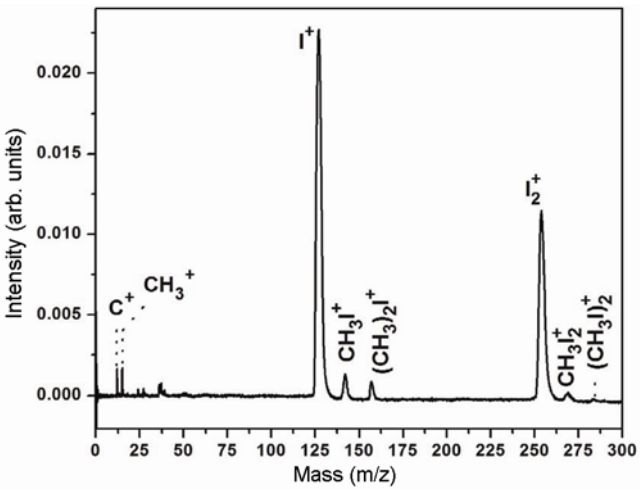

Figure 2. Time-of-flight mass spectra of methyl iodide clusters upon multiphoton excitation at 266 nm.

What is Coulomb explosion?

Clusters have high local density of electrons and atoms due to which they interact efficiently with laser radiation. This efficient coupling of intense pulses with clusters has led to several interesting consequences, including the phenomenon of Coulomb explosion of highly charged clusters, which leads to the generation of multiply charged energetic ions and electrons[31,32], higher order harmonics[33], enhanced emission of X-rays[34] and even neutrons[35]. Coulomb explosion occurs when an intense field of laser interacts with the cluster and removes several electrons causing the constituents of the cluster to become highly charged. The highly charged cluster then experiences Coulomb repulsion due to close proximity of ionic charges within the cluster. When the Coulomb repulsion forces between these highly charged constituents within the cluster exceed its total cohesive energy, the cluster explodes (disintegrates) into multiply charged fragment ions which carry large kinetic energy. In the past, Coulomb explosion of atomic and molecular clusters has been reported using intense, ultrashort laser pulses, typically of duration ≤ 100 fs with intensities in the range 10^{14}–10^{20} W/cm^2 over a wide range of wavelengths[36–38]. Under these conditions, for the case of xenon clusters, highly charged atomic species like Xe^{m+} ($m \leq 40$) having kinetic energy up to 1 MeV have been reported[39,40]. Generation of these multiply charged ions and observation of other non-linear processes like higher harmonic and X-ray generation cannot be explained by usual ionization processes, i.e. multiphoton ionization, optical field ionization, etc. This led to the development of different models like coherent electron motion model (CEMM)[41,42], ionization ignition model (IIM)[43], charge resonance enhanced ionization[44], etc. which satisfactorily explain the Coulomb explosion mechanism and other associated processes upon interaction of clusters with femtosecond laser pulses of intensity $\sim 10^{14}$–10^{15} W/cm^2. Each of these models explains some part of the overall interaction process which the cluster undergoes after being irradiated by an intense femtosecond pulse. For example, IIM, put forth by Rose-Petruck and coworkers, considers that several electrons are ejected upon initial ionization of the cluster, leaving behind several ion cores confined within the cluster. These ion cores coupled with the electric field of the intense laser pulse generate an inhomogeneous electric field within it, suppressing the ionization barrier within the cluster. Thus, they facilitate the ejection of additional electrons, leading to enhancement of charged state on the cluster. This sequence of events continues until the total cohesive energy of the cluster is surpassed by the Coulombic repulsive forces, resulting in Coulomb explosion of cluster. Hence, IIM can explain the generation of multiply charged energetic atomic ions. This model also explains the wavelength dependence of the Coulomb explosion phenomenon, as it depends on the ease with which the initial ion core is generated.

On the other hand, CEMM, proposed by Rhodes and co-workers[41,42], explains the generation of X-rays as a result of interaction of rare-gas clusters with intense laser pulses. It considers that the electrons initially produced upon ionization of the cluster, move coherently around the charged cluster under the influence of the intense laser field, causing further ionization by electron stripping (even from the inner shell). This electron heating process ultimately results in Coulomb explosion of the highly charged cluster along with generation of X-rays.

All the models discussed above deal with interaction of cluster with intense/ultraintense laser fields of the order of 10^{14}–10^{20} W/cm^2 and currently, there are no theoretical models to explain the Coulomb explosion under low intensity such as the one observed in the present work. This article portrays different systematic studies carried out by our group to realize the occurrence of Coulomb explosion in molecular clusters at such low laser intensities ($\sim 10^9$ W/cm^2) and the parameters which affect this phenomenon.

Instrumentation

Figure 3 illustrates a schematic diagram of the cluster set-up designed and fabricated indigenously at the Chemistry Division, Bhabha Atomic Research Centre (BARC)[45]. A pulse valve mounted in the expansion chamber acts as a cluster source for the generation of molecular clusters. In this set-up, typically an inert carrier gas (helium or argon) at a stagnation pressure of 1–8 bar is bubbled through the liquid organic sample of interest for the formation of the desired clusters. The resultant gas mixture is then supersonically expanded through a pulsed nozzle. Under these jet-cooled conditions, translational and rotational temperatures drop to a few Kelvin. At such low translational temperatures, condensation of atoms and molecules can lead to the formation of clusters[46,47]. The resultant supersonic jet is skimmed with the help of a skimmer (a truncated cone) and a cold beam of molecular clusters is introduced in the analyser chamber, where these clusters are subjected to mildly focused nanosecond laser pulses from a Nd : YAG laser mostly operating at 532 nm (second harmonic). The ions produced upon laser–cluster interaction are accelerated by a double field assembly and mass-separated in a time-of-flight mass spectrometer.

