# Collision-free multiple photon ionization of atoms and molecules at 193 nm

T. S. Luk, U. Johann, H. Egger, H. Pummer, and C. K. Rhodes
*Department of Physics, University of Illinois at Chicago, P.O. Box 4348, Chicago, Illinois 60680*
(Received 4 February 1985)

The nonlinear coupling of 193-nm radiation to a range of atomic and molecular materials has been experimentally explored up to a maximum intensity on the order of $\sim 10^{17}$ W/cm$^2$. Studies of collision-free ion production clearly exhibit anomalous behavior which strongly implies that the atomic shell structure is the principal determinant in the observed response. On the basis of the observed coupling strength and the measured atomic-number ($Z$) dependence, the experimental evidence points to a coherent atomic motion involving several electrons, possibly an entire shell, as the main physical mechanism enabling the scale of energy transfers seen. Therefore, states representing multiple excitations appear to play a central role in the coupling, a consideration that fundamentally distinguishes the nonlinear interaction of a multielectron atom from that of a single-electron system. Comparison of the experimental findings with standard theoretical treatments, of either a perturbative or nonperturbative nature, does not produce satisfactory agreement. Conversely, the formulation of a simple classical estimate qualitatively conforms to several features of the observed behavior including the shell character of the interaction, the maximum energy transfer, the dependence of the average energy transfer on the intensity of irradiation, the frequency dependence of the observed energy transfer, and the weak influence of polarization.

## I. INTRODUCTION

The initial studies[1,2] of the $Z$ dependence of collision-free multiphoton ionization of atoms at 193 nm clearly exhibited anomalous behavior in terms of the gross rate of energy transfer. The general class of physical processes studied was

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

A prominent feature of these studies was the unusually strong nonlinear coupling found characteristic of certain heavy materials such as Xe and U. In the case of U, the maximum observed values of $N$ and $q$ were found to be 99 and 10, respectively. By comparison with theoretical approaches based on perturbation theory,[3–5] these experiments clearly demonstrated that standard theoretical techniques were incapable, by a discrepancy as great as several orders of magnitude, of describing the observed results. Subsequent work,[6] conducted at a wavelength of 1.06 $\mu$m, has confirmed the anomalous nature of the coupling strength.

## II. EXPERIMENTAL CONSIDERATIONS

For the studies of multiple ionization conducted since the earlier studies[1,2] were completed, the 193-nm ArF* laser used for irradiation[7] ($\sim$5 psec, $\sim$3 GW) was focused by an appropriate lens to generate intensities in the range of $10^{15}$–$10^{17}$ W/cm$^2$ in the experimental volume. In order to produce the highest intensities used, an $f/2$ aspheric focusing element was necessary. The ions are created in a vacuum vessel which is evacuated to a background pressure of $\sim 10^{-9}$ Torr.

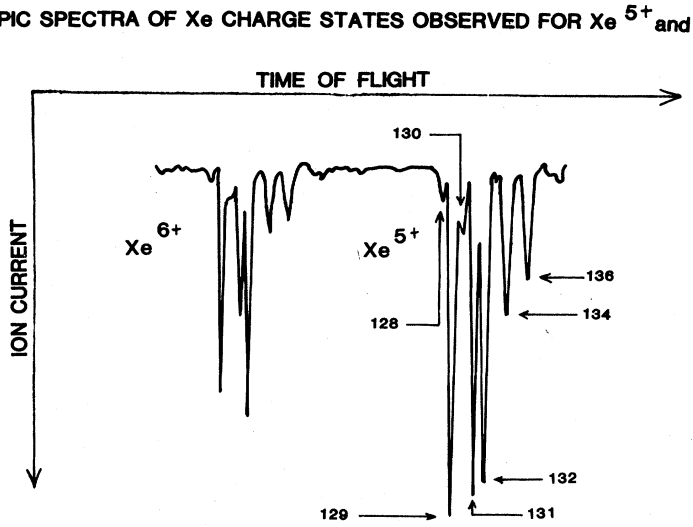
In contrast to the earlier work,[1,2] the ion analyzer had a greatly extended time-of-flight drift region which permitted significantly superior mass and charge discrimination.[8] In this case, the isotopic signature of heavy atoms was readily distinguished.[9] This aspect provided a clear identification of the signal and enabled unambiguous separation of the desired ion current from any spurious signals originating from the background gas.

Figure 1 illustrates the characteristic isotopic pattern observed for $Xe^{5+}$. Note the close correspondence of the individual isotopic peaks to the strengths expected on the basis of the isotopic natural abundance.[10] Under typical experimental conditions, the ions formed in the focal region were collected by the analyzer with an extraction field in the range of 100—5000 V/cm, and a microchannel plate located at the exit of the time-of-flight region served as the ion detector. In addition, a laser-evaporation technique has been incorporated[11] into the apparatus to enable the study of elements, such as the lanthanides, which are not conveniently available in gaseous form, and preliminary experiments involving Eu and Yb have been conducted.

## III. EXPERIMENT RESULTS ON ION PRODUCTION

The basic information obtained by observation of the ion spectra pertains to the scale of the energy transfer, for both average and peak values, communicated to the target atom $X$ by the radiation field. An examination of the $Z$ dependence of the average energy transfer is informative. Figure 2 illustrates the dependence observed at 193 nm for an intensity of irradiation in the range of $10^{15}$–$10^{16}$ W/cm$^2$. The comparison in the average energy absorbed for the adjacent elements, I ($Z=53$) and Xe ($Z=54$), is remarkable. This difference, which is approximately a factor of 4, cannot reasonably be attributed to experimental error, since only the strong, easily registered ion-signal




(a) ISOTOPIC ABUNDANCES OF XENON ISOTOPES

Insert (a) shows the comparison of the observed and natural abundances.

| ISOTOPIC WEIGHT | 128 | 129 | 130 | 131 | 132 | 134 | 136 |
|---|---|---|---|---|---|---|---|
| NATURAL ABUNDANCE | 0.07 | 0.98 | 0.15 | 0.8 | 1.0 | 0.39 | 0.33 |
| OBSERVED $Xe^{5+}$ | 0.1 | 1.1 | 0.2 | 1.03 | 1.0 | 0.46 | 0.36 |

FIG. 1. Isotopic spectra of $_{54}Xe^{5+}$ and $_{54}Xe^{6+}$ are shown, and their relative abundance is compared with the natural abundance.

components figure appreciably in the calculation of the average energy. Furthermore, since the two elements are close in atomic mass, the ion velocities of the two materials, for a given charge state, are nearly identical, rendering corrections in the sensitivity of the channel-plate detector due to differences in velocities negligible. We conclude that some factor involving the basic atomic structure of the materials must account for the observed differences in energy transfer and that this factor can vary rapidly in atomic number.

The ion production in several elements has been studied for a range in atomic number spanning He ($Z=2$) to U ($Z=92$) at intensity levels above those used in the initial work.[1,2] A typical ionic spectrum for xenon is illustrated in Fig. 3. In this case, there is the clear presence of eight charge states, the first five of which are seen to have approximately comparable abundances. An overall summary of the species observed is presented in Fig. 4. As represented in this figure, the maximum observed energy transfers are on a scale of several hundred electron volts

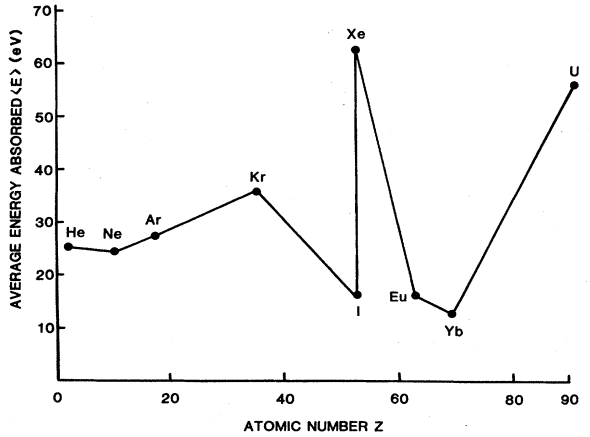



FIG. 2. Average energy absorbed per atom under collision-free conditions for irradiation at 193 nm with an intensity in the range of $10^{15}$–$10^{16}$ W/cm$^2$.

