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Generation of multiply charged tin and carbon ions in low intensity Coulomb explosion of tetramethyl tin clusters: Role of screening effects

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ABSTRACT

Present work reports multiple ionization and subsequent Coulomb explosion of tetramethyl tin clusters induced by gigawatt intensity laser pulses. The time-of-flight mass spectra and charge density measurements revealed that the efficiency of laser–cluster interaction depends on ionization wavelength. Extent of energy absorbed from optical pulses by the cluster medium was found to increase with laser wavelength. Experimental results obtained in the present study have been rationalized on the basis of three stage cluster ionization model, i.e. multiphoton ionization ignited – inverse bremsstrahlung heating (IBS) – electron ionization. In addition to the experiments, theoretical calculations have been performed to account for screening effects in clusters. Our calculations suggest that the charged particles, generated upon initial multiphoton ionization of cluster constituents, significantly lower the Coulombic barrier of atoms/molecules that are present in its vicinity. This, in turn, decreases the ionization energy of cluster constituents, during subsequent steps of ionization, ultimately increasing the ionization level of clusters via the process of enhanced ionization due to ion shielding. Thus, above calculations predict dominant role of screening effects in evolution of higher charge state atomic ions during laser–cluster interaction.

1. Introduction

Clusters undergo Coulomb explosion upon interacting with highly energetic electrons [1], particles [2] or photons [3,4]. This phenomenon occurs due to extensive stripping of electrons from constituent atoms/molecules of clusters resulting in buildup of excessive positive charge on cluster. When the repulsive Coulombic energy of clusters, arising from positive charges, overcomes the total cohesive energy, cluster disintegrates violently resulting in generation of multiply charged atomic ions. Initial report on Coulomb explosion dates back to 1981 when Sattler et al. [1] observed doubly charged species upon electron impact ionization of metallic and vander Waal clusters. In 1994, Castleman and co-workers [5] observed extensive ionization and generation of multiply charged atomic species (I^{17+} and Ar^{8+}) upon interaction of $(HI)_n(Ar)_m$ clusters with intense femtosecond laser pulses. Subsequent studies on Coulomb explosion by other research groups [6–10] revealed the dependence of cluster size, laser wavelength, intensity, pulse duration, etc. on efficiency of energy transfer from optical field into the cluster medium.

Several ionization mechanisms such as Ionization Ignition Model (IIM) [11], Coherent Electron Motion Model (CEMM) [12,13], Charge Resonance Enhanced Ionization (CREI) [14], etc., have been proposed to account for occurrence of Coulomb explosion under high intensity laser fields ($I \sim 10^{15}$ W/cm^2). However, these ionization models could not explain low intensity ($I \sim 10^{9}$ W/cm^2) induced Coulomb explosion of clusters [15–20]. In order to rationalize the phenomenon of Coulomb explosion at gigawatt laser intensity, a three stage cluster ionization model, i.e. multiphoton ionization ignited – inverse bremsstrahlung heating (IBS) – electron ionization, has been proposed [18,19]. According to this model, Coulomb explosion is initiated via multiphoton ionization of atoms/molecules present in clusters. Subsequently, electrons released via inner ionization process are caged within the clusters. These quasi free electrons, under the influence of Coulombic field, extract energy from laser pulse via inverse bremmsstralung process. Once the quasi free electrons gain enough energy, further ionization takes place via electron ionization resulting in generation of multiply ionized species within clusters. Finally, these charged clusters undergo Coulomb explosion due to strong electrostatic repulsion.

Based on the above proposed three stage cluster ionization model, the quasi free electrons, generated upon initial MPI of cluster constituents, needs to acquire the energy equal to or greater than the ionization energy (I.E.) of neighbouring species, so as to

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cause further ionization. Hence the maximum electron energy, generated during this interaction process, was expected to be equal to or greater than the ionization energy (I.E.) of highest observed charge state. However, experimentally measured maximum electron energy for different cluster systems was significantly lower than the I.E. of highest observed charge state. For instance, photo-ionization of $(CH_3I)_n$, at 532 nm, resulted in generation of multiply charged state atomic ions up to C^{3+} (I.E. = 47.8 eV). While the maximum electron energy measured for methyl iodide cluster system under similar irradiation condition was ~30 eV [21]. Similar behaviour was observed in other cluster systems such as benzene [19] and diethyl ether [20]. Hence, in order to account for generation of high I.E. atomic species even at lower electron energies, screening effects in clusters ought to be considered. Screening effect arises due to presence of ions and quasi free electrons in clusters [22], resulting in lowering of I.E. of cluster constituents. This process subsequently facilitates generation of high I.E. species, even at lower electron energy.

In the present study, we demonstrate wavelength dependent photo-ionization behaviour of an organometallic cluster system, i.e. tetramethyl tin ($Sn(CH_3)_4$, abbreviated as TMT). Further, in order to determine the extent of lowering of I.E. of the species, we have calculated I.E. of multiply charged atomic ions [Sn^{n+} (n = 2–5) and C^{n+} (n = 2–4)] taking into consideration the screening effects in clusters. Our calculation suggests significant lowering in I.E. of multiply charged atomic ions due to presence of charged particles in its vicinity. As a result, electrons of particular energy are able to generate ions which are otherwise not feasible if one considers the ion in isolated state. Further, our calculation also predicts dependence of electron energy, charge state and atomic number of ions on the extent of lowering in ionization energy (I.E.) of the species which are present inside a cluster following multiphoton ionization.

