Studies of multiphoton production of vacuum-ultraviolet radiation in the rare gases

A. McPherson, G. Gibson, H. Jara, U. Johann, T. S. Luk, I. A. McIntyre, K. Boyer, and C. K. Rhodes

Department of Physics, University of Illinois at Chicago, P.O. Box 4348, Chicago, Illinois 60680

Received November 1, 1986; accepted December 18, 1986

Measurements of the vacuum-ultraviolet (<80-nm) radiation produced by intense ultraviolet (248-nm) irradiation (10^{15}–10^{16} W/cm^2) of rare gases have revealed the copious presence of both harmonic radiation and fluorescence from excited levels. The highest harmonic observed was the seventeenth (14.6 nm) in Ne, the shortest wavelength ever produced by that means. Strong fluorescence was seen from ions of Ar, Kr, and Xe, with the shortest wavelengths observed being below 12 nm. Furthermore, radiation from inner-shell excited configurations in Xe, specifically the $4d^9 5s5p \rightarrow 4d^{10}5s$ manifold of Xe^{7+} at ~17.7 nm, was detected. These experimental findings, in alliance with other studies concerning multielectron processes, give evidence for a role of electron correlations in a direct nonlinear process of inner-shell excitation.

1. INTRODUCTION

The nonlinear response of matter to an intense radiation field is an active area of study. The basic process under examination is the reaction

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

in which multiply charged ions X^{q+}, photoelectrons qe^-, and photons γ' are produced. In order to provide a basis for understanding the physical mechanism of coupling involved, the properties of ion-charge-state distributions[1–3] and electron energy spectra[4] were previously examined in a collision-free environment. Recently, harmonic radiation[5] and fluorescence[6,7] produced in a gas jet by irradiation of atoms with intense ultraviolet radiation were also investigated. Information on the earlier studies concerning the ion and electron distributions, conducted at several different wavelengths, is thoroughly documented in Refs. 1–6 and associated citations. In this discussion, further results on the generation of short-wavelength radiation arising from the nonlinear interaction will be emphasized.

2. EXPERIMENTAL APPROACH

The experimental arrangement used to conduct the studies[8] of the radiation produced is illustrated in Fig. 1. The source used for irradiation of the target gas was KrF* (248-nm) laser system[9] that produces pulses having a maximum energy of ~20 mJ and a minimum pulse duration[10] of ~350 fsec. A 23-cm (f/10) focal-length lens focuses the 248-nm laser radiation into a gaseous target produced by a modified Lasertechnics pulsed gas jet. With this optical system, the intensity in the focal region is estimated to be in the range of ~10^{15}–10^{16} W/cm^2. The gas jet is mounted 11.5 cm in front of the entrance slit of a 2.2-m grazing-incidence spectrometer (McPherson Model 247) equipped with a 600-line/mm gold-coated spherical grating blazed at 120 nm. A single-stage microchannel plate with a phosphored fiber-optic anode serves as the detector. Mounting of the detector tangentially to the Rowland circle of the spectrometer allows the observation of radiation between 7.5 and 80 nm. The FWHM resolution and accuracy of the spectrometer–detector system are typically 0.1 nm. The pulsed-gas valve, which was modified to allow a backing pressure up to 5.17×10^4 Torr (1000 psi), was typically operated in the range of 1.03×10^4 to 3.10×10^4 Torr (200–600 psi) with a pulse repetition rate of 2 Hz. Background pressures in various parts of the apparatus are indicated in Fig. 1. The laser was focused to a position a few hundred micrometers above the nozzle tip that has a diameter of 0.5 mm and a throat depth of 1 mm. The estimated gas density in the interaction region was ~10^{18} cm^{-3}.

3. EXPERIMENTAL FINDINGS

The nonlinear coupling represented by reaction (1) can lead to the generation of radiation. In our experiments, we observe the presence of two nonlinear mechanisms leading to the production of radiation in the vacuum-ultraviolet range. They are (a) harmonic generation, a parametric scattering process, and (b) fluorescence arising from excited ionic states.

