

Production of Multiply Charged Argon Ions in Moderate Nanosecond Laser Fields: An Open Question or a Forgone Conclusion?

Reply to “Generation of Multiply Charged Argon Ions in Nanosecond Laser Field Ionization of Argon Clusters” by Rajesh K. Vatsa and Deepak Mathur

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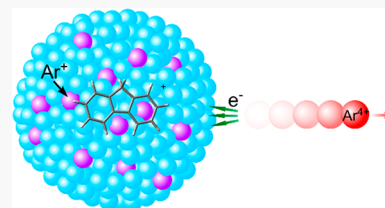
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ABSTRACT: We reply to the Viewpoint by Vatsa and Mathur on our publication reporting the observation of multiply charged atomic ions from argon clusters doped with aromatic chromophores in a moderate nanosecond laser field. Vatsa and Mathur raised three concerns about the proposed explanation and offered additional ideas for the reported process. We agree with some of their concerns and welcome the addition of information, and we also clarify a few misunderstandings of our intention, perhaps caused by our implicit assumption of contextual relations. While the experimental results are indisputable, the interpretation is still a topic of debate, subject to further experimental investigations and theoretical modeling.



Vatsa and Mathur (VM) commented on our publication titled “Coulomb Explosion in Nanosecond Laser Fields”. In a nanosecond laser field of $\sim 10^{12}$ W/cm², we have observed Arⁿ⁺ ($1 \leq n \leq 7$) and Cⁿ⁺ ($1 \leq n \leq 4$) from argon clusters containing an aromatic chromophore such as fluorene or halogenated fluorenes.¹ The statements of VM on the difficulties facing the explanation of the experimental results, i.e., extensive production of multiply charged atomic ions (MCAIs) in laser fields orders of magnitude lower than those typically considered possible, are in agreement with our assessment of the situation. The mechanism from intense fields on MCAI production runs into trouble on several fronts in moderate nanosecond laser fields, including the plasma model of energy absorption, the classical treatment of inverse bremsstrahlung scattering (IBS) when the ponderomotive energy is much lower than the photon energy, and the unavoidable expansion of the charged cluster in the long (nanosecond) laser field. The primary concern of VM on our report centers on our explanation of the formation mechanism of the MCAIs. In our original publication, we proposed a pathway for the ionization of Ar⁺ and ultimately the formation of Arⁿ⁺. Our explanation was intended only for the systems that we have studied, i.e., argon clusters doped with aromatics, and our calculation is meant only for estimates on the order of magnitude. The goal is to draw attention from the community for discussions. In their Viewpoint, VM posed several major concerns with regard to our interpretation: some are of additional value to our explanation, while others are due to misunderstandings—perhaps caused by our over reliance on the context which is not entirely clear to the readers. Moreover, VM also posit an alternative explanation: they

suggest that electrons inside clusters can be direct absorbers of optical energies via collisions with the cations inside the cluster and that coherent superposition of collisions can enhance the absorption by orders of magnitude.^{2,3} The thus energized electrons are the source of ionization in forming MCAIs.

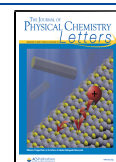
Among the three major points raised by VM, we are in full agreement with the authors on the limited role of the chromophore and the beneficial effect of resonance for the formation of Ar⁺. In the introduction of our Letter,¹ references to a variety of compounds investigated by three other groups are listed,^{4–12} and the lack of a common structural motif among the compounds implies that a chromophore is not the prerequisite to observe MCAIs. Our path of ionization for Ar⁺ is specific only to our own experiment and is not intended to be general: the path with the resonances is the enhanced path, offering a higher probability of excitation than otherwise. In addition, similar observations of pure krypton and xenon clusters,⁵ and more recently in our own laboratory, pure argon clusters, have also been achieved. These are further proof that the role of the dopant is limited in the formation of MCAIs.