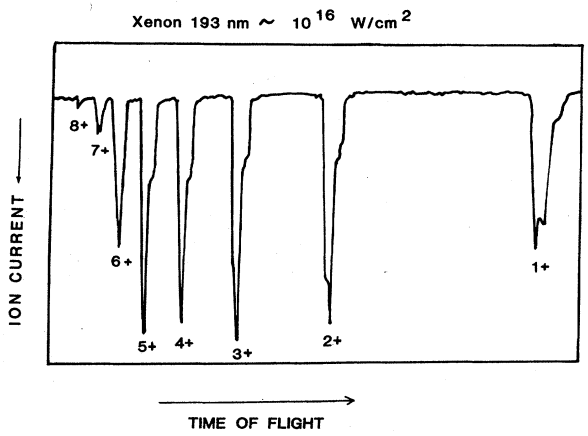



FIG. 3. Time-of-flight ion spectrum of xenon irradiated at $\sim 10^{16}$ W/cm$^2$ at 193 nm.

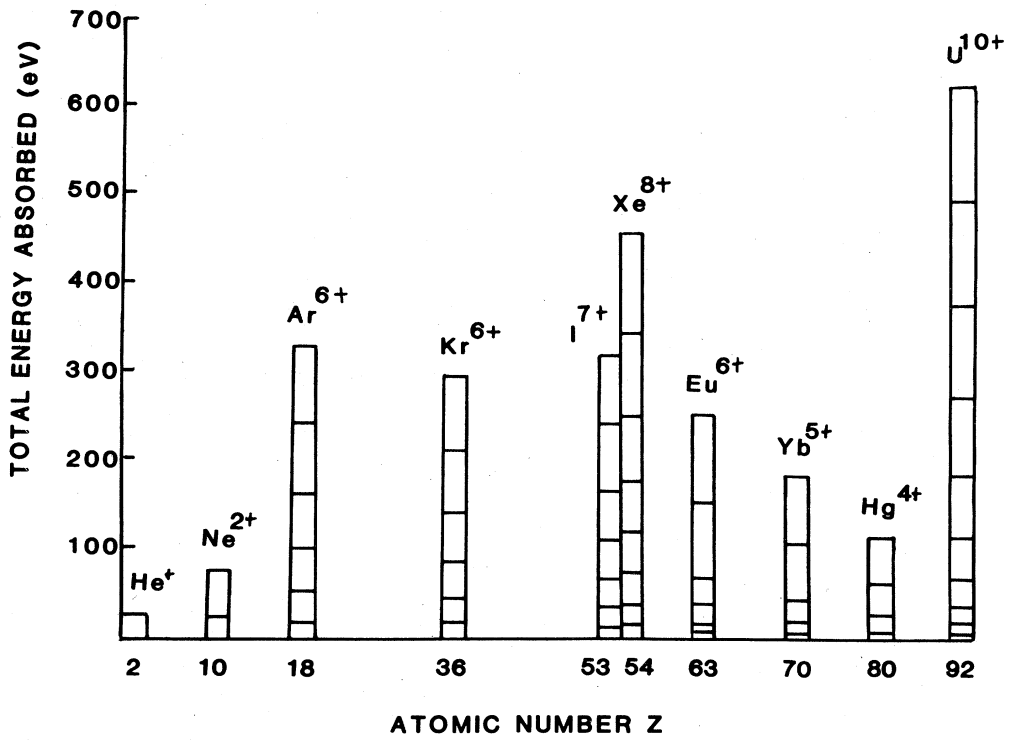



FIG. 4. Data concerning the multiple ionization of atoms for irradiation at 193 nm. Plot of total ionization energies of the observed charge states as a function of atomic number ($Z$). $_{53}I^{7+}$ was not positively identified because it coincides with an $H_2O^+$ background signal.

for the heavy materials. In the earlier experiments[1] conducted at $\sim 10^{14}$ W/cm$^2$, an examination of the ionization energies[12,13] of the species involved failed to suggest any consistent picture for the understanding of the stages of ionization produced. Furthermore, the subsequent work reported herein shows that this situation continues to exist at intensity levels as high as the $10^{16}$–$10^{17}$ W/cm$^2$ range. For example, the ionization of the second electron from He, which is not detected, requires an energy of $\sim 54.4$ eV, a value less than that necessary to remove the fifth electron from Xe, a process which is clearly seen. 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. Clearly, this strong variation in coupling strength cannot be explained by standard perturbative and unperturbative theories.

Another clear characteristic of these data is the shell dependence manifested in the behavior of the heavier rare gases. For Ar, Kr, and Xe, the maximum charge states observed would correspond to the complete removal of atomic subshells. For these materials they are the $3p$, the $4p$ and both the $5s$ and $5p$ shells, respectively. Similarly, if the $I^{7+}$ signal is present under the $H_2O^+$ peak, then that also implies complete removal of the $5s$ and $5p$ shells.

The hint provided by the role of the shell structure described above led to the hypothesis that it was mainly the number of electrons in the outer subshells that governed the coupling. A measurement of the response of elements in the lanthanide region, with the use of a method involving laser-induced evaporation to provide the material, enabled this view to be checked. As one moves from La ($Z=57$) to Yb ($Z=70$) in the lanthanide sequence, aside from slight rearrangements involving the $5d$ shell for Gd ($Z=64$), $4f$ electrons are being added to interior regions of the atoms. The data illustrated in Fig. 4 for $_{63}$Eu ($4f^7 6s^2$) and $_{70}$Yb ($4f^{14} 6s^2$), which differ by seven $4f$ electrons, indicated that these inner electrons play a small role in the direct radiative coupling, a fact that is in rapport with the observed dependence on the outer-shell structure.

The intensity dependence of these ion spectra, corrected for the relative sensitivity of different charge states,[14] has also been examined, and Fig. 5 illustrates the nature of this response for xenon. Over the range of intensities studied ($\sim 10^{15}$–$10^{17}$ W/cm$^2$), higher intensity translates generally into an increased yield of ions of a particular charge, although not necessarily an increase in the maximum charge state observed. For example, the ion $_{54}Xe^{8+}$, with ground-state[15] configuration $4d^{10}$, is the greatest charge state detected at $\sim 10^{16}$ W/cm$^2$, and although its abundance increases at $\sim 10^{17}$ W/cm$^2$, no $_{54}Xe^{9+}$ appears at the higher intensity. The average energy communicated to the atom also increases at the higher intensities, although clearly not as rapidly as the intensity. In the case of xenon, as shown in Fig. 5, the average ener-

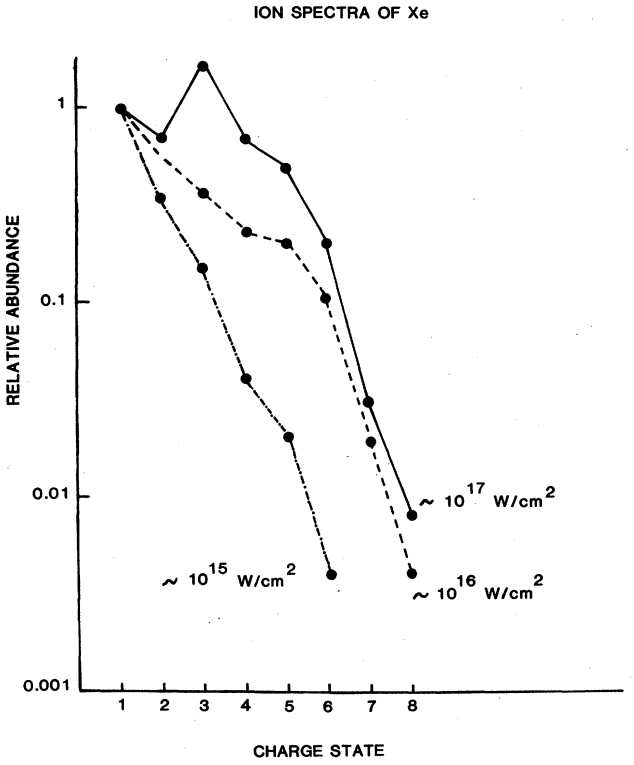



FIG. 5. Relative abundance of charge-state distributions observed in the ion spectra of xenon in the intensity range $10^{15}$–$10^{17}$ W/cm$^2$ at 193 nm.