Generation of multiply charged atomic ions with large kinetic energy upon interaction of $(CH_3I)_n$ and $(CS_2)_n$ clusters at 532 nm

Figure 4 shows a typical time-of-flight mass spectrum of methyl iodide clusters irradiated with gigawatt intensity 532 nm laser pulses. In addition to the parent ion peak, CH_3I^+ ($m/z = 142$), and daughter ions like CH_3^+ and I^+, broad asymmetric peaks at $m/z = 63.5$, 42.3, 12, 6 and 4 are

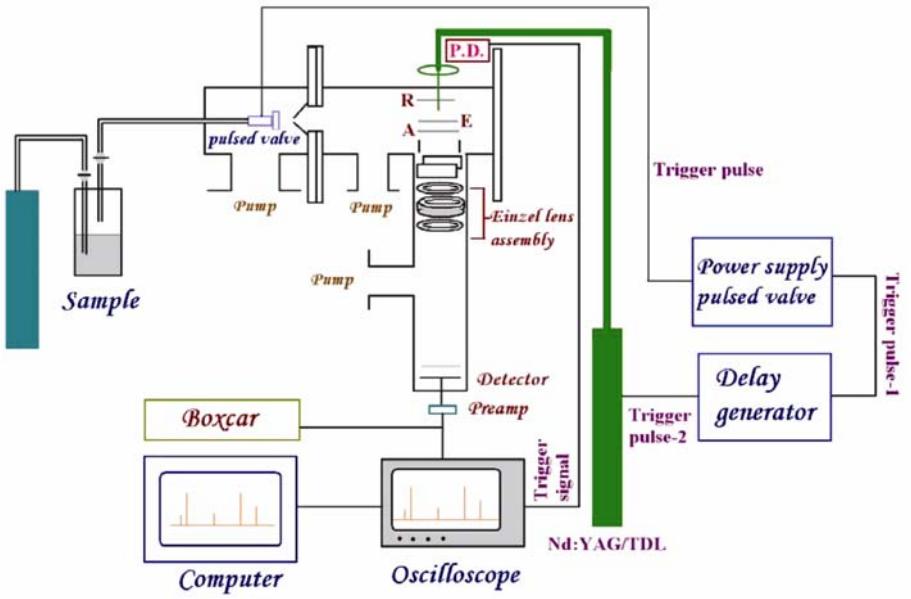

Figure 3. Schematic layout of cluster set-up designed and fabricated at the Chemistry Division, Bhabha Atomic Research Centre, Trombay.

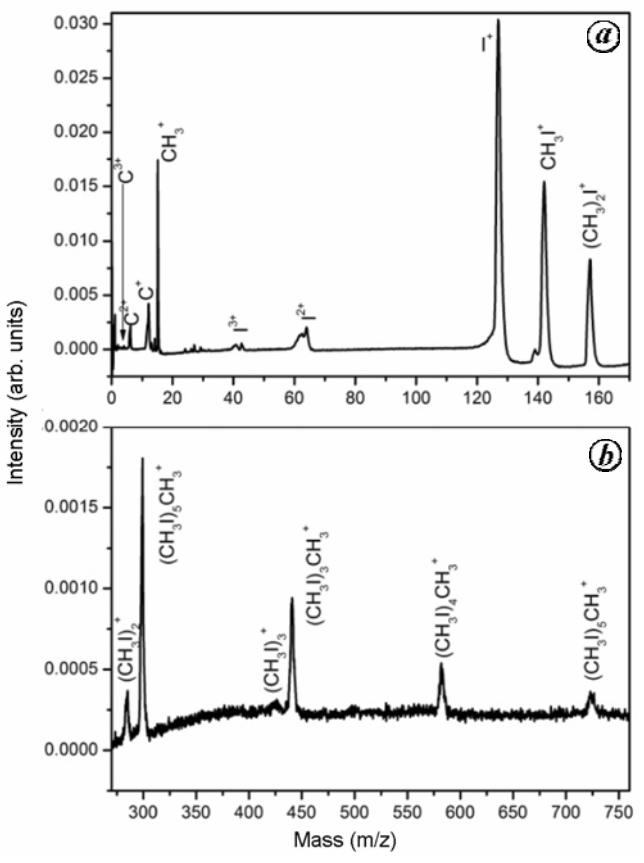

Figure 4 ***a, b.*** Time-of-flight mass spectra of methyl iodide clusters subjected to 532 nm laser pulse of intensity ~ 10^9 W/cm^2.

also observed (Figure 4 *a*). These broad asymmetric peaks can be assigned to *m*/*z* values corresponding to multiply charged ions of iodine (I^{2+}, I^{3+}) and carbon (C^{2+}, C^{3+}), which have large ionization energy. Further, additional low-intensity peaks corresponding to $(CH_3I)_2^+$ and $(CH_3)(CH_3I)_n^+$ (n = 1–5; Figure 4 *b*) due to cluster fragments are also observed. It can be seen that the multiply charged atomic ion peaks are broad and doubly split, indicating that a large amount of kinetic energy is associated with these ions[20].

In case of CH_3I clusters, synergistic contribution from the large size of the iodine atom and hence ease of polarizability as well as the dipole moment, can efficiently couple laser energy with the cluster and lead to Coulomb explosion in $(CH_3I)_n$ at gigawatt laser intensities. In order to check if the dipole moment, polarizablity and hydrogen bonding played an important role, further experiments were carried out with a molecule which has a zero dipole moment in the ground state and is devoid of hydrogen bonding. Carbon disulphide (CS_2), which is a linear molecule in the ground electronic state with net zero dipole moment was chosen. CS_2 also has an extensive absorption spectrum from the vacuum-ultraviolet (VUV) to the near visible region, and the excited states could be accessed by multiphoton excitation using the harmonics of a Nd : YAG laser. $(CS_2)_n$ clusters, when subjected to gigawatt laser intensity pulses at 532 nm, were also found to exhibit Coulomb explosion phenomenon resulting in the formation of multiply charged atomic ions of sulphur and carbon[48], suggesting that dipole moment, polarizablity and hydrogen bonding are not important for the observation of this phenomenon. Figure 5 shows a typical time-of-flight mass spectrum of carbon disulphide clusters irradiated with gigawatt intensity laser pulses of 532 nm. In addition to the parent ion peak, CS_2^+ (*m*/*z* = 76), and fragments like CS^+ and S_2^+ (Figure 5 *b*), broad asymmetric peaks at *m*/*z* = 32, 16, 10.6, 8, 6.4, 5.3,

12, 6, 4 and 3 are also observed (Figure 5 *a*). These broad asymmetric peaks can be assigned to *m*/*z* values corresponding to S^{n+} (*n* = 1–6) and C^{m+} (*m* = 1–4).

