Xenon Clusters in Intense VUV Laser Fields

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A simple model is developed that quantitatively describes intense interactions of a VUV laser pulse with a xenon cluster. We find good agreement with a recent experiment [H. Wabnitz et al., Nature 420, 482 (2002)]. In particular, the large number of VUV photons absorbed per atom—at intensities significantly below $10^{16} \text{ W/cm}^2$—is now understood.

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Little is known about laser–cluster interactions at UV or higher photon energies. The destructive impact of laser pulses with a peak intensity of almost $10^{19} \text{ W/cm}^2$ at a wavelength of 248 nm was demonstrated by McPherson et al. [1]. However, intense laser fields at even higher photon energies have not been accessible until very recently. In 2000, the first lasing—in a free-electron laser (FEL)—at $\lambda = 109$ nm was reported [2]. The FEL is part of the TESLA Test Facility (TTF) in Hamburg, Germany. One of the major objectives of the TTF is the development of the technology for an ultrabright x-ray laser [3]. The new VUV laser source has already displayed its capability for exploring interesting physics:

Motivated by the outstanding properties of the radiation generated by the TTF FEL, documented in Ref. [4], researchers in Hamburg exposed xenon atoms and clusters to the intense VUV laser pulses [5]. Each laser pulse had a duration of about 100 fs and consisted of 12.7-eV photons. The highest intensity in the experiment was about $7 \times 10^{13} \text{ W/cm}^2$ [6]. Under these conditions, isolated Xe atoms are found to be only singly ionized. This observation is compatible with one-photon absorption, as the ionization threshold of Xe is 12.1 eV [7]. Multiphoton processes apparently are of no relevance. Clusters of 1000 atoms or more, on the other hand, behave in a strikingly different way: They absorb at least 30 VUV photons per atom. The clusters are completely destroyed, and ion charge states of up to $8^+$ can be detected.

It is the purpose of this Letter to elucidate the physics underlying the experimental observations. We show that the high efficiency of VUV photon absorption in xenon clusters is due to inverse bremsstrahlung [8,9,10] in combination with atomic-structure and plasma-screening effects. Nonlinear optical processes do not play a role.

Considering the relatively low intensity of the TTF FEL, the experimental findings are rather surprising. Producing similarly pronounced ionization and fragmentation phenomena in noble gas clusters using near-infrared lasers requires pulse intensities of $10^{16} \text{ W/cm}^2$ or higher [11]. Under these circumstances, the clusters are turned into microplasmas, and x-ray emission [12] and highly energetic electrons [13] and ions [14] can be observed.

The high intensity at long wavelengths serves two purposes [15,16,17,18]. On one hand, even though a noble gas atom cannot be ionized by single near-infrared photons, some of the valence electrons can tunnel through, or even escape over the potential barrier generated by the ionic core and the strong quasistatic electric field of the laser. On the other hand, the average kinetic energy, or ponderomotive potential, of an electron oscillating in the laser field can easily be of the order of 1 keV. This energy can be released in collisional ionization, i.e., $(e, 2e)$ type reactions. Moreover, in energetic electron–ion collisions a substantial number of photons can be absorbed from the laser field. This heating mechanism is referred to as inverse bremsstrahlung (IBS).

At VUV photon energies, however, the ponderomotive potential is only on the order of 10 meV. Indeed, numerical simulations and estimates in Ref. [2], which are based on methods developed in the context of low-frequency lasers [15,17], predict the absorption of only a few photons per atom. This differs from the experimental result by more than an order of magnitude.

The photoionization cross section of neutral Xe at $\hbar \omega = 12.7$ eV is roughly 50 Mb [19]. Hence, a pulse with an intensity of $10^{15} \text{ W/cm}^2$ ionizes all atoms in a cluster within 10 fs. The resulting plasma bears some similarity to a metal: The plasma electrons can move freely, but because of the high atomic density there is a high probability for electron–ion and electron–electron collisions. Free electrons cannot absorb photons; neither can photons be absorbed in electron–electron collisions [10].

However, electron–ion collisions can extract energy from the laser field via IBS. Since we are considering relatively moderate intensities and rather short wavelengths, it is legitimate to treat this process perturbatively. Using second-order perturbation theory (first order in electron–ion and electron–photon coupling, respectively) and assuming a cluster of infinite spatial extension but constant atomic density, one can derive a quantum-mechanical formula for the heating rate per plasma electron. In our implementation of the IBS heating rate, we avoided making use of the classical limit $\hbar \rightarrow 0$, which is often taken in the weak-field case (see, for example, Ref. [2]), but which is inappropriate for VUV photons. We exploit, however, the fact that due to numerous collisions with ions and electrons all directionality imprinted on the plasma electrons by the linear polarization of the VUV laser field is lost and thermal equilibrium among the plasma elec-
tronized prior to the laser pulse. The average initial kinetic energy of a plasma electron is 0.01 hartree. The laser pulse, having a peak intensity of $7.3 \times 10^{13}$ W/cm$^2$, is Gaussian. It is centered at $t = 0$; its FWHM is 100 fs. If the electrons are scattered by simple (Debye-screened) Coulomb potentials, only one photon per atom is absorbed from the laser field. About 30 photons are absorbed, however, if a more realistic atomic scattering potential is taken.