gy increased by only approximately a factor of 7 when the intensity was increased 100-fold. It is important, however, to be aware of the experimental uncertainty involved in the intensity dependence, since low-charge states can be disproportionately produced in the outer regions of the focal volume. This particular effect is expected to be somewhat more significant for materials, such as $_{63}$Eu and $_{70}$Yb, which can be ionized by a single 193-nm photon. Nevertheless, the data illustrated in Fig. 5 clearly show a relatively weak intensity scaling for the high-order ($N$) process that produces the higher-charge-state species observed.

Several existing types of nonperturbative calculations predict a variety of different laws governing the intensity ($I$) scaling of the transition probabilities. For a field strength comparable to or greater than the binding field $E_b$ of the electrons, Pert[16] and Mittleman[17] derived $I^{-1/2}\ln(I/I_0)$ and a $I_0/N^2I$ relationships, respectively, in which $I_0$ represents the intensity corresponding to the value of the electronic-binding field $E_b$. Moreover, under conditions for which the radiative-field strength is small compared to the electronic-binding field $E_b$, Keldysh[18] obtained a $I^{1/4}$ scaling. Furthermore, for the experiments under consideration, it is not apparent that the analyses of Pert[16] and Mittleman[17] can be validly applied to the production of the higher observed charge states, since the intensity $I$ is much less than the corresponding $I_0$ for those species. Finally, we note that, in the weak-field limit corresponding to applicability of the Keldysh[18] approach, the model predicts a substantial abundance of $He^{2+}$, a conclusion that stands in contrast to the experimentally observed absence of this charge state.

The frequency dependence of the coupling has also been examined by comparison of our results at 193 nm with other studies performed[19,20] at 1.06 $\mu$m and 0.53 $\mu$m. The comparison, conducted at an intensity of $\sim 10^{14}$ W/cm$^2$ for both krypton and xenon, indicates that the average energy absorbed is reduced at the longer wavelengths. Figures 6 and 7 illustrate these comparative differences for krypton and xenon, respectively.

The influence of laser polarization has been studied for xenon. With the use of a quarter-wave plate, the linearly polarized radiation normally produced by the 193-nm source[7] can be conveniently transformed into circularly polarized radiation. The ion spectra observed for xenon were found to be negligibly modified by the change from linear to circular polarization. This result is in contrast to that expected on the basis of perturbation theory analysis[3] in the single-electron picture of the interaction. In that case, for high-order processes, the much greater abundance of available channels for linear polarization produces a substantially greater ionization rate in comparison to that characteristic of circular polarization. Nonperturbative treatments[21] also indicate that greater ionization rates are commonly associated with linear polarization.

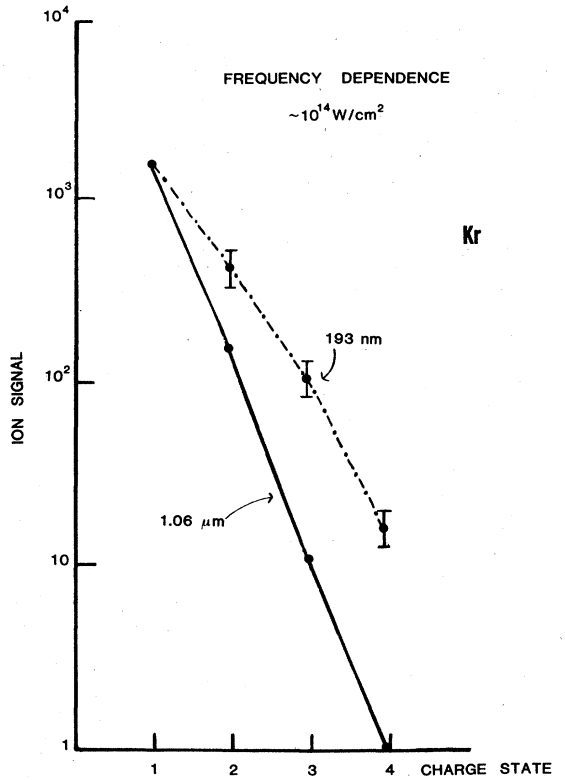



FIG. 6. Comparison of charge-state spectra observed for krypton at an intensity of $\sim 10^{14}$ W/cm$^2$ at 1.06 $\mu$m and 193 nm. The data shown for 1.06 $\mu$m irradiation is taken from Ref. 19.

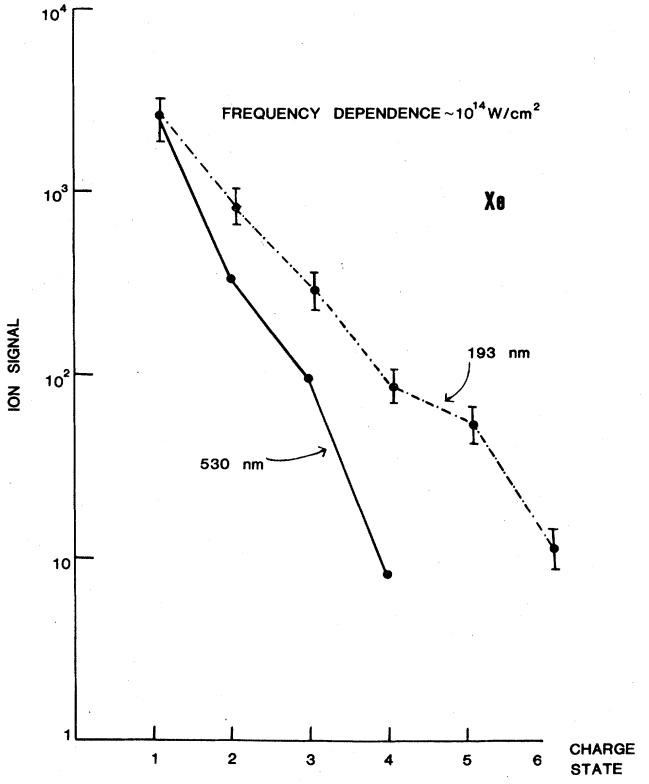



FIG. 7. Comparison of charge-state spectra observed for xenon at an intensity of $\sim 10^{14}$ W/cm$^2$ at 0.53 $\mu$m and 193 nm. The data shown for 0.53 $\mu$m irradiation is taken from Ref. 20.

We comment further that, at sufficiently high-electromagnetic fields, all angular momentum states become accessible,[22] a fact that will certainly alter the polarization dependence.[17]

## IV. DISCUSSION OF RESULTS

### A. Ion production

In broad terms, we now discuss and interpret these experimental findings. In the data represented in Figs. 2, 4, and 5, two salient characteristics exhibited by the experiments involving ion production are (i) the large coupling strength for heavy materials and (ii) the sharp variations present in the average energy transfer as a function of $Z$, such as that illustrated by the comparison of iodine and xenon in Fig. 2.