As mentioned earlier, signals from multiply charged ions exhibit significant peak broadening, indicating the release of large amounts of kinetic energy during the disassembly of a highly charged cluster. This is a typical feature of Coulomb explosion[25,26]. Upon Coulomb explosion for ions with the same *m*/*z*, the ions liberated along the time-of-flight axis towards the detector arrive early in time (forward component), whereas those liberated towards the repeller plate are first decelerated, stopped and then back accelerated towards the detector and hence arrive late at the detector (backward component). Thus, based on time-of-flight equations, the kinetic energy gained by the ions from the Coulomb explosion process can be readily determined from the time separation between the forward and backward components of the ion peaks using the following formula:

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

where Δt (in ns) represents the time difference between the split peaks for the same mass, *F* the static electric field for ion extraction in V cm^{-1}, *n* the charge and *m* the mass (in amu) of the fragment[25,49]. Using eq. (2), kinetic energies of different multiply charged atomic ions produced during Coulomb explosion of methyl iodide and carbon disulphide clusters have been calculated and are listed in Table 1.

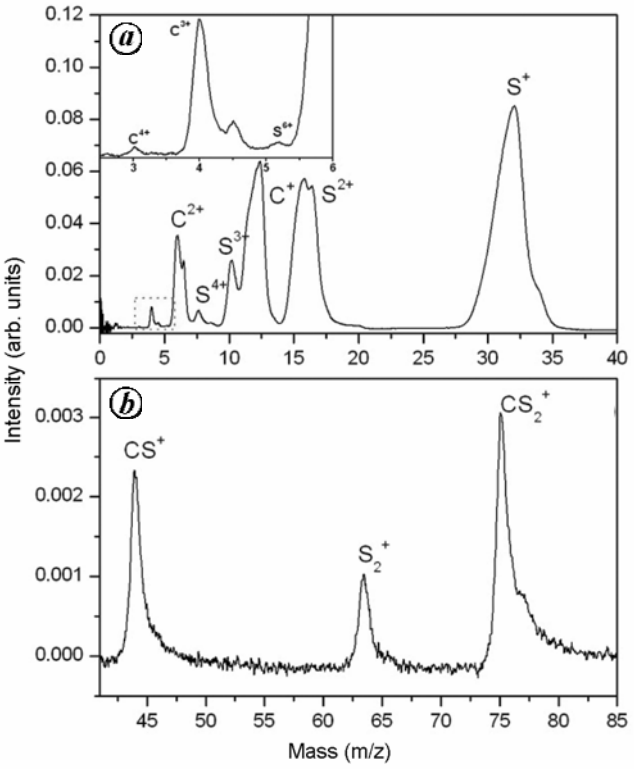

Figure 5 ***a, b.*** Time-of-flight mass spectra of carbon disulphide clusters subjected to 532 nm laser pulse of intensity ~ 10^9 W/cm^2.

Role of clusters in the Coulomb explosion process

To understand if the presence of clusters in the molecular beam is essential for the observation of multiply charged ions in the time-of-flight mass spectra, we varied the delay time between the opening of the pulse valve and the arrival of the laser pulse to sample both the clustered and unclustered zones of the gas pulse that interact with the focused laser beam. Figure 6 illustrates the time-of-flight mass spectra of methyl iodide clusters recorded at different delay times using gigawatt laser intensity pulses of 563 nm. The figure also depicts the variation in multiply charged atomic ion signals as the laser pulse interacts selectively with different regions of the molecular beam. When the laser beam interacts with the gas pulse on the trailing or leading edge, where monomers are predominant, we only observed the molecular ion and some dominant fragment ions like CH_3^+ and I^+ (ref. 50). Multiply charged fragment ions were observed only when the cluster beam was sampled at the peak of the gas pulse.

Clusters are produced during supersonic expansion as a result of three-body collisions between the molecules and the carrier gas. The rate of three-body collisions (Z_3) can be defined as:

$$Z_3 \propto P_0^2 d / T_0^2, \quad (3)$$

where P_0 is the stagnation pressure, *d* the nozzle diameter and T_0 the temperature (K). The above relation suggests that the probability of cluster formation increases with increase in the stagnation pressure and the nozzle diameter. Based on eq. (3), we carried out pressure-dependent studies on methyl iodide clusters. Figure 7 illustrates that increasing the stagnation pressure results in an increase of multiply charged fragment ion signal.

In another set of experiments, we varied the nozzle diameter to increase the average cluster size. Figure 8 *a* shows the time-of-flight mass spectrum of acetone clusters obtained using a 0.5 mm nozzle subjected to 532 nm laser pulse of intensity ~ 4.3×10^9 W/cm^2. It is seen that clusters generated using a smaller diameter (0.5 mm) nozzle exhibit a multiphoton dissociation/ionization behaviour, resulting in the generation of fragment ions like CH_3CO^+, $(CH_3COCH_3)_n^+$ (*n* = 1–4), $(CH_3COCH_3)_nCH_3CO^+$ (*n* = 1–3), etc. In contrast, acetone clusters generated using a 0.8 mm nozzle and subjected to 532 nm laser pulse under identical intensity conditions (Figure 8 *b*) exhibited Coulomb explosion resulting in the generation of multiply charged atomic ions of carbon and oxygen, C^{m+} (*m* = 1–4) and O^{n+} (*n* = 1–3), in addition to other fragment ions[51].

