Anomalous Collision-Free Multiple Ionization of Atoms with Intense Picosecond Ultraviolet Radiation

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Collisionless multiphoton absorption, resulting in multiple atomic ionization and exhibiting anomalously strong coupling, has been studied in the region spanning atomic number $Z = 2$ (He) to $Z = 92$ (U). The highest ion state identified is U^{10+}, corresponding to absorption of 99 quanta (~ 633 eV). Models of stepwise ionization using standard theoretical techniques are incapable of describing these results. A mode of interaction involving radiative coupling to a collective motion of an atomic shell is proposed.

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The availability of spectrally bright picosecond ultraviolet light sources enables the study of nonlinear coupling mechanisms in that spectral range under experimental circumstances unaffected by collisional perturbations. In this Letter, the results of the first experiments examining the atomic-number dependence of processes of multiple ionization of atoms X with intense ($\lesssim 10^{14}$ W/cm^2) picosecond 193-nm radiation under *collision-free* conditions are reported.

The general physical process studied is

$$N\gamma + X \rightarrow X^{q+} + qe^- \quad (1)$$

for which observed values of N and q range as high as 99 and 10, respectively. Of particular significance is the behavior of the amplitude for Reaction (1) as a function of atomic number (Z). Accordingly, the response of materials spanning the range in atomic number from He ($Z=2$) to U ($Z=92$) has been measured. Similar processes involving the irradiation of Kr at 1.06 μm have recently been described by L'Huillier *et al.*,[1] in addition to other studies concerning the characteristics[2] of Xe and Hg.

The experiments reported herein exhibit two salient features. These are (1) an unexpectedly strong coupling for extraordinarily high-order processes, and (2) a coupling strength which is dramatically enhanced at higher Z values.

The experimental arrangement used to detect the production of the highly ionized species consists of a double-focusing electrostatic energy analyzer (Comstock) operated as a time-of-flight mass spectrometer. The analyzer is positioned in a vacuum vessel which is evacuated to a background pressure of $\sim 10^{-7}$ Torr. The materials to be investigated are introduced into the chamber in a controlled manner at pressures typically from $\sim 3\times 10^{-7}$ to 10^{-5} Torr. The 193-nm ArF* laser used for irradiation[3] ($\sim$10 psec, $\sim$4 GW) is focused by a $f=50$-cm lens in front of the entrance iris of the electrostatic analyzer, producing an intensity of $\lesssim 10^{14}$ W/cm^2 in the experimental volume. The number of atoms in the focal volume is estimated to be $\sim 10^4$ at 10^{-5} Torr. Therefore, any ion produced with a probability less than $\sim 10^{-4}$ cannot be detected without extensive signal averaging. Ions formed in the focal region are collected by the analyzer with an extraction field in the range of 50–500 V/cm and detected with a microchannel plate at the exit of the electrostatic device.

Representations of the experimental results are given in Figs. 1(a) and 1(b) and Table I. Figure 1(a) shows a sample of typical time-of-flight ion current data for Xe. Table I contains the normalized relative abundances of the observed ion charge states for Xe, derived from Fig. 1(a) and uncorrected for detector sensitivity. Experiments indicate that the detector is about four times as sensitive for Xe^+. Similar data have been recorded for He, Ne, Ar, Kr, I, Hg, and U. In Fig. 1(b), the observed ions and the total energies required for their generation in the electronic ground state are given.