Qualitatively, several aspects of the basic interaction emerge clearly. With reference to xenon, for example, a 100-fold increase in 193-nm intensity from $\sim 10^{15}$–$10^{17}$ W/cm$^2$ does not drastically increase either the maximum charge state observed or the average energy transferred. Over this range of intensity, the charge state $q$ advances from $q=6$ to 8, and the average energy transferred in the interaction increases by approximately a factor of 7. Within the experimental uncertainty over this range of intensity, the average energy appears to grow approximately linearly to the magnitude of the radiative electric field, a fact we comment on further below. Furthermore, since the charge state does not increase beyond the apparent removal of the full $5p$ and $5s$ subshells, tentatively we can conclude that the $n=5$ shell is an important agent coupling the xenon atom to the 193-nm radiation field. It is also known, however, particularly from photoionization studies involving multiple-electron ejection,[23,24] that the $5p$, $5s$, and $4d$ shells exhibit substantial intershell coupling and behave in a collective fashion in a manner resembling a single supershell.[25] In this connection it is also known that the spatial dependence of the self-consistent field[26] experienced by the atom is expected to contribute to the $Z$ dependence of the atomic response.

In this picture, the increase in multiphoton coupling strength results directly from the larger magnitude of the effective charge involved in the interaction. In this way, a multielectron atom undergoing a nonlinear interaction responds in a *fundamentally different fashion* from that of a single-electron atom.[18,27,28] This interpretation involving a collective atomic response with several coupled atomic shells is exhibited most prominently for Xe, but is also apparent in the nature of the Ar and Kr spectra.

We now briefly consider the magnitude of the coupling strength. A strong implication of the studies reported initially[1] and noted above, and which is reinforced by the additional data illustrated in Figs. 2 and 4, is that the atomic-shell structure is a principal determinant in the atomic response. Indeed, all the conspicuous characteristics of the experimental findings can be consolidated by this single principle. Surprisingly, the order $N$ of the nonlinear process appeared as relatively unimportant. Furthermore, the data strongly indicated that a collective response of an entire shell, or a major fraction thereof, was directly involved in the nonlinear coupling. Collective responses of atomic shells, as noted above, have been discussed in relation to the mechanism of single-photon photoionization. The present studies simply point to a *nonlinear analog* of this basic electronic mechanism. With this picture, the outer atomic subshells are envisaged as being driven in *coherent* oscillation by the intense ultraviolet wave. Of course, such a model can only be valid if the damping rate, presumably by electron emission, is sufficiently low. Consequently, that assumption is naturally implied in this description. We note that an oscillating atomic shell, quantum mechanically, would be represented by a *multiply* excited configuration. The simplest examples are doubly excited levels of the type commonly observed in the extreme ultraviolet spectra of the rare gases such as argon.[29] Naturally, higher stages of multiple excitation can be considered such as those discussed in the context of planetary atoms.[30]. Therefore, if this type of description is a valid representation of the radiative coupling, then it would follow that multiply excited configurations would be prodigiously generated and, therefore, be prominent features in any excited-state populations produced. We shall see below that additional evidence supports this interpretation in the case of xenon and krypton.

Within the framework of the above picture, it is possible to make a simple estimate of the energy absorbed by an atom and the corresponding scaling law describing the intensity dependence. For this we imagine an atom com-

posed of two parts: (i) an outershell of $n$ electrons driven by the radiative field at frequency $\nu$ and (ii) an atomic core. The outer electrons could, through "inelastic collisions" at frequency $\nu_c$, transfer energy to the core. Assuming a mean free path $\delta$ for the electrons between two collisions, and for large collision frequencies ($\nu_c > \nu$), the work done by the radiative field between two collisions is $neE\delta$. The total energy transferred to the core during the lifetime $\tau$ of the highly excited atomic configuration represented by the coherently driven outer shell is then given by

$$neE\,\delta\nu_c\,\tau = \hbar\omega_x \ . \tag{2}$$

Here, this energy is written in the form of a quantum with magnitude $\hbar\omega_x$. Using $\delta\nu_c = v$ and estimating the average velocity $v$ by equating the kinetic energy of an electron with the potential energy lost between two collisions

$$\tfrac{1}{2}mv^2 = eE\delta \ , \tag{3}$$

one obtains for the optical electric field

$$E = \frac{1}{e}\left[\frac{\hbar\omega_x}{n\tau}\sqrt{m/2\delta}\right]^{2/3} \ . \tag{4}$$

As an example, if we take $\hbar\omega_x = 1$ keV, $n = 6$ representing a closed $p$ shell, $\delta = 0.1$ Å, and $\tau = 10^{-15}$ sec, then $E = 2.0\times10^9$ V/cm, corresponding to an intensity $I = 10^{16}$ W/cm$^2$.

The value taken for the mean free path $\delta$ requires some discussion. It is predicted on the mean free path associated with the scattering of an electron, having an energy considerably above the Fermi energy, interacting through a screened Coulomb potential in an electron gas. The cross section $\sigma_0$ for this process, estimated, for example, in the case of sodium,[31] by Pines,[32] to have a value $\sigma_0 \sim 17\pi a_0^2$, in combination with the electron density $\rho_e$ characteristic of the xenon $n = 5$ shell, yields a scale length $\delta \sim (\rho_e\sigma_0)^{-1} \sim 10^{-9}$ cm. Interestingly, if we examine the data for xenon in Figs. 4 and 5, we observe that the maximum charge state $Xe^{8+}$, which corresponds to $\sim$450 eV total energy,[13] was seen for an intensity in the range of $10^{16}$–$10^{17}$ W/cm$^2$, figures not far from those represented by Eq. (4). Finally, since Eq. (4) is independent of the frequency $\nu$, a weak dependence on frequency is expected. As shown in Figs. 6 and 7 frequency does not appear to exert a strong influence on the average energy transfer. Certainly, no quantitative accuracy can be claimed for the estimate made above; its only significance is that the general nature of the atomic response and the qualitative scales of the physical quantities, for what appear to be reasonable choices of atomic parameters, are roughly that observed in actual experiments.

It is informative to consider the case representing the high-intensity limit.[17,22] At an intensity of $\sim 10^{19}$ W/cm$^2$, which we anticipate will be available soon with the use of subpicosecond rare-gas halogen lasers, the peak ultraviolet electric field is more than tenfold $e/a_0^2$, so that loosely bound outer electrons can be approximately modeled as free particles. In this case, the problem reduces to that of the acceleration of electrons in focused laser fields,[33] an issue that, incidentally, is related to the acceleration of cosmic rays by rotating neutron stars.[34] Simple estimates indicate that for intensities of that magnitude, the outer electrons would approach relativistic velocities ($\sim$50–80 keV) and that oscillating atomic-current densities on the order of $10^{14}$–$10^{15}$ amps/cm$^2$ could be established as a result. Actually, in this high-intensity limit it appears to be possible to estimate the coupling of the coherently driven outer electrons with the remaining atomic core by a relatively simple procedure. Since the electron-kinetic energies are considerably above their corresponding binding energy, it appears possible to use a first-order Born approximation[35] in a manner similar to that used to the study of electron collisions for $K$- and $L$-shell ionization[36] and shell specific ionization processes in highly charged ions.[37,38] Indeed, in the case of xenon ions, cross sections for electron-impact ionization are available.[39] It also seems possible to account for the transition from adiabatic to sudden excitation of core electrons with a rather simple procedure.[40]

The results illustrated in Fig. 2 indicate a complex and rapidly varying $Z$ dependence for heavy materials. It has not been possible to formulate a reasonable explanation of this behavior solely on the basis of the systematics of valence-shell properties.[1,2,9] These results again point to the significance of intershell couplings. Such couplings are manifested in an obvious way, for example, in Coster-Kroning processes.[41] Indeed, if we consider, as specific cases, giant Coster-Kronig (GCK) processes of the type

$$n\underline{s} \rightarrow n\underline{p}^2 nd, \epsilon d \tag{5}$$

and super Coster-Kronig (SCK) processes like

$$n\underline{p} \rightarrow mf, \epsilon f \ , \tag{6}$$

it is well established that strong perturbations[42] are present and that the single-electron picture seriously breaks down.[43] These processes are sensitive to systematics of the shell-energy levels and, therefore, can exhibit sharp variation in their dependence on atomic number. In particular, many-electron effects are prominent when there is a degeneracy between single- and double-vacancy states that are strongly coupled. These requirements are commonly fulfilled and strong collective behavior arises, for example, in single-photon photoionization.[25,44,45] Significantly, in comparison with the results illustrated in Figs. 2 and 4 these effects are known to be of importance[43,46] over certain regions of the atomic number from argon to the heavier part of the Periodic Table. A particular case involves double photoionization of Ga in the energy region near the $3d$ ionization threshold.[47]