Table 1. Kinetic energy of different ions produced upon Coulomb explosion of CH_3I and CS_2 clusters at 532 nm

Cluster system	Laser energy	Kinetic energy of multiply charged ions (eV)						
		I^+	I^{2+}	I^{3+}	C^+	C^{2+}	C^{3+}	
$(CH_3I)_n$	12 mJ	18	114	376	29	115	325	
		S^+	S^{2+}	S^{3+}	S^{4+}	C^+	C^{2+}	C^{3+}
$(CS_2)_n$	12 mJ	13	74	484	602	15	170	638

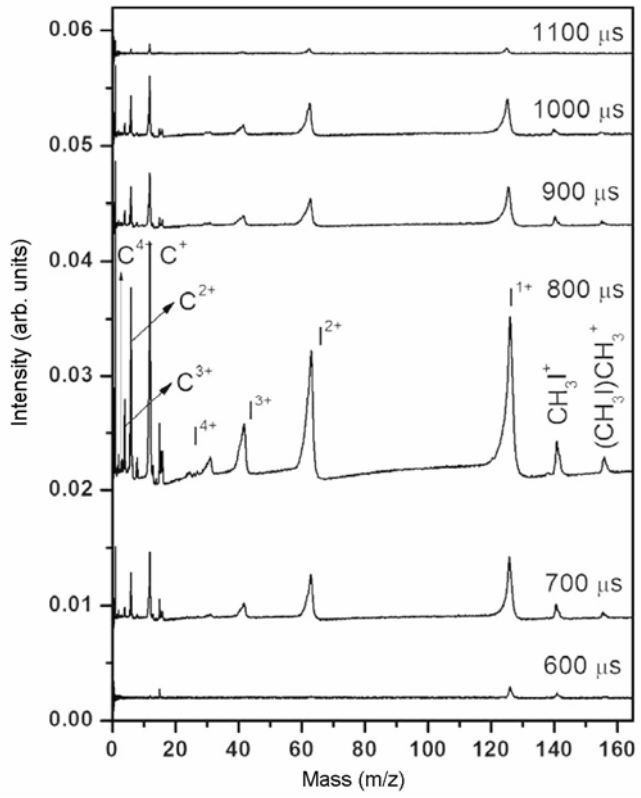

Figure 6. Variation in ion signal of multiply charged ions as a function of delay between pulsed valve and laser firing for clusters of methyl iodide at 563 nm.

The above experiments clearly demonstrate size-dependent photochemical behaviour of clusters. Based on these studies it can be concluded that for a cluster to exhibit Coulomb explosion, a characteristic threshold cluster size is required. For the case of acetone clusters, the cluster size distribution in both the expansion conditions is broad (i.e. using 0.5 and 0.8 mm). However, it is expected to be somewhat different in the two cases. For the same duration of pulse valve opening, a greater amount of gas load is forced through in the case of a 0.8 mm nozzle. So the average cluster size is expected to be larger for clusters obtained using the 0.8 mm nozzle, and it probably lies above the critical threshold cluster size required for the acetone cluster to exhibit Coulomb explosion. These large clusters interact efficiently with the low-intensity laser radiation leading to the generation of multiply charged energetic ions via Coulomb explosion.

Effect of laser wavelength on Coulomb explosion

At high intensity ($\sim 10^{15}$ W/cm^2), the Coulomb explosion is found to be independent of wavelength over a wide spectral region spanning from infrared to VUV. This can be easily understood since the electric field associated with the laser pulse is high and is responsible for the removal of several electrons in a short time. In order to examine how the wavelength affects Coulomb explosion at 10^9 W/cm^2, time-of-flight mass spectra of CH_3I clusters exposed to different selected wavelengths in the region of 266–640 nm at a fixed laser intensity of $\sim 4.6 \times 10^9$ W/cm^2 were also recorded and results are presented in Figure 9. At 266 and 355 nm, no evidence of multiply charged atomic carbon or iodine was observed (Figure 9 *a* and *b*). At 532 nm, low-intensity peaks for I^{2+}, I^{3+} and C^{2+} could be observed (Figure 9 *c*). With increase in the wavelength to ~ 560 nm region, multiply charged states up to I^{5+} and C^{4+} were observed. A representative mass spectrum recorded at 563 nm is shown in Figure 9 *d*. Further increasing the wavelength to 640 nm, a small additional signal of I^{6+} also starts appearing (Figure 9 *e*). These results thus provide clear evidence that Coulomb explosion of CH_3I clusters under our experimental conditions has an onset wavelength and is enhanced at longer wavelengths.

Understanding the mechanism responsible for Coulomb explosion at gigawatt laser intensity

Till date, various theoretical models and computational studies have been proposed to explain the Coulomb explosion process operative in clusters[41,52,53]. However, all these deal with interaction of the cluster with intense/ultraintense laser fields of the order 10^{14}–10^{20} W/cm^2. Although the high-intensity Coulomb explosion is reasonably well understood, the understanding of gigawatt laser-induced Coulomb explosion at present is meagre. It is not clear as to how such low laser fields of ~ 10^9 W/cm^2 can give rise to the formation of ions with high ionization

energy possessing large kinetic energies. There must be a highly efficient energy-absorption mechanism which couples the optical field and the cluster. Recently, a three-stage model comprising 'multiphoton ionization ignited-inverse bremsstrahlung heating and electron impact ionization' has been proposed to explain different facets of Coulomb explosion occurring on the interaction of molecular clusters with nanosecond laser pulses with intensity $\sim 10^9$–10^{11} W/cm^2 (refs 54, 55). This model assumes that the nanosecond laser-induced Coulomb explosion of the cluster is initiated by multiphoton ionization (MPI) of the constituent molecules within the neutral clusters. Subsequently, some of the ionized electrons which are caged inside the cluster, extract energy from the laser field via inverse bremsstrahlung process, i.e. absorption of energy from the electromagnetic laser field on collision with neutral and ionic species within the cluster. Once these caged electrons gain enough energy to surpass the corresponding ionization energy of the ions, multiple ionization process may start via stepwise electron impact ionization resulting in the generation of multiply ionized species within the cluster. Finally, these multiply ionized clusters undergo Coulomb explosion due to strong electrostatic repulsion resulting in the generation of multiply charged atomic ions with large kinetic energies.