Similarly, the second concern of populating a specific Rydberg state of Ar for ionization is also not an emphasis of our original intent. The overall 5-photon process involving

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dopant ionization (3 photons required) and subsequent dopant ion excitation (2 additional photons required) is only an energy accumulation pathway, and energy transfer between the superexcited neutral dopant and a surrounding argon atom can facilitate Ar excitation. This can be a coherent process with no actual quasi-free electrons nor ions produced—resonantly enhanced multiphoton absorption. Once again we provide only a possible enhanced pathway, with no intention of emphasizing nor generalizing any particular energy levels. The role of resonance is to provide a facile pathway of ionization for Ar, and given the field strength and the related line-broadening, many levels can come into resonance and achieve the resonant enhancement of coherent multiphoton absorption. In fact, we believe that this is exactly the case for neat molecular clusters with many vibronic levels available for resonant enhancement.^{4,6–12}

A potential problem of our explanation is on the electron stripping process in forming Ar^{n+} , and here the concern of VM is quite relevant. In our original publication, we just assumed that the cluster was highly charged, but we did not offer any evidence or mechanism to explain this statement. We estimated the rate of electron transfer and the mean-free-path of a low-energy electron from multiphoton ionization and found that an electron should experience no collision on its way out of the cluster. However, any electron should also be affected by the field of the overall cluster, so the mechanism of outer ionization was missing in our original explanation. Our estimate of the fast ionization rate of Ar^+ due to the resonant absorption of Ar_3^+ is therefore applicable only to inner ionization, but not for outer ionization. It is not the mechanism of producing the highly positively charged cluster. Moreover, our values of electron transfer are only estimates to confirm if electron escape is possible, and our estimate is not meant to be quantitative in any sense, because experimental conditions vary case by case; hence, actual values of charge transfer differ.^{13,14}

The general idea of plasma heating offered by VM is certainly a welcome addition to our explanation.¹⁵ However, before a plasma can be heated, it has to be formed; that is, a charge accumulation process has to occur first. The facile inner ionization mechanism through resonant absorption of Ar_3^+ could therefore be the prior step for plasma heating. Here we also need to clarify another misunderstanding on “the primary mode of energy absorption”. We stated that “due to resonant absorption of Ar_3^+ , the number of Ar_3^+ would rise exponentially”, implying that the primary mode of energy absorption is the resonant absorption of Ar_3^+ , not “resonant multiphoton absorption by the dopant molecule in their Ar cluster” as interpreted by VM.

We are unclear about the statement of “strong enhancement in collisional absorption ... is known to occur because of coherent superposition of collisions in clusters” from VM. Based on the original publication by Mulser, Kanapathipillai, and Hoffmann,² this effect applies to extensively ionized clusters in much stronger laser fields, and the enhancement refers to the comparison between a cluster and an equal number of isolated atoms. The enhancement in the absorption cross section for a 5 nm cluster is 4.1×10^2 obtained at an electron temperature of 1 keV in a field of $\leq 10^{15}$ W/cm² at a level of 100% inner ionization and 98% outer ionization. This condition is clearly different from our situation. Moreover, this collision process as described by VM is very similar to IBS in terms of its dependence on the laser intensity and wavelength, i.e., the ponderomotive energy, and the efficiency of this

process in producing MCAs awaits further quantitative modeling in moderate nanosecond laser fields.

One caveat in comparing the work of Schütte et al.¹⁶ and ours is the different nature of states accessed at different excitation wavelengths: an extreme UV photon (EUV) in the experiment of Schütte et al. can directly ionize any atomic species, some directly into excited ionic states, and preform a plasma before the arrival of the near-infrared (NIR) laser, whereas a visible photon at 532 nm in our experiment cannot. The mechanism of the initial charge accumulation step should be quite different in these two experiments.

On the other hand, as reported by several groups including us,^{1,6–8,10,12,17–19} MCAI formation in moderate nanosecond laser fields is wavelength-dependent, i.e. the longer the wavelength (visible and longer), the higher the charge states of the observed MCAs. This dependence seems to support resonant absorption of a plasma: the resonant frequency of a plasma increases with increasing charge density;^{20,21} hence, as the charges accumulate in the cluster, the resonant wavelength shifts from infrared to visible. Resonant conditions are reached earlier in the excitation process for longer-wavelength laser fields. In the meantime, the cluster expands because of the Coulomb field inside the cluster or the hydrodynamic pressure;²² hence, it is possible that before resonance is reached for a short-wavelength laser in the ultraviolet, for example, the cluster has already disintegrated. Consequently, the formation of MCAs is more conducive in fields of longer-wavelength lasers. We did not address any phenomenon related to the laser wavelength in the publication,¹ because the Letter was meant to be a short report on our own observation.