The degeneracies of single- and double-hole states occur at particular values of the atomic number. Figure 8, which was derived from calculations[48] of neutral-atomic binding energies performed with a relaxed-orbital relativistic Hartree-Fock-Slater analysis, illustrates the region from $_{29}$Cu to $_{40}$Zr. Near degeneracies in the $n = 3$ shell are indicated for $_{32}$Ge, $_{36}$Kr, and $_{37}$Rb. Moreover, since the $3p$ and $3d$ orbitals both have their maximum charge densities at nearly identical radii,[49] strong coupling between these subshells is expected to occur. Indeed, such couplings are known[50] to produce discontinuous behavior in the $L_\alpha$ and $L_{\beta 1}$ satellite fractions as well as in the

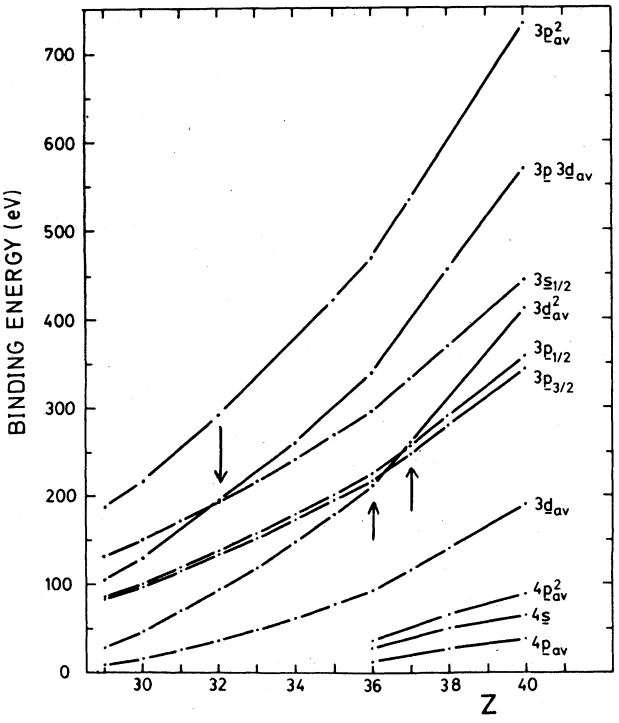



FIG. 8. Atomic, relativistic ΔSCF single- and double-hole levels for $_{29}$Cu to $_{40}$Zr. The energies were obtained from Ref. 48 and the figure has been adapted from Fig. 17 of Ref. 43 appearing on p. 28. The arrows indicate the locations of near degeneracies between single- and double- vacancy states. Figure reprinted by permission.

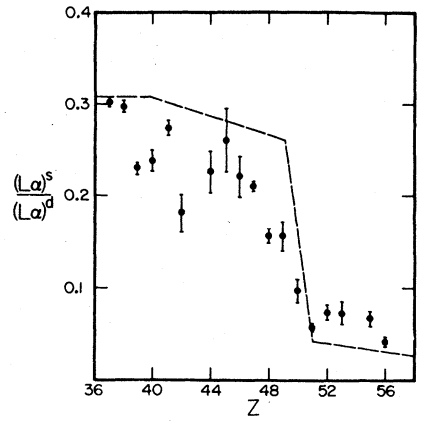



FIG. 9. $L\alpha$ satellite $(L\alpha)^s$ to diagram $(L\alpha)^d$ line ratio as a function of atomic number $Z$. The data are taken from Ref. 50. The dashed curve corresponds to a theoretical treatment adapted from a calculation performed in Ref. 51. Figure reprinted by permission.

$L_{\beta 3,4}/L_\alpha$ and $L_{\beta 1}/L_\alpha$ intensity ratios as a function of atomic number $Z$. The data illustrated in Fig. 9 convey this effect for the $L_\alpha$ features for atomic number in the vicinity of $Z=50$. In this case, the observation[50] is consistent with a critical atomic number of $Z\simeq 50$ for the $L_1$-$L_3M_{45}$ Coster-Kronig transition. The dashed line appearing in Fig. 9 is a theoretical curve related to the calculation of Krause *et al.*[51] The discontinuous behavior in $Z$ characteristic of the data shown in Fig. 9 has a striking similarity to that exhibited in Fig. 2. Similarly sharp variations in atomic number have been calculated in the Auger width associated with a $2s$ vacancy.[52] Interestingly, it has been predicted[52] that plasma-shielding effects can have a strong influence on autoionizing widths by causing an energetic closing of the channel for Coster-Kronig transitions, although no such behavior has ever been actually observed. For a $2s$ vacancy with an argon-like configuration, a sharp change in the $2s$ width is estimated for $Z=22$ at an electron density of $\sim 5\times 10^{20}$ cm$^{-3}$. It should be possible to achieve such a plasma density, under controlled conditions, with the use of a subpicosecond rare-gas halogen source. We note that several informative accounts of vacancy distributions[53] and the behavior of autoionizing widths are available.[54,55]

Normally, relaxation mechanisms involving intershell coupling, such as Coster-Kronig and Auger processes, are experimentally observed by initially producing an inner-shell vacancy which subsequently relaxes, generally producing multiple vacancies and excitation in outer shells. In principle, the initial vacancy can be produced with radiative excitation,[56,57] electron collisions,[58,59] beam-foil methods,[60] ion collisions,[61] and nuclear-decay processes such as $K$ capture.[62,63] To these alternatives, the results of these experiments suggest that multiquantum processes may now conceivably be added. Furthermore, the nature of Coster-Kronig processes provides a hint at the mechanism that could make this possible. In simple terms, this can be viewed as a *reverse* Coster-Kronig process[43] in which *multiple* excitations in outer shells generate excitations in more tightly bound shells. In this fashion we use the term "excitation" in a broad sense to include both bound excited levels and continuum states (vacancies). For double and single excitations or vacancies, this mechanism is basically represented by the reverse reactions of processes (5) and (6), namely,

$$n\underline{s} \leftarrow n\underline{p}^2 nd, \epsilon d \ , \tag{5'}$$

$$n\underline{p} \leftarrow n\underline{d}^2 mf, \epsilon f \ . \tag{6'}$$

Indeed, since these intershell couplings are sensitive to the systematics of the shell binding energies, resonance effects[43,64] are expected in certain regions of atomic number $Z$ for the reasons stated above. In summary, the similarity of the discontinuous character of the data represented in Figs. 2 and 9 mentioned above plainly, although tentatively, suggest a common origin for this general type of behavior, namely, the possibility that the electrons involved in the nonradiative relaxation of an atom in the forward reaction (5) could, in the *reverse* process (5'), if driven by coupling to a sufficiently intense radiation field, generate a corresponding transfer of energy *into* an atom.

Finally, we comment on some aspects of this general line of inquiry which deserve exploration. It is of natural and fundamental interest to further examine the properties of the ionization process (i) with different ultraviolet

frequencies, specifically 248 nm, since it is readily available at high intensities, (ii) over a greater variation in $Z$, particularly in regions for which the intershell couplings are believed to be large, and (iii) at intensities above $10^{17}$ W/cm$^2$. Studies of this nature, therefore, are obviously an important element of our current activity. Examples of specific materials which appear as promising candidates for study are Ba, on account of the known[65–67] sensitivity of the $4f$ orbital to the state of ionization; the lanthanides, on account of the unusual systematics associated with the filling of the $4f$ shell and the effects of configuration interaction[68,69] prominent for certain members of that sequence; and $_{90}$Th and $_{92}$U, the heaviest materials[70] available for practical study. Finally, since molecular binding is known to have an influence on the behavior of inner-shell transitions, sometimes with rather dramatic effects, such as that known for the $5d$-$f$ absorption of uranium,[71] a comparison of the ionization properties of certain molecular and atomic species is planned.