To test this proposition, we carried out different sets of studies which are discussed below.

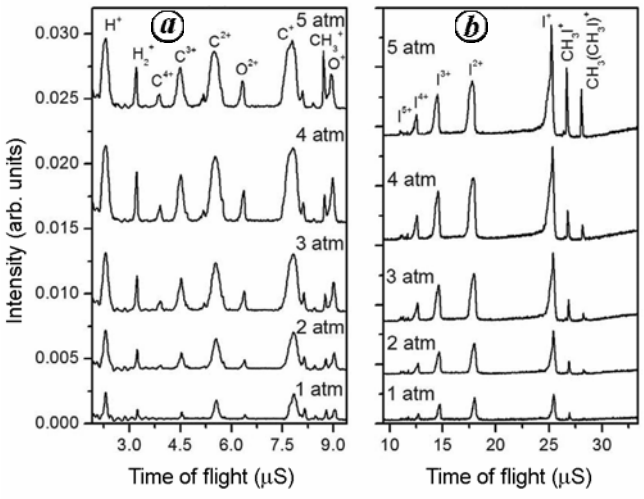

Figure 7. Variation in ion signal of multiply charged ions as a function of helium back-up pressure for methyl iodide clusters: ***a***, C^{p+} ($p \le 4$) and ***b***, I^{q+} ($q \le 5$).

Role of excited intermediate states

Ionization in molecules and clusters can occur through MPI and/or field ionization (FI) mechanism (tunnelling, barrier suppression ionization) and subsequently followed

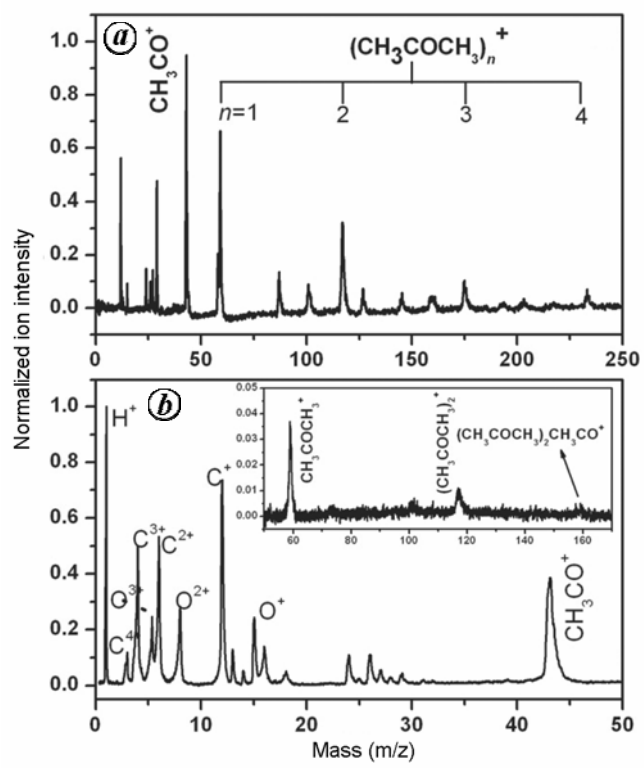

Figure 8. Time-of-flight mass spectra recorded for acetone clusters at 532 nm using (***a***) 0.5 mm and (***b***) 0.8 mm diameter nozzle.

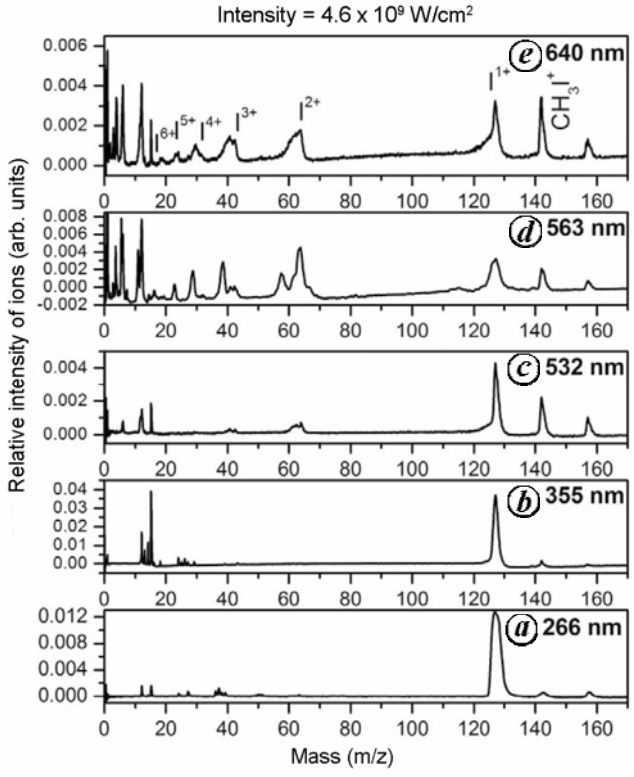

Figure 9 *a–e*. Time-of-flight mass spectra of methyl iodide clusters as a function of laser wavelength at a fixed laser intensity $\sim 4.6 \times 10^9$ W/cm^2.