2. Experimental

Details of the experimental setup have been described in our earlier publications [15–17,21] and only a brief account is given here. TMT clusters were generated via supersonic expansion of $Sn(CH_3)_4$ vapours seeded in Ar, at a backup pressure of 1–6 bar, at room-temperature. A pulse valve with 800 μm nozzle diameter and 350 μs pulse duration was used for generation of cluster. The supersonic jet produced in this way was skimmed at a distance of 5 cm from the nozzle. Clusters were ionized 17 cm downstream from the skimmer by 266, 355 or 532 nm output of a pulsed Nd:YAG nanosecond laser (Quanta System, Olona, Italy; GIANT G790-10; FWHM = 10 ns). The ions generated were accelerated and guided into a 100 cm field-free region of home built time-of-flight mass spectrometer based on Wiley–McLaren ion optics and detected using a Channel Electron Multiplier (CEM). The mass resolution of the instrument is ~300. Signal from the CEM was recorded on a digital storage oscilloscope. Typically ~500 laser shots were averaged for each time-of-flight mass spectrum. For weak signals, ~1000 shots were averaged. The averaged signal was finally transferred to a computer for further processing.

In order to quantify total number of ions generated within the ionization volume upon laser–cluster interaction, experiments were carried out in which the charge density was measured using parallel plate method [23]. In this setup, a sufficiently high positive voltage was applied to one of the plates (anode) in order to repel the ions towards the collector plate (cathode) and the ion current was measured across a suitable resistor (10 kΩ). It was ensured that all the experimental parameters were kept identical in the time-of-flight and charge density studies, so that the results could be correlated.

3. Results

3.1. Time-of-flight measurements at different laser wavelengths

In the initial set of experiment, TMT clusters were irradiated with laser pulses at selected wavelengths ranging from UV to Visible region, to investigate the effect of laser wavelength on photo-ionization. The time-of-flight mass spectrum obtained on interaction of TMT clusters, with laser wavelength of 266 nm, is depicted in Fig. 1a. The mass spectrum shows an intense ion peak corresponding to Sn^+. The broad nature of this ion peak is due to the presence of several isotopes (m/z ranging from 112 to 122) of Sn. Of these, isotopes of Sn with higher abundance are ^{116}Sn (14.5%), ^{118}Sn (24.2%), ^{119}Sn (8.6%) and ^{120}Sn (32.6%) In addition to Sn^+, low intensity ion signals corresponding to $Sn(CH_3)^+$ and $Sn(CH_3)_3^+$ could also be observed in the mass spectrum. On changing the laser wavelength from 266 nm to 355 nm, in addition to the above ion signal, the mass spectrum (Fig. 1b) revealed generation of Sn^{2+}. Also cluster fragment ions, i.e. Sn_2^+ and $[(CH_3)_4Sn]_n[Sn(CH_3)_3]^+$ (n = 1), could be detected in the mass spectrum at this ionizing wavelength. For 532 nm photo-ionization, in addition to singly charged species, multiply charged atomic ions of Sn^{n+} (n = 2–5) and C^{n+} (n = 2–4), could be seen in the mass spectrum (Fig. 1c).

The complete absence of molecular ion at all the ionizing wavelengths could be ascribed to the fact that TMT has a tetrahedral geometry and possesses triply degenerate highest occupied molecular orbitals. Removal of an electron from these orbitals generates an ion whose geometry, according to the Jahn–Teller theorem, must distort to lift the orbital degeneracy. This makes the molecular ion unstable, leading to its dissociation into methyl radical and $(CH_3)_3Sn^+$ [15]. An interesting feature observed in the above photo-ionization studies is that the charge state of atomic ions increases with laser wavelength. At 266 nm photo-ionization, highest observed charge state of Sn is +1 (I.E. = 7.3 eV). While 355 and 532 nm ionization resulted in generation of multiply charged atomic ions upto Sn^{2+} (I.E. = 14.6 eV) and Sn^{5+} (I.E. = 77.2 eV), respectively. These results suggest that in case of low intensity laser fields, the extent of energy transfer from optical pulses into cluster medium, and subsequent level of ionization, increases with laser wavelength.

3.2. Charge density measurements at different laser wavelength

In addition to time-of-flight studies, charge density measurements (using parallel plate method) were also performed at different laser wavelength to quantify the number of ions generated during the laser-interaction process [23]. Fig. 2 represents experimentally measured charge density as a function of applied electric field between the parallel plates at three different wavelengths. For all the wavelengths, the charge density initially increases up to a certain value of applied electric field and then saturates. Under low applied electric field, the ions having high kinetic energy are not collected efficiently resulting into a low charge density. With increasing electric field, the collection of ions is more efficient and hence the charge density increases. Finally, the saturated region signifies complete collection of charges on the collector plate. The charge densities measured from the saturated region of the graph at 266, 355 and 532 nm are $\sim 5 \times 10^{10}$, $\sim 1.5 \times 10^{11}$ and $\sim 8 \times 10^{11}$ charges/cm^3, respectively. Due to the higher energy per photon, ionization at 266 and 355 nm would require less number of photons and one would expect higher charge density at 266 and 355 as compared to 532 nm for a fixed laser intensity of 5×10^9 W/cm^2. However, the measured values show that the charge density is lower at 266 and then increases ~3 times for 355 nm and finally at 532 nm the overall charge density is about ~16 times higher than that at 266 nm. It should be noted here that ionization at