### B. Radiative properties

Measurements of emission produced by the highly excited states provide important information on the nature of the coupling mechanism involved. Specifically, if the interpretation discussed above in Sec. IV involving a collective atomic response with coupled atomic shells has any validity, detectable emission at short wavelengths or energetic electrons would be expected.

Indeed, in a recent, although preliminary, experiment examining the properties of the xenon ions produced in the ion studies discussed in Secs. III and IV A which was designed to detect extreme ultraviolet radiation, significant levels of spontaneous radiation and/or energetic electrons have been observed.[72] The spectral width observed in the radiation channel was determined by the 1500-Å aluminum filter (10—80 eV) used. The schematic of the apparatus employed in these studies and the signal observed are shown in Fig. 10. The signal occurs precisely

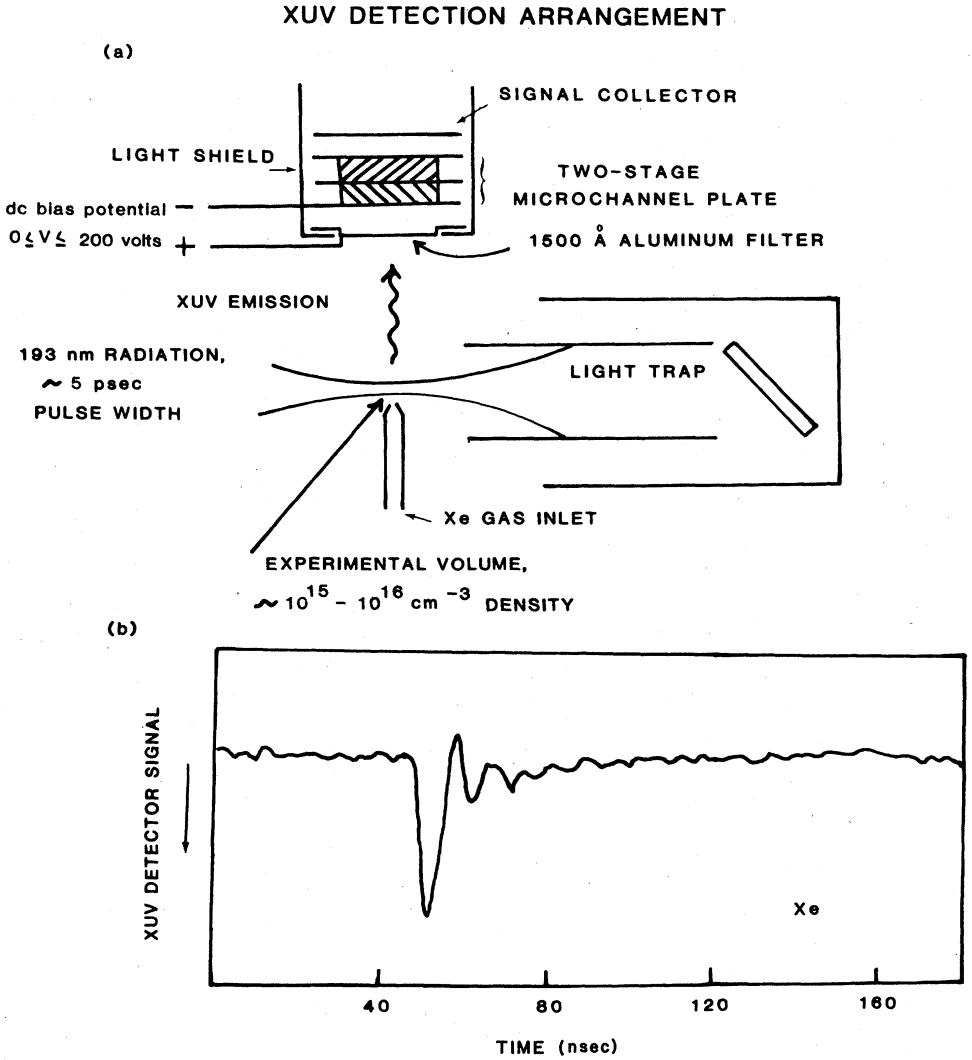



FIG. 10. (a) Experimental arrangement used to detect xuv radiation from highly excited atoms excited by 193-nm radiation at an intensity of $\sim 10^{16}$—$10^{17}$ W/cm$^2$. (b) xuv signal observed from xenon in the 10—100 eV range with $\sim$100-V bias between the aluminum filter and the microchannel plate; some ringing of the detector circuit is evident.

at the time of irradiation of the gas with the 5-psec 193-nm radiation, vanishes if the xenon flow is terminated, and is not observed if the xenon is replaced by other materials, such as krypton or hydrogen. In order to eliminate the influence of electrons that could be produced by photoemission from the surface of the aluminum filter facing the microchannel plate from reaching the detector, a dc electrical bias of 200 V was applied to retard the motion of electrons moving in that direction. Some evidence of an electron-induced signal was observed if no negative-bias potential was used. Judging from the spectral transmission and the electron stopping power of the 1500-Å Al filter, we conclude that only xuv photons in the region of 10—100 eV and energetic electrons exceeding a few hundred electron volts could possibly contribute to the observed signal. This observation is consistent with the excitation of an inner-shell electron state, presumably the $4d$ level in xenon, by atomic processes of the nature described above. Significantly, recent experiments[73] measuring the photoelectron spectra under identical experimental conditions have ruled out the presence of electrons with sufficient energy to produce the observed signal. In addition, the photoelectron measurements[73] reveal the presence of several lines in the xenon spectrum which closely match the pattern expected from $N_{4,5}$-$OO$ Auger transitions, a finding which strongly reinforces the interpretation given above. Naturally, further experiments are being prepared to determine the electron and photon spectra of the observed emission more accurately.

Another class of experiments, intended to observe stimulated emission from highly excited states, has also been performed.[74–77] In the experiment designed to observe amplification in Kr in the extreme ultraviolet range, intense stimulated emission was detected on five transitions spanning the range from 91.6—100.3 nm. An examination of the linewidths and tuning behavior of these transitions led to a possible identification of the upper levels as autoionizing neutral levels involving both singly excited inner-shell excitations[75] and doubly excited configurations.[74,76,77] This is the first indication of stimulated emission arising from such electronically unstable states. Finally, if we reason that the anomalous increase in this coupling is connected with the presence of multiply excited configurations and if we recall that coherently excited shells, in quantum-mechanical language, are described in terms of multiple excitations,[78,79] then the results of the ion-production experiments and the observation of stimulated emission in krypton can be viewed in a unified manner.

## V. CONCLUSIONS

The nonlinear coupling of 193-nm radiation to a range of atomic systems has been studied up to a maximum intensity on the order of $\sim 10^{17}$ W/cm$^2$. Studies of ion production, under collision-free conditions, exhibit anomalous behavior which implicate the atomic-shell structure as the principal determinant in the observed response. On the basis of the coupling strength observed and the measured $Z$ dependence, the experimental evidence points to a collective coherent atomic motion involving several electrons, possibly an entire shell, as the main physical mechanism enabling the scale of the energy transfers seen. In quantum-mechanical language, states representing multiple excitations appear to play a central role in the coupling, a consideration that *fundamentally* distinguishes the nonlinear interaction of a multielectron atom from that of a single-electron system.