by collisions between rescattered electrons and ions, depending on the laser wavelength and intensity. The factor which distinguishes between MPI and FI regimes is the Keldysh parameter (γ).

$$\gamma = (\mathrm{IE}/2U_p)^{1/2}, \quad (4)$$

where IE is the ionization energy and U_p $\{= 9.33 \times 10^{-14} I(\mathrm{W/cm^2})\lambda^2(\mu\mathrm{m}^2)\}$ the ponderomotive energy in eV for a given laser intensity (I) and wavelength (λ). For $\gamma > 1$, ionization is attributed to MPI processes, whereas for $\gamma < 1$ it is attributed to the FI mechanism[56]. Based on Keldysh parameter, all our studies fall in the MPI regime, since $\gamma \gg 1$. Hence, in order to shed light on the mechanism which leads to the generation of these multiply charged ions, we carried out laser power dependence studies for different ions generated upon the interaction of 532 nm laser pulse with methyl iodide and acetone clusters.

Figures 10 and 11 show the logarithmic plot of laser energy and integrated ion signal for different ions. For methyl iodide clusters a power dependence of ~3 was obtained, whereas for acetone clusters a power dependency of ~4 was observed. Based on these plots, we conclude that the rate limiting step to the generation of these multiply charged ions is a three-photon excitation process for CH_3I to Rydberg C state at ~7 eV, while for acetone clusters four-photon excitation to the Rydberg state $[1/2]6s\sigma_g$ at ~9.32 eV was identified as the rate determining process. The wavelength dependence that we have observed in our experiments strongly suggests that resonance excitation is important and the role of the excited states is crucial for the initiation of Coulomb explosion in clusters under gigawatt intensity laser fields. This observation is different from the high-intensity results and somewhat ignored aspect of laser cluster interactions.

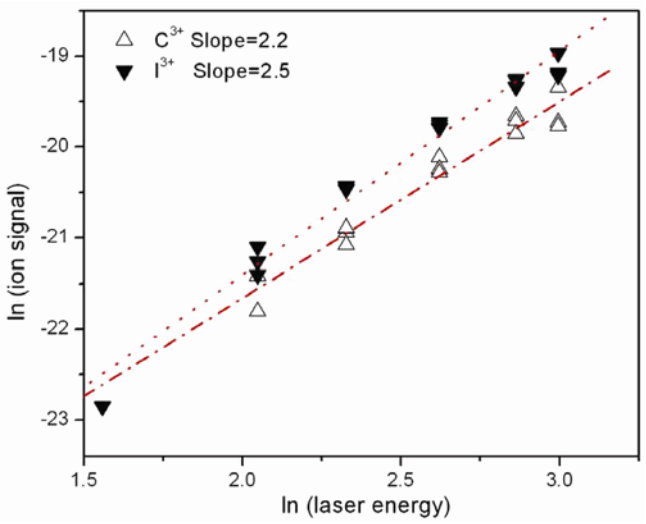

Figure 10. ln–ln plot of laser energy versus signal intensity of multiply charged fragment ions (C^{3+} and I^{3+}) that are produced upon interaction of CH_3I clusters with 532 nm laser pulse of ~10^9 W/cm^2 intensity.

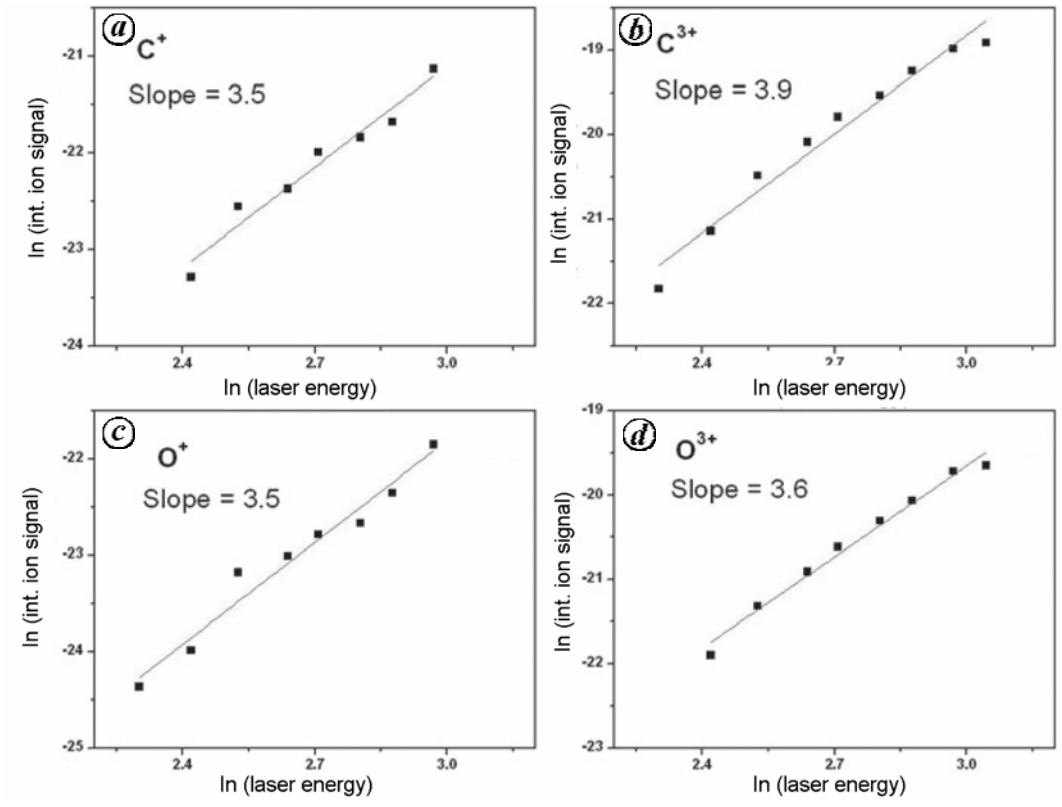

Figure 11. ln–ln plots for multiply charged ions generated upon interaction of 532 nm laser pulse with acetone clusters.