Let all atoms in the cluster be singly ionized (we treat the combined effect of photoionization and IBS later), and let the atomic density be that of liquid xenon. To a first approximation, the plasma electrons are scattered by point-like ions of charge +1. Additionally, the plasma electrons can screen the ionic field. Using a Debye-shielded Coulomb potential $20$, we calculated the number of VUV photons absorbed per atom via IBS, a plasma electron having an average initial kinetic energy of 0.01 hartree. (Screening due to ions as well as ionic motion during the laser pulse are neglected throughout.) The result, as a function of time, is shown in Fig. 1. Our data are based on a Gaussian laser pulse, centered at $t = 0$ with a FWHM of 100 fs. The peak intensity is $7.3 \times 10^{13}$ W/cm$^2$. After the pulse is over, each plasma electron has absorbed only a single photon, which is clearly in disagreement with experiment, but analogous to the estimate quoted in Ref. 8.

The probability of finding a neutral atom in the cluster is $n_0$; $n_1$ and $n_2$ refer to singly and doubly ionized species, respectively. The same laser parameters as in Fig. 1 are used. Plasma screening, which is responsible for efficient double photoionization of xenon, is taken into account. Collisional ionization is not included.

So far we have restricted ourselves to a preformed plasma interacting with a laser pulse. In order to arrive at a more complete picture, we need to follow the time evolution of photoionization and collisional heating. Since we anticipate plasma screening effects to lower the simple Coulomb field. A more realistic treatment of the atomic potential is needed. We use the form

$$V_i(r) = -\frac{1}{r} \left( i + [Z - i] \exp(-\alpha_i r) \right) \exp(-r/\lambda_D),$$

where $i$ is the ionic charge state, $Z = 54$ the nuclear charge, and $\lambda_D$ the Debye length. The parameter $\alpha_i$ controls the transition from the exterior of the ion to its interior, where a colliding electron experiences an effective charge higher than $i$. We adjust $\alpha_1$ in such a way that the binding energy of a 5$p$ electron in the potential $V_1(r)$ (for $\lambda_D \to \infty$) equals the ionization potential of neutral Xe. That the resulting potential is useful for quantitative predictions can be illustrated by calculating the photoionization cross section: At 12.7 eV, we find agreement with experiment to within 10%. (Both the binding energy and the photoionization cross section are calculated by numerically diagonalizing the one-electron Hamiltonian based on $V_i(r)$.) If we now suppose that a plasma electron scattered by Xe$^+$ experiences the same potential, $V_1(r)$, then the number of absorbed VUV photons per atom turns out to be about 30. This is illustrated in Fig. 2. The mechanism of IBS is, thus, indeed capable of explaining the huge amount of VUV laser energy deposited in a large xenon cluster.
ionization thresholds, our treatment is not restricted to single photoionization. We formulate a set of coupled rate equations for the time-dependent probabilities \( n_i(t) \) \((i \geq 0)\) of finding \( \text{Xe}^{i+} \) in the cluster:

\[
\begin{align*}
\dot{n}_0(t) &= -\sigma_1(t) j_{ph}(t) n_0(t) \\
\dot{n}_1(t) &= \sigma_1(t) j_{ph}(t) n_0(t) - \sigma_2(t) j_{ph}(t) n_1(t) \\
&\vdots
\end{align*}
\]

Here, \( j_{ph}(t) \) is the photon flux. These rate equations require knowledge of the photoionization cross sections \( \sigma_i+1(t) \) of the \( \text{Xe}^{i+} \) species embedded in the Debye plasma. Taking the double \( \text{21} \), triple \( \text{22} \), and quadruple \( \text{23} \) ionization thresholds from the literature, we can determine, in addition and in analogy to \( \alpha_1 \), the parameters \( \alpha_2, \alpha_3, \) and \( \alpha_4 \) (see Eq. 11). (In so doing, we imply that the various 5p levels have—at least approximately—the same energy.) With this information, the photoionization cross sections of \( \text{Xe}, \text{Xe}^{+}, \text{Xe}^{++}, \) and \( \text{Xe}^{3+} \) can be calculated as a function of time. Note that the Debye length in Eq. 1 is time-dependent, for it is a function of the temperature and density of the plasma electrons.