Comparison with standard theoretical treatments of nonlinear processes, of either perturbative or nonperturbative nature, does not produce agreement with the experimental findings. Conversely, the formulation of a simple classical estimate qualitatively conforms to several features of the observed behavior. They are, with particular reference to xenon, the shell character of the interaction, the maximum energy transfer, the dependence of the average energy transfer on the intensity of irradiation, the frequency dependence of the energy transfer, and the weak influence of polarization. Furthermore, it is postulated that the sharp variations in $Z$ noted for the heavy materials is due to a reverse Coster-Kronig mechanism in which inner-shell excitations are produced by interaction with multiply excited outer shells. These points naturally imply the existence of a systematic trend in nonlinear properties which extends throughout the Periodic Table. This would then constitute a principle of classification which appears to bear some analogy to that developed earlier for electron potentials, binding energies, and electron scattering phase shifts.[80]

## ACKNOWLEDGMENTS

The authors wish to acknowledge the expert technical assistance of M. J. Scaggs, J. R. Wright, and D. M. Gustafson. This work was supported by the U.S. Air Force Office of Scientific Research under Contract No. F49630-83-K-0014, the U.S. Department of Energy under Grant No. DE-AS08-81DP40142, the U.S. Office of Naval Research, the National Science Foundation under Grant No. PHY-81-16626, the U.S. Defense Advanced Research Projects Agency, and the Avionics Laboratory, U.S. Air Force Wright Aeronautical Laboratories, Wright Patterson Air Force Base, Ohio.

[1]T. S. Luk, H. Pummer, K. Boyer, M. Shahidi, H. Egger, and C. K. Rhodes, Phys. Rev. Lett. **51**, 110 (1983).

[2]T. S. Luk, H. Pummer, K. Boyer, M. Shahidi, H. Egger, and C. K. Rhodes, in *Excimer Lasers—1983,* edited by C. K. Rhodes, H. Egger, and H. Pummer (American Institute of Physics, New York, 1983), Vol. 100, p. 341.

[3]P. Lambropoulos, in *Advances in Atomic and Molecular Physics,* edited by D. R. Bates and B. Bederson (Academic, New York, 1976), Vol. 12, p. 87.

[4]H. B. Bebb and A. Gold, Phys. Rev. **143**, 1 (1966).

[5]Y. Gontier and M. Trahin, J. Phys. B **13**, 4384 (1980); Phys. Rev. **172**, 83 (1968).

[6]A. L'Huillier, L-A. Lompré, G. Mainfray, and C. Manus, in *Proceedings of the Conference on Laser Techniques in the Extreme Ultraviolet,* edited by S. E. Harris and T. B. Lucatorto (American Institute of Physics, New York, 1984), Vol. 119, p. 79.

[7]H. Egger, T. S. Luk, K. Boyer, D. F. Muller, H. Pummer, T. Srinivasan, and C. K. Rhodes, Appl. Phys. Lett. **41**, 1032 (1982).

[8]W. C. Wiley and I. H. McLaren, Rev. Sci. Instrum. **26**, 1150 (1955).

[9]H. Egger, T. S. Luk, W. Müller, H. Pummer, and C. K. Rhodes, in *Proceedings of the Conference on Laser Techniques in the Extreme Ultraviolet,* edited by S. E. Harris and T. B. Lucatorto (American Institute of Physics, New York, 1984), Vol. 119, p. 64.

[10]*Table of Isotopes,* 7th ed., edited by C. Michael Lederer and Virginia S. Shirley (Wiley, New York, 1978).

[11]T. S. Luk, U. Johann, H. Jara, and L. Haddad (private communication).

[12]R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).

[13]T. A. Carlson, C. W. Nestor, Jr., N. Wasserman, and J. McDowell, At. Data **2**, 63 (1970).

[14]B. L. Schram, A. J. H. Boerboom, W. Kleine, and J. Kistemaker, *Amplification Factors of a Particle Multiplier for Multiply Charged Noble Gas Ions,* in *Proceedings of the 7th International Conference on Phenomena in Ionized Gases (Beograd, 1965),* edited by B. Perović and D. Tosić (Gradevinska Knjiga House, Beograd, 1966), Vol. 1, p. 170.

[15]J. Blackburn, P. K. Carroll, J. Costello, and G. O'Sullivan, J. Opt. Soc. Am. **73**, 1325 (1983).

[16]G. J. Pert, J. Phys. B **8**, L173 (1975).

[17]J. Gersten and M. H. Mittleman, Phys. Rev. A **10**, 74 (1974).

[18]L. V. Keldysh, Zh. Eksp. Teor. Fiz. **47**, 1945 (1964) [Sov. Phys.—JETP **20**, 1307 (1965)].

[19]A. L'Huillier, L-A. Lompré, G. Mainfray, and C. Manus, Phys. Rev. Lett. **48**, 1814 (1982).

[20]A. L'Huillier, L-A. Lompré, G. Mainfray, and C. Manus, Phys. Rev. A **27**, 2503 (1983).

[21]H. S. Brandi, L. Davidovich, and N. Zagury, J. Phys. (Paris) Colloq. **43**, C2-397 (1982).

[22]S. Geltman and M. R. Teague, J. Phys. B **7**, L22 (1974).

[23]M. J. Van der Wiel and T. N. Chang, J. Phys. B **11**, L125 (1978).

[24]M. Ya Amusia, in *Advances in Atomic and Molecular Physics,* edited by D. R. Bates and B. Bederson (Academic, New York, 1981), Vol. 17, p. 1.

[25]M. Ya. Amusia and N. A. Cherepkov, in *Case Studies in Atomic Physics 5,* edited by E. W. McDaniel and M. R. McDowell (North-Holland, Amsterdam, 1975), p. 47.

[26]A. Zangwill and P. Soven, Phys. Rev. A **21**, 156 (1980); Phys. Rev. Lett. **45**, 204 (1980); W. Ekardt and D. B. Tran Thoai, Phys. Scr. **26**, 194 (1982); A. Zangwill, Ph.D. thesis, University of Pennsylvania, 1981.

[27]H. R. Reiss, Phys. Rev. A **1**, 803 (1970); Phys. Rev. Lett. **25**, 1149 (1970); Phys. Rev. D **4**, 3533 (1971); Phys. Rev. A **6**, 817 (1972).

[28]H. S. Brandi and L. Davidovich, J. Phys. B **12**, L615 (1979).

[29]R. P. Madden, D. L. Ederer, and K. Codling, Phys. Rev. **177**, 136 (1969).

[30]I. C. Percival, Proc. R. Soc., London Ser. A **353**, 289 (1977).

[31]C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1983), p. 116.

[32]David Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1984).

[33]Marc J. Feldman and Raymond Y. Chiao, Phys. Rev. A **4**, 352 (1971); E. S. Sarachik and E. R. Schappert, Phys. Rev. D **1**, 2738 (1970).

[34]James E. Gunn and Jeremiah P. Ostriker, Phys. Rev. Lett. **22**, 728 (1969).

[35]N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1965); H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1969), Vol. 1; H. A. Bethe, Ann. Phys. (Leipzig) **5**, 325 (1930).

[36]James H. Scofield, Phys. Rev. A **18**, 963 (1978).

[37]L. B. Golden, P. H. Sampson, and K. Omidvar, J. Phys. B **11**, 3235 (1978).

[38]L. B. Golden and D. H. Sampson, J. Phys. B **13**, 2645 (1980).

[39]D. C. Gregory and D. H. Crandall, Phys. Rev. A **27**, 2338 (1983); C. Achenbach, A. Müller, E. Salzborn, and R. Becker, J. Phys. B **17**, 1405 (1984).

[40]T. Darrah Thomas, Phys. Rev. Lett. **52**, 417 (1984).

[41]E. J. McGuire, in *Atomic Inner-Shell Processes,* edited by B. Crasemann (Academic, New York, 1975), Vol. 1, p. 293.

[42]T. Aberg, in *Photoionization and Other Probes of Many-Electron Interactions,* edited by F. J. Wuilleumier (Plenum, New York, 1976), p. 273.