Measurement of electron energy

In order to shed light on the proposed electron heating mechanism of clusters leading to Coulomb explosion, it was essential to measure the energy of electrons librated upon interaction of the laser with the clusters. In an independent experiment, we measured the kinetic energy of ions and electrons produced due to laser–cluster interaction using an entirely different apparatus designed and fabricated at the Tata Institute of Fundamental Research (TIFR), Mumbai, which incorporated arrival time measurements coupled with a retarding field[57]. In this set-up, ions/electrons generated due to the laser–cluster interaction traversed a distance of ~ 19 cm under field-free condition before reaching the detector. The ions reached the detector due to the high kinetic energy gained by them as a result of Coulomb explosion of the clusters. To measure the kinetic energy of the ions and electrons, a retarding potential assembly (0–V–0 grid) was inserted in the path of ions/electrons just before the detector. In these experiments, the measured kinetic energy of the ions upon interaction of the 532 nm laser with methyl iodide clusters was in line with those reported in Table 1, obtained using the split peak method based on time-of-flight mass spectrometer. Similarly, the kinetic energy of electrons was also measured. Figure 12 shows the functional dependence of the integrated electron signal on retarding voltage. Electrons up to 20–25 eV kinetic energies can be readily observed from this figure[20]. Observation of electrons with kinetic energy up to 20–25 eV clearly suggests that the electrons generated upon multiphoton ionization of clusters gain energy from the laser fields.

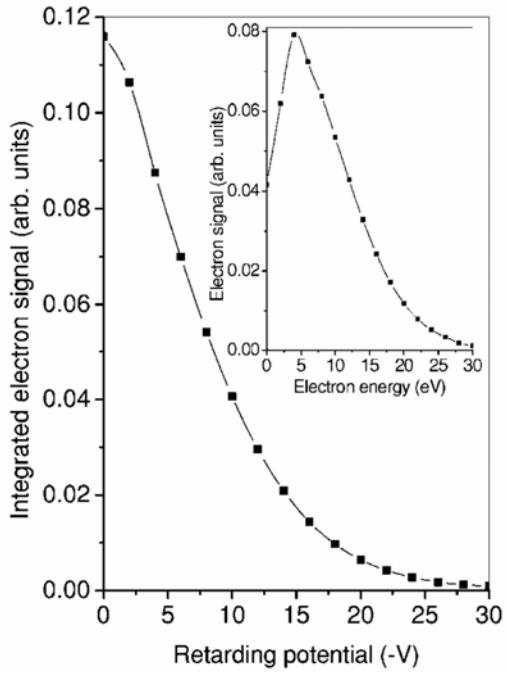

Figure 12. Integrated electron signal as a function of retardation potential for methyl iodide clusters at 532 nm. (Inset) Area-normalized electron energy distribution generated from the integrated data.

Effect of laser polarization

In order to understand the effect of laser polarization on Coulomb explosion of clusters under our experimental conditions, mass spectra were recorded under different polarizations. Figure 13 *a* and *b* illustrates time-of-flight mass spectra of CH_3I clusters recorded under parallel (0°) and perpendicular (90°) laser polarization with respect to the time-of-flight axis at 532 nm. The multiply charged ions C^{2+}, C^{3+}, C^+, I^{3+} and I^{2+} exhibit asymmetric peak profile, whereas for I^+ ions the asymmetry is not well-resolved due to lower kinetic energy associated with it[58]. Since the fragmentation pattern as well as the ion intensity distribution is found to be nearly identical for parallel and perpendicular polarizations, it can be concluded that Coulomb explosion under gigawatt intensity laser fields is isotropic in nature.

Effect of doping

Based on our above studies, it can be concluded that for generation of multiply charged ions upon Coulomb explosion it is essential that the molecular cluster under-

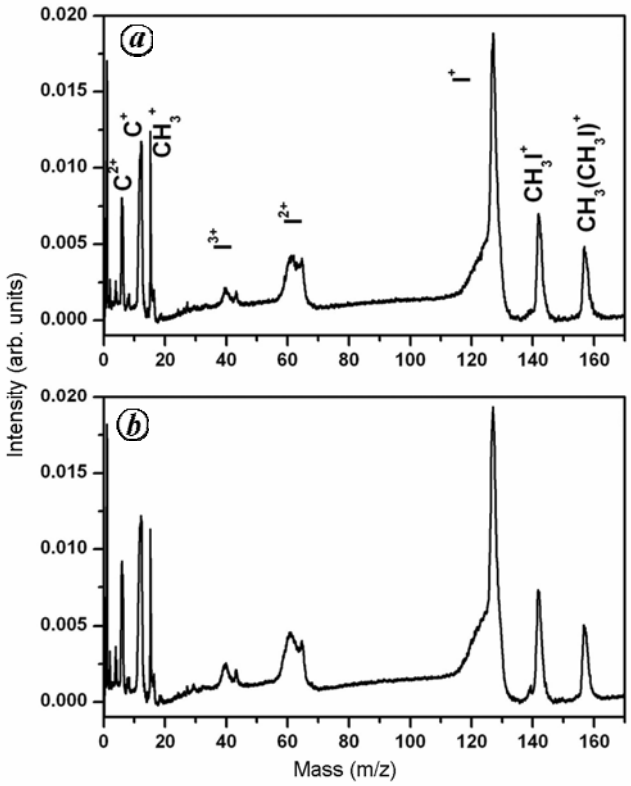

Figure 13. Time-of-flight mass spectra of CH_3I clusters at 532 nm under (***a***) parallel (0°) and (***b***) perpendicular (90°) polarization.