A remarkable feature of the data is the magnitude of the total energy which can be communicated to the atomic systems, especially for high-Z materials. The total energy investment[4-7] of $\sim$633 eV, a value equivalent to 99 quanta, needed to generate U^{10+} from the neutral atom, with neglect of the small contribution associated with molecular binding[8] in the experimental material UF_6, represents the highest energy value reported for a collision-free nonlinear process. The removal of the tenth electron from uranium, which requires[5] $\sim$133 eV if viewed as an independent process, requires a minimum of 21 quanta. The coupling strength implied by this scale of energy transfer at an intensity of $\sim 10^{14}$ W/cm^2 very sub-

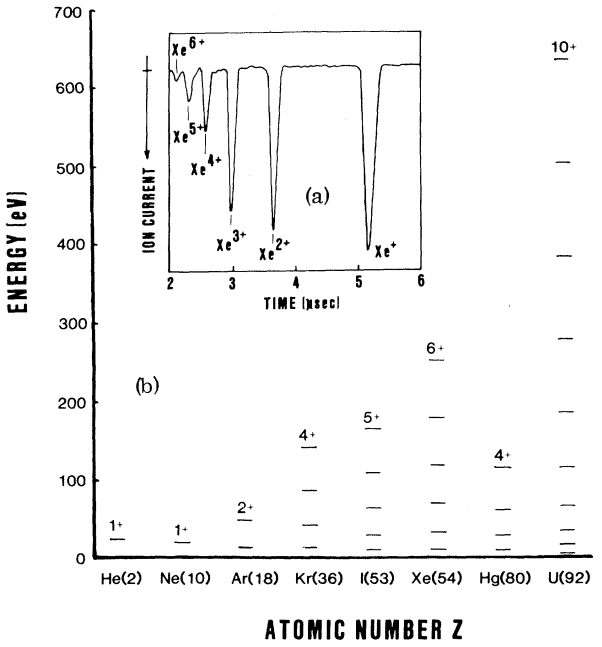

FIG. 1. Data concerning multiple ionization of atoms for 193-nm irradiation at $\sim 10^{14}$ W/cm^2. (a) Inset: typical time-of-flight ion current signal for xenon. (b) Plot of total ionization energies of the observed charge states as a function of atomic number (Z).

stantially exceeds that anticipated from conventional theoretical formulations describing multiquantum ionization.

Aside from the magnitude of the observed excitation energies, the general and strong tendency for increased coupling for materials heavier than argon and the similarity in the response of I and Xe, for which the maximum charge state observed in both cases corresponds to complete loss of the $5p$ shell, are significant. An examination of the ionization energies[4,5] for the species involved fails to suggest any consistent picture for this behavior. For example, the ionization of the second electron from He, which is not detected, requires an energy of ~54.4 eV, a value less than that necessary to remove the fifth electron from Xe. We are led to the conclusion that some factor other than the magnitude of the ionization potentials corresponding to the different species, or equivalently, the order of the nonlinear process, governs the strength of the coupling.

An explanation based simply on the density of states is also unconvincing. A comparison of the excited-state structures[9,10] for He and Ne quickly shows that the density of levels for Ne is very large in comparison to that for He, but only singly

TABLE I. Charge-state distribution of xenon derived from Fig. 1(a).

Charge state	Relative abundance
1+	44
2+	26
3+	20
4+	7
5+	5
6+	1

ionized species are observed for both materials. Likewise, the comparison of Xe and Hg leads to the conclusion that the density of states is not a key factor in determining the coupling strength.

Conversely, all the conspicuous characteristics of Fig. 1(b) can be consolidated if the shell structure of the atom is the principal physical property determining the magnitude of the coupling. The considerable change seen in the atomic response observed between Ar and Kr implicates a role for the $3d$ shell which is filled in that region. A very similar variation between Ar and Kr, that has been observed in the amplitude for single-quantum multiple photoionization,[11] has been attributed to correlation effects arising from the d shell. A significant shell-dependent effect is also suggested by the comparative behavior of I and Xe, since complete removal of the valence $5p$ shell is observed in both cases although the total energies required differ substantially. We note that I and Xe exhibit similar and unusually intense $4d$ absorptions[12,13] in the region ~100 eV, strongly implicating correlated[14-16] motions in that shell.

The most elementary mechanism that could lead to the production of the observed ionic charge states is the stepwise removal of the individual electrons by conventionally described multiphoton ionization. A given charge state (e.g., Xe^{6+}) then requires the generation of all lower charge states, thereby linking the probability for its occurrence directly to the rates of production of these other species. The appearance of Xe^{6+} would require a sequence of 2-, 4-, 6-, 8-, 10-, and 12-photon processes of ionization.