[43]G. Wendin, *Breakdown of the One-Electron Pictures in Photoelectron Spectra,* Vol. 45 of *Structure and Bonding* (Springer, Berlin, 1981); S. Lundquist and G. Wendin, J. Electron. Spectrosc. Relat. Phenom. **5**, 513 (1974).

[44]G. Wendin, in *Vacuum Ultraviolet Radiation Physics,* edited by E. E. Koch, R. Haensel, and C. Kunz (Pergamon, Braunschweig, 1974), p. 225.

[45]G. Wendin, in *Photoionization and Other Probes of Many-Electron Interactions,* edited by F. J. Wuilleumier (Plenum, New York, 1976), p. 61; H. P. Kelly and S. L. Carter, Phys. Scr. **21**, 448 (1980).

[46]J. A. R. Samson and G. N. Haddad, Phys. Rev. Lett. **33**, 875 (1974); J. A. R. Samson, in *Photoionization and Other Probes of Many-Electron Interactions,* edited by F. J. Wuilleumier (Plenum, New York, 1976), p. 419.

[47]J. P. Connerade, J. Phys. B **10**, L239 (1977).

[48]Ken-Ning Huang, Michio Aoyagi, Mau Hsiung Chen, Bernd Crasemann, and Hans Mark, At. Data Nucl. Data Tables **18**, 243 (1976).

[49]Frank Herman and Sherwood Skillman, *Atomic Structure Calculations* (Prentice-Hall, Engelwood Cliffs, 1963).

[50]B. L. Doyle and S. M. Shafroth, Phys. Rev. A **19**, 1433 (1979).

[51]M. O. Krause, F. J. Wuilleumier, and C. W. Nestor, Jr., Phys. Rev. A **6**, 871 (1972).

[52]B. F. Rozsnyai, V. L. Jacobs, and J. Davis, Phys. Rev. A **21**, 1798 (1980).

[53]P. Venugopala Rao, Mau Hsiung Chen, and Bernd Crasemann, Phys. Rev. A **5**, 997 (1972).

[54]S. Southworth, U. Becker, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, S. Owaki, and D. A. Shirley, Phys. Rev. A **28**, 261 (1983).

[55]Masahide Ohno, Phys. Rev. B **29**, 3127 (1984); A. Fahlman, M. O. Krause, and T. A. Carlson, J. Phys. B **17**, L217 (1984).

[56]T. A. Carlson, W. E. Hunt, and M. O. Krause, Phys. Rev. **151**, 41 (1966).

[57]T. S. Axelrod, Phys. Rev. A **13**, 376 (1976); T. Åberg, in *Proceedings of the International Conference on Inner-Shell Ionization and Future Applications, Oak Ridge, 1972,* edited

by R. W. Fink, S. T. Manson, J. M. Palms, and P. V. Rao, Natl. Tech. Info. Service Spec. Publ. No. CONF-720 (U.S. Dept. of Commerce, Springfield, VA, 1972), p. 404; John W. Cooper, in *Atomic Inner-Shell Processes,* edited by B. Crasemann (Academic, New York, 1975), Vol. I, p. 160.

[58]T. A. Carlson, W. E. Moddeman, and M. O. Krause, Phys. Rev. A **1**, 1406 (1970).

[59]L. M. Middleman, R. L. Ford, and R. Hofstadter, Phys. Rev. A **2**, 1429 (1970); K. Ishii, M. Kamiya, K. Sera, S. Morita, H. Tawan, M. Cyamada, and T. C. Chu, Phys. Rev. A **15**, 906 (1977).

[60]I. Martinson, in *Beam-Foil Spectroscopy,* edited by S. Bashkin (Springer, Berlin, 1976), p. 33.

[61]D. H. Madison and E. Merzbacher, in *Atomic Inner-Shell Processes,* edited by B. Crasemann (Academic, New York, 1975), Vol. I, p. 1; U. Fano and W. Lichten, Phys. Rev. Lett. **14**, 627 (1965); M. Barat and W. Lichten, Phys. Rev. A **6**, 211 (1972); P. Ziem, R. Bruch, and N. Stoltefoht, J. Phys. B **8**, L480 (1975); J. M. Hansteen, in *Advances in Atomic and Molecular Physics,* edited by D. R. Bates and B. Bederson (Academic, New York, 1975), Vol. I, p. 299; P. H. Mokler and F. Folkmann, in *Structure and Collisions of Ions and Atoms,* edited by I. A. Sellin (Springer, Berlin, 1978), p. 201.

[62]Robert J. Walen and Chantel Briancon, in *Atomic Inner-Shell Processes,* edited by B. Crasemann (Academic, New York, 1975), Vol. I, p. 233; M. S. Freedman, in *Photoionization and Other Probes of Many-Electron Interactions,* edited by F. J. Wuilleumier (Plenum, New York, 1976), p. 255.

[63]W. Bambynek, H. Behrens, M. H. Chen, B. Crasemann, M. L. Fitzpatrick, K. W. D. Ledingham, H. Genz, M. Mutterer, and R. L. Intemann, Rev. Mod. Phys. **49**, 77 (1977).

[64]C.-O. Almbladh and L. Hedin, in *Handbook on Synchrotron Radiation,* edited by Ernst-Eckhard Koch (North-Holland, Amsterdam, 1983), Vol. 16, p. 607.

[65]T. B. Lucatorto, T. J. McIlrath, J. Sugar, and S. M. Younger, Phys. Rev. Lett. **47**, 1124 (1981).

[66]J. P. Connerade, K. Dietz, M. W. D. Mansfield, and G. Weymans, J. Phys. B **17**, 1211 (1984); B. Sonntag, T. Nagata, Y. Satow, A. Yagistita, and M. Yanagihara, J. Phys. B **17**, L55 (1984).

[67]K. Nuroh, M. J. Shott, and E. Zaremba, Phys. Rev. Lett. **49**, 862 (1982).

[68]S.-T. Lee, S. Süzer, E. Matthias, R. A. Rosenberg, and D. A. Shirley, J. Chem. Phys. **66**, 2496 (1977); R. D. Cowan, Nucl. Instrum. Methods **110**, 173 (1973).

[69]Ernst-Rudolf Radtke, Dissertation, Universität Bonn, December, 1980.

[70]H. R. Moser, B. Delley, W. D. Schneider, and Y. Baer, Phys. Rev. B **29**, 2947 (1984).

[71]M. Pantelouris and J. P. Connerade, J. Phys. B **16**, L23 (1983).

[72]T. S. Luk and K. Boyer (private communication).

[73]U. Johann, T. S. Luk, H. Egger, H. Pummer, and C. K. Rhodes (unpublished).

[74]K. Boyer, H. Egger, T. S. Luk, H. Pummer, and C. K. Rhodes, J. Opt. Soc. Am. B **1**, 3 (1984).

[75]T. Srinivasan, H. Egger, T. S. Luk, H. Pummer, and C. K. Rhodes, in *Laser Spectroscopy VI,* edited by H. P. Weber and W. Lüthy (Springer, Berlin, 1983), p. 385.

[76]H. Egger, T. S. Luk, W. Müller, H. Pummer, and C. K. Rhodes, "Collision-Free Multiple Ionization of Atoms and XUV Stimulated Emission in Krypton at 193 nm," *AIP Conference Proceedings on Laser Techniques in the Extreme Ultraviolet, Boulder, Colorado, 1984* (AIP, New York, in press).

[77]H. Pummer, H. Egger, T. S. Luk, and C. K. Rhodes, SPIE J. **461**, 53 (1984).

[78]M. E. Kellman and D. R. Herrick, Phys. Rev. A **22**, 1536 (1980).

[79]A. R. P. Rau, J. Phys. B **16**, L699 (1983).

[80]A. R. P. Rau and U. Fano, Phys. Rev. **167**, 7 (1968).