The rate equations governing the populations \( n_i(t) \) are complemented by a rate equation that describes heating of the plasma electrons:

\[
\dot{E}_{\text{kin}}(t) = \frac{3}{2} q(t) \dot{T}(t) + \sum_i \varepsilon_i(t) \sigma_i(t) j_{ph}(t) n_{i-1}(t),
\]

where \( q(t) \) is the average number of plasma electrons per atom, \( T(t) \) the electron temperature (in units of energy), and \( \dot{E}_{\text{kin}}(t) = \frac{3}{2} q(t) \dot{T}(t) \). \( \varepsilon_i(t) \) denotes the kinetic energy of a photoelectron leaving \( \text{Xe}^{i+} \) behind. Two contributions are taken into account in Eq. 3: the collisional heating rate due to IBS (\( \dot{T}(t) \)) and the kinetic energy of photoelectrons newly added to the plasma. This rate equation also depends on the neutral and ionic populations as well as the respective photoionization cross sections.

Starting with a cluster of neutral atoms in their ground state, we numerically integrate the entire set of coupled rate equations (Eqs. 2 and 3). For laser pulse parameters identical to the ones employed for Fig. 1, the probabilities \( n_i(t) \) shown in Fig. 2 are obtained. As expected, the neutral population is completely depleted after just 10 fs or so. It is more interesting to observe that singly ionized xenon also vanishes on the same timescale. Due to plasma screening, the production of \( \text{Xe}^{++} \) becomes energetically accessible. Higher ionic charge states, however, cannot be generated by direct photoionization.

According to Fig. 2, all xenon atoms are doubly ionized before the laser pulse even reaches its maximum. Therefore, each atom contributes two electrons to the plasma, which results in enhanced energy absorption: Almost 70 photons per atom are taken from the VUV laser field at a peak intensity of \( 7.3 \times 10^{13} \) W/cm\(^2\), as can be seen in Fig. 3. Also shown in that figure are the corresponding data for lower laser intensities. Clearly, reduced intensities lead to a smaller number of plasma electrons and to less collisional heating. On the log–log scale of Fig. 3, the effect may appear to be dramatic. However, the relationship between the number of absorbed photons and the peak intensity of the laser pulse is really a linear one. The solid line in Fig. 3 represents a linear fit to the data.

There is no optical nonlinearity involved. In fact, our model of photoionization and IBS does not contain true multiphoton physics. Nevertheless, at high intensity, many photons are absorbed by each plasma electron. But this does not happen in a single step. Each plasma electron is scattered many times and can absorb only a single photon during a collision with an ion.

Up to this point, we have ignored collisional ionization. This effect can be incorporated \textit{a posteriori} by noticing that electron–ion collisions facilitate a thermal equilibrium among the plasma electrons and the ions. Thus, the electron gas is cooled, and energy is transferred to the ions. In order to quantify this picture, the first eight ionization potentials of xenon are needed. To this end, we made use of the complete-active-space self-consistent-field code implemented in the \textit{ab initio} package MOLPRO \( 24, 25 \) and of the effective core potential by LuJohn et al. \( 26 \). Our first four ionization potentials are in agreement with experiment \( 21, 22, 23 \) at a level of a few percent. We assign a similar accuracy to our calculation of the energies required to turn a neutral xenon atom into even more highly charged ions: 156 eV for \( \text{Xe}^{5+} \), 220 eV.
for Xe$^{6+}$, 310 eV for Xe$^{7+}$, and 414 eV for Xe$^{8+}$. (It is justified to use unscreened ionization potentials at the end of the laser pulse, in view of the fact that at high intensities the electron kinetic energies are rather high and at low intensities there are just a few electrons that could contribute to shielding.)

From the solution of our coupled rate equations, we determine the total laser energy stored in the electrons and ions. This energy is then redistributed assuming: a Boltzmann distribution for the ionic charge states; thermal kinetic energies for electrons and ions; the existence of a common temperature. A statistical weight is introduced for each ionic charge state by simply counting the number of ways the valence electrons can be distributed over the $5p$ spin orbitals (Xe, ..., Xe$^{5+}$; the 5s level being doubly occupied) or over the 5s spin orbitals (Xe$^{6+}$, Xe$^{7+}$). A single state is assigned to Xe$^{8+}$. (Other electronic states of the Xe$^{i+}$ are neglected.) The ionic populations resulting from this procedure are plotted in Fig. 4 together with experimental data taken from Ref. 5. Considering the simplicity of our approach, it is amazing how well the experimental Xe$^{i+}$ populations for various laser intensities can be reproduced. We learn from Fig. 4 that the experimental signal, obtained after fragmentation of the clusters, basically reflects the thermal ionic distribution in the plasma.

In this Letter, we have demonstrated that some of the concepts familiar from low-frequency laser–cluster physics can be transferred to higher photon energies. However, this transfer requires a more detailed description of atoms in plasmas than previously anticipated. Similar care is therefore necessary when evaluating the potential of future x-ray lasers for imaging of single molecules. If not all physically relevant processes are taken into account, for example interatomic electron-correlation phenomena following core-hole relaxation, then the degree of damage caused in a large biomolecule, for instance, can be easily underestimated.

We believe that the theoretical description presented here provides insight into the nature of intense laser–cluster interactions at VUV wavelengths. Yet we anticipate that, in this new laser regime of higher photon energies, many more surprises are likely to emerge.

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