The additional question on the Supporting Information from VM is confusing. To extract the MCAs with high kinetic energies from the laser field, an electric field on the order of 10^3 V/cm is needed. The high field is to ensure that the MCAs can reach the detector before hitting the wall of the flight tube. Previous reports including those from the Vatsa group²³ and from the Li group⁹ on MCAs also used the same approach, and we do not see what the concern raised by VM is. If the electrons produced in the laser field can be accelerated by the extraction field, they could, although very unlikely because of the low particle density, collide with the cluster and produce more ions. The pulsed extraction field with a time delay is to eliminate this possibility for the formation of MCAs, following the same idea of zero kinetic energy photoelectron spectroscopy:²⁴ the delay time between laser excitation and the pulsed electric field allows the photoionized electrons to fly out of the interaction region, eliminating the possibility of secondary ionization. Altogether there are 3 electrostatic fields that are of concern in our situation: the Coulomb field of the overall cluster, the Coulomb field of the nucleus of Ar^{n+} , and the DC field for ion extraction. The supplementary experiment only confirms that the latest field is not related to the production of MCAs.

The order of magnitude estimate by VM on the number of charges in the cluster and the average charge state of xenon atoms do not seem to bear any relation to the extraction field, pulsed or DC. The statements seem to have missed the fundamental assumption of our idea: if 10% of the atoms in the cluster of 11 000 ($R = 5$ nm ≈ 94 Bohr radius) are outer ionized, the total charge on the cluster will be $Q = 1100$ atomic units (au), and the Coulomb field of the highly charged cluster ($Q/R \approx 11.7$ hartree) is stronger than the field from the nucleus ($Z = 2–8$ au) of a departing Ar^+ ($r = 0.07$ nm ≈ 1.3

Bohr radius) at $Z/r \approx 1.5$ – 6.2 hartree. Therefore, electrons from the departing Ar^+ should be attracted to the cluster, resulting in Ar^{n+} with $n = 2$ – 8 .

The two suggestions by VM on the experiment and interpretation are unclear to us. Measurements on kinetic energies of electrons from this process have been carried out by the Li and Vatsa groups,¹² with a resulting value of tens of electronvolts. We do not see the necessity of performing the same measurement using the same experimental method. We were concerned of the role of these electrons in the mass spectrometer and hence performed the delayed pulsed extraction experiment to eliminate this possibility. We are uncertain of the statement by VM on the possibility that the leading edge of the laser pulse with an even lower intensity than the reported peak value can ionize Ar, and the “ionized matter” can have secondary and tertiary ionization events in the laser field.

We believe that whether the formation of Ar^{n+} is due to electron impact ionization or electron stripping of the departing Ar^+ is still an open question. If an inner ionized electron has a kinetic energy to ionize Ar^{3+} to form Ar^{4+} at 59.81 eV,²⁵ it should also be able to escape the Coulomb field of a cluster containing 141 unit charges with a radius of 3.4 nm (4000 atoms total), achieving outer ionization and resulting in a cluster containing 142 charges. Similarly, if the electron can directly ionize Ar to form Ar^{4+} at 143.94 eV,²⁵ it should also be able to escape the Coulomb field of the same cluster containing 340 unit charges. If so, even if the plasma is initially quasi-neutral, the cluster should become increasingly more positively charged as the plasma is (or the inner ionized electrons are) being heated. The relative contribution of each pathway, electron impact ionization or electron stripping from ejected ions, is the answer we are seeking.

We understand that the prevailing theory on the formation of Ar^+ in strong fields is electron impact ionization,^{15,26–28} and we are fully ready to accept the possibility that this electron-stripping pathway in moderate fields may not have any sizable yield. We are also accumulating further experimental data to elucidate the process. For example, one recent result from our laboratory is the laser power dependence of the different atomic ions: while Ar^{n+} with $n > 1$ demonstrate a similar power law dependence on the laser intensity, Ar^+ has a higher exponent than those with $n > 1$. We believe that the verdict is still out, and more evidence from different angles is still needed before we take the prevailing theory from ultrafast strong fields as the truth in moderate nanosecond fields.

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Notes

The authors declare no competing financial interest.

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