A. Harmonic Radiation

The general scattering mechanism[11]

$$N\gamma(\omega) + X \rightarrow \gamma'(N\omega) + X, \qquad (2)$$

arising from the nonlinear nature of the atomic susceptibility at high field strengths for frequency ω, leads to the generation of harmonic radiation[12] of frequency $N\omega$. For our studies, the system X could represent either a neutral atom or an ion. In the electric-dipole approximation for a spatially homogeneous medium, it is well known that the harmonic order N is restricted to odd integers. For these initial studies, all the rare gases have been used as target materials.

Previously, with radiation at 248 nm in pulses of ~15-psec duration, 35.5-nm radiation was produced as the seventh harmonic[13] in He. In the present experiment, conducted with intensities ranging from 10^{15} to 10^{16} W/cm^2, harmonic generation was observed at considerably higher orders in the

0740-3224/87/040595-07$2.00

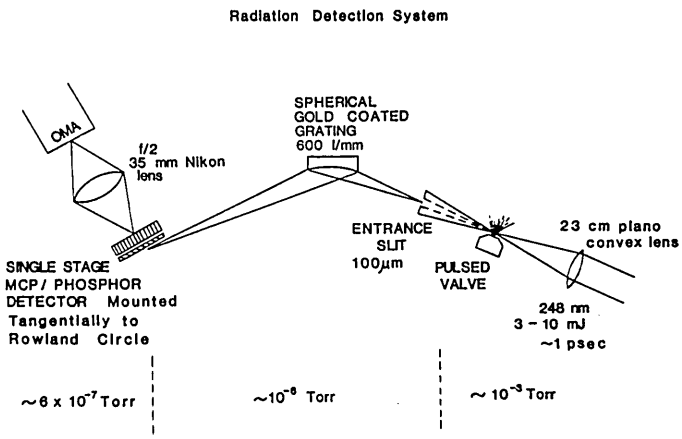

Fig. 1. Schematic of pulsed-gas jet and spectrometer–detector assembly used in studies of emitted radiation. The laser was operated to produce 3–10 mJ of energy with a pulse width of ~1 psec. Typical background pressures are indicated.

Table 1. Summary of Harmonic Production and Maximum Charge States Observed in the Rare Gases with 248-nm Radiation at an Intensity of $\sim 10^{15}$–10^{16} W/cm^2 and a Pulse Length of ~1 psec

Material	Maximum Harmonic Order Observed	Maximum Charge State Observed	Energy Coupling Associated with Charge State (eV)
He	13 (19.1 nm)	2	79
Ne	17 (14.6 nm)	4	224
Ar	7 (35.5 nm)	8	627
Kr	7 (35.5 nm)	8	544
Xe	9 (27.6 nm)	9	630

Table 2. Estimated Values of Several Harmonic Scattering Cross Sections σ_N for the Rare Gases Observed with 248-nm Radiation at an Intensity of $\sim 10^{15}$–10^{16} W/cm^2 and a Pulse Length of ~1 psec

Material	Harmonic Scattering Cross Sections σ_N (cm^2)			
	σ_5	σ_9	σ_{13}	σ_{17}
He	$\sim 1 \times 10^{-25}$	$\sim 1 \times 10^{-27}$	$\sim 1 \times 10^{-29}$	–
Ne	$\sim 2 \times 10^{-25}$	$\sim 6 \times 10^{-28}$	$\sim 6 \times 10^{-29}$	$\sim 3 \times 10^{-29}$
Ar	$\sim 5 \times 10^{-27}$	–	–	–
Kr	$\sim 3 \times 10^{-26}$	–	–	–
Xe	$\sim 8 \times 10^{-26}$	$\sim 6 \times 10^{-29}$	–	–

lighter materials He and Ne. Furthermore, it was found that the signal strength fell rather slowly as the harmonic order increased. For example, in our experiments in He and Ne with 248-nm pulses of ~1-psec duration, the decrease in intensity of adjacent orders was approximately a factor of 20 or less, a finding that contrasts with the earlier work[13] performed in He at an intensity of $\sim 10^{15}$ W/cm^2 that exhibited a decrement of several hundred between adjacent orders. Table 1 summarizes the maximum harmonic orders and corresponding wavelengths observed in the rare gases and, for comparison, the corresponding maximum charge state observed in the ion-charge-state experiments and the minimum energy transfer needed to produce this charge state.