The probabilities for multiphoton transitions calculated with standard perturbative approaches[17] and procedures valid in the high-field limit[18] have been discussed for single-electron systems. From these calculations, it can be shown that, at the 193-nm intensity of $\sim 10^{14}$ W/cm^2 used in these experiments, the transition rates for N-

photon processes decrease very rapidly with increasing N. An estimate shows that for $N=3, 5, 7$, the relative transition probabilities scale as $1:\sim 10^{-4}:\sim 10^{-8}$. On this basis, the expected ionic distributions should decrease very sharply towards higher charge states. Indeed, the abundances of ions in charge states $q>3$ would fall below the detection limit of the apparatus used. It follows that the results obtained from single-electron models for multiquantum processes of this nature do not represent the observed experimental findings involving charge states $q>3$. This conclusion holds for all materials studied that are heavier than Ar. Conversely, inspection of the experimental data indicates that the low-Z materials, essentially up to Ar, exhibit behavior in reasonable accord with that predicted by conventional theory. This interpretation can be reconciled with the presence of two different coupling mechanisms, one dominating in the low-Z region and the other providing enhanced coupling in the higher-Z materials. From our data, the division between these two regimes appears to occur between Ar and Kr.

The very substantial underestimate provided by standard theoretical models of the coupling strength observed and the envelope of the Z dependence both conspire to support an interpretation involving an alternative mode of coupling. The enhanced and anomalous strength of the radiative interaction points to a collective response of the atom. Such a collective response, or atomic plasmon,[19] is anticipated to be favored in the outer subshells of high-Z materials for which the correlation energy becomes a more substantial fraction of the total electronic energy.[4,20] The coherent motion envisaged has a counterpart in nuclear matter known as the giant dipole,[21] although giant multipoles higher than the dipole are known.[22]

All aspects of the experimental findings can be unified if an important mode of nonlinear coupling involves a direct multiquantum interaction with an atomic shell which undergoes a collective response. In this picture, it would follow naturally that the shell structure of the material would be reflected as an important property governing the coupling to the radiation field. Collective inner-shell responses have been discussed in relation to processes of single-photon ionization.[23] It is generally found that in cases for which the electronic correlations are important, the single-particle spectrum is very greatly altered, leading to a collectively enhanced many-electron process. In this regard, the xenon $4d^{10}$ shell[24,25] and the lanthanides[26] have been studied extensively. Recent analyses of collective responses in atomic and molecular systems have been given by Brandt and co-workers,[27-29] Wendin,[14,16,24] and Amusia and co-workers.[15,30] The results of our current studies simply indicate a nonlinear analog of this basic electronic mechanism. In the present experiments, the implication of the d-shell electrons seems particularly strong given the sharp change in behavior seen between Ar and Kr. Naturally, f electrons[31] would be expected to behave similarly, a consideration that clearly motivates study of the lanthanide sequence. Finally, the spatial dependence of the self-consistent field experienced by the atom[23] is expected to give rise to a complex Z dependence of the atomic response, an aspect that may be related to the relatively low value of maximum energy indicated in Fig. 1(b) for Hg.

In summary, studies examining the nonlinear coupling of intense ultraviolet radiation to atomic systems, spanning the atomic number range $Z=2$ to $Z=92$, reveal several important characteristics of this interaction. It is concluded that the conventional treatments of multiquantum ionization do not correspond to our experimental findings for high-Z materials. The essential findings are (1) an unexpectedly large amplitude for collision-free coupling, (2) a strong enhancement in the coupling strength for the heavy elements, and (3) the inference, based on the atomic-number dependence and the anomalous coupling strength, that a collective motion of d and f shells may play an important role in these phenomena. With this physical picture, selectivity in the population of excited ionic states is expected on the basis of photoelectron studies.[32]

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