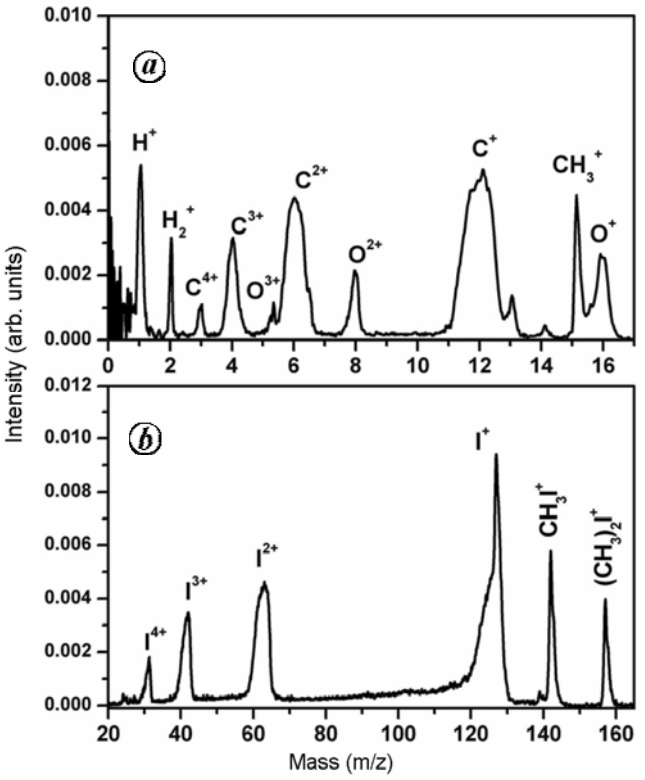

Figure 14 ***a, b.*** Time-of-flight mass spectra of CH_3I–H_2O mixed clusters when subjected to 563 nm laser pulse at an intensity of ~ 10^9 W/cm^2.

goes ionization and the librated electrons extract additional energy from the laser pulse leading to multiple ionization of the cluster which finally results in Coulomb explosion. The latter process of electron heating is expected to be isotropic and would cause homogeneous ionization of the cluster. To ascertain the validity of the conjecture, we carried out studies on methyl iodide clusters doped with water. Water was chosen due to its much lower vapour pressure compared to that of methyl iodide. On co-expansion, the methyl iodide clusters would have minor contribution from dopant water molecules. As a result the cluster size distribution is not expected to be very different with respect to pure methyl iodide clusters. Also due to higher ionization energy of water molecules (12.62 eV) compared to that of methyl iodide (9.54 eV), the multiphoton ionization probability of the water molecules/clusters compared to that of methyl iodide molecules/clusters would be diminutive. When the water-doped methyl iodide clusters which were generated by supersonic expansion of CH_3I and water sample mixed in 9 : 1 ratio (by volume) were subjected to 563 nm laser radiation, they were found to undergo Coulomb explosion resulting in the generation of energetic multiply charged atomic ions of oxygen (up to O^{4+}) in the time-of-flight mass spectra along with other multiply charged atomic ions of carbon and iodine (Figure 14). Here it is worth mentioning that in an independent study when pure water clusters were made to interact with 563 nm laser pulse of gigawatt intensity, no ion signal could be observed under our experimental conditions. Therefore, this study demonstrates that doping of methyl iodide clusters with water leads to induction of Coulomb explosion in dopant water molecules also which now form an integral part of the methyl iodide cluster. We would like to mention here that doped systems are important since they not only help in understanding the ionization process, but also provide other strategies to engineer clusters which could absorb laser energy with enhanced efficiency. Jha *et al.*[59] reported a significant enhancement in the yield of argon (Ar) K-shell X-rays when water-doped argon clusters were irradiated with femtosecond pulses in comparison to pure Ar clusters. The reason for the enhancement was suggested to be the presence of easily ionizable water molecules which change the ionization dynamics. The above-mentioned results using nanosecond and femtosecond lasers show that Coulomb explosion is a collective property of the cluster as a whole and individual molecular properties do not play a significant role.

Conclusion

Clusters are embryos of matter held together by weak forces, i.e. van der Waals forces, hydrogen bonds, etc. These are generally intermediate in size between individual atoms/molecules and aggregates large enough to be called bulk matter. From a technological point of view, clusters exhibit unique physico-chemical properties which originate mainly from the fact that they are composed of a finite number of atoms/molecules, most of which are located on their surface. Irradiation of clusters by intense laser pulses opens the door to a new challenging phenomenon, i.e. Coulomb explosion. In this domain of physics, the interactions between the clusters and the radiation is so strong that it leads to severe ionization and extensive fragmentation. The present study suggest that at gigawatt laser intensities, clusters exhibit complex yet efficient laser–cluster interaction mechanism resulting in the generation of multiply charged atomic ions with large kinetic energies. Further, isotropic disintegration of the multiply ionized atomic ions as a function of laser polarization, coupled with induction of Coulomb explosion in clusters doped with water molecules having higher ionization energy compared to that of the host matrix, i.e. methyl iodide, suggests that the mechanism leading to Coulomb explosion is a collective property of the cluster as a whole and does not discriminate between the constituents of the cluster. The recently proposed three-stage model comprising ‘multiphoton ionization ignited-inverse bremsstrahlung heating and electron impact ionization’ qualitatively explains the experimental observations of Coulomb explosion at gigawatt laser intensity. The present study, however, clearly shows that much more

detailed experimental and theoretical studies are needed before a comprehensive picture of the nanosecond laser-induced Coulomb explosion in clusters can emerge. In addition, the crucial role of multiphoton excited resonant electronic states which directly influence the ionization probability of the clusters, as well as the role of cluster size essential for confinement of the ionized electron for the duration of the laser pulse to have efficient extraction of energy from the laser field cannot be overlooked.

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