On the basis of the observed harmonic intensities, it is possible to estimate the effective scattering cross sections σ_N for the production of radiation corresponding to reaction (2). Table 2 contains the specific values for the rare gases. As an example, the coupling strength shown for the thirteenth harmonic in Ne represents an efficiency of energy conversion of approximately 2×10^{-11}.

Interestingly, the data contained in Tables 1 and 2 indicate that a significant change in the harmonic scattering properties occurs between Ne and Ar, the same point at which, in earlier studies,[6] the observed energy-transfer rates for ionization appeared to change appreciably in magnitude. Basically, He and Ne, materials with relatively low rates for energy transfer and ionization, generate harmonics copiously, whereas the opposite relationship holds for the heavier atoms Ar, Kr, and Xe.

An additional property of the mechanism of harmonic production is revealed by a plot of the energy-conversion efficiency in Ne, the data for which are shown in Fig. 2. A clear break in the curve is evident between the ninth and the eleventh harmonics, a feature that cannot be accounted for by systematic effects in the wavelength response of the spectrometer–detector system. However, it is just in this energy region,[14] ~45.5 eV, that excitation of the 2*s* orbital becomes possible. This finding invites the interpretation that the harmonic production in Ne, under the conditions of irradiation studied, is governed for $N \leq 9$ mainly by the 2*p* electrons, while the higher harmonics observed ($11 \leq N \leq 17$) are produced by motions induced in the 2*s* subshell. Furthermore, since the atomic potential in which the 2*s* electrons move tends to be both stronger and of shorter range than that corresponding to the 2*p* electrons, a flatter harmonic spectrum such as that illustrated on Fig. 2 is expected.

B. Fluorescence

Electronically excited ions can be produced directly by process (1). Collision-free photoelectron spectra[4] of Xe have

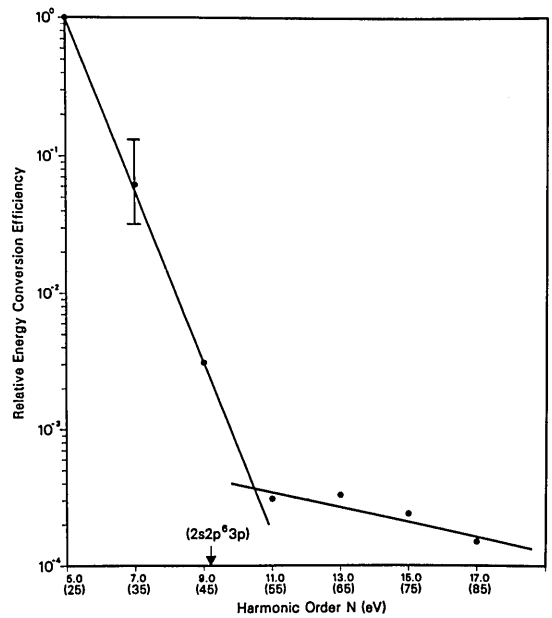

Fig. 2. A plot of the relative energy-conversion efficiency for harmonic generation in Ne shows a sharp change in slope between the ninth and eleventh harmonics. The arrow indicates the energy at which a 2*s* electron in the neutral becomes excited. For the seventh harmonic, the typical error bar is shown. The efficiency of the thirteenth harmonic is $\sim 2 \times 10^{-11}$.

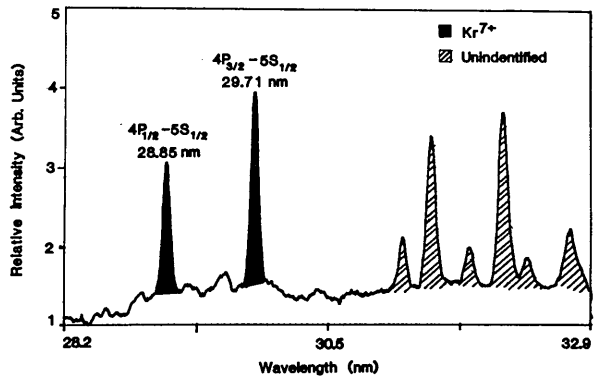

Fig. 3. A section of the Kr spectrum near 30 nm illustrates identified features from Kr^{7+} and unidentified lines of comparable strength.

Table 3. Main Properties of the Fluorescence Observed from Ar, Kr, and Xe with 248-nm Radiation at an Intensity of ~10^{15}–10^{16} W/cm^2 and a Pulse Length of ~1 psec

Material	Ar	Kr	Xe
Ionic charge states observed	4+, 5+, 6+, 7+	6+, 7+, 8+	6+, 7+, 8+
Wavelength range of emissions (nm)	12.0–47.1	9.9–45.3	9.8–48.1
Typical identified transitions	7+ $4f \rightarrow 3d$	7+ $5p \rightarrow 4s$	7+ $6s \rightarrow 5p$ 7+ $4d^9 5s5p \rightarrow 4d^{10}5s$
Unidentified emissions	Many	Many	Many
References	15, 31–34	15, 24–30	16–20, 21–23

explicitly demonstrated the generation of excited electronic levels for both Xe^{2+} and Xe^{3+} but only of the ground-state configuration. In the current studies employing a gas jet, fluorescence shorter than 50 nm from orbitally excited ions of Ar, Kr, and Xe has been observed. A region of the spectrum obtained for Kr is shown in Fig. 3, which illustrates two general features of the observed spectra. They are identified radiation from high charge states and an abundance of unidentified lines. Although He and Ne, on the basis of the charge states known to be produced in the ion spectra,[1–3] could emit characteristic line radiation[15] from excited ions produced either by recombination or other processes, no emission of any kind, other than the harmonic radiation, was observed in the spectral region 20–50 nm for these two materials.

Table 3 summarizes the main properties of the observed fluorescence in Ar, Kr, and Xe.[16–34] In all three cases a large number of emissions was seen. Although specific identification is often possible, as illustrated in Fig. 3 and Table 3, a considerable fraction of the observed transitions cannot be associated with the known spectra of any ionic species. It seems possible that multiple excited levels and/or core-excited states could account for some of these anomalous spectral features. At present, the information on the properties of such states, particularly for ionic spectra,[35,36] is quite meager.

From a comparison of the data shown in Tables 1 and 3, we see that the harmonic production and fluorescence are anticorrelated. Specifically, fluorescent emissions are seen only from atoms that are relatively poor generators of harmonic spectra, and the best materials for harmonic generation exhibit no fluorescence below 50 nm. Moreover, the change in the behavior occurs between Ne and Ar, a division that matches that observed and discussed above in relation to the ionization rate.[6] The strong radiators are consistently the materials that exhibit high energy-transfer rates in the studies of collision-free ionization.

It has been suggested[37] that the tendency of the heavier rare gases to cluster[38] could be a factor in the comparative behavior of the fluorescence from those materials, in comparison to that observed for the lighter atoms He and Ne. Given the measured properties[39,40] of the multiphoton absorption of Kr_2 and Xe_2, which are expected to be approximately those of corresponding molecular clusters, and the characteristics of the detailed temporal profile of the 248-nm irradiation, it is possible to estimate the influence of this effect. The fluorescence has been observed with two different pulse shapes. One involved a pedestal-free irradiation with pulse lengths in the 0.5–1.0-psec range. The other had

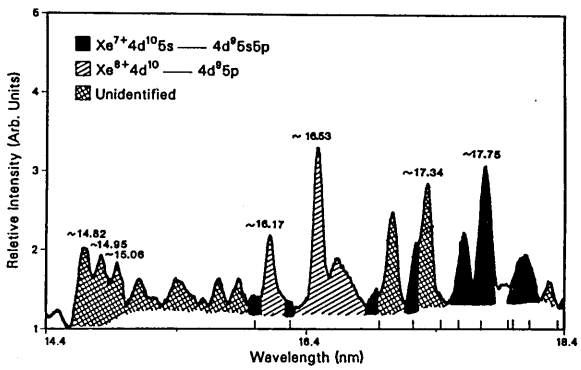

Fig. 4. Xe spectrum illustrating the characteristic emissions produced by 248-nm radiation at an intensity of ~10^{15}–10^{16} W/cm^2 with a pulse length of ~1 psec. Features involving transitions in Xe^{7+} and Xe^{8+} are shown along with a group of unidentified lines. The tick marks indicate the positions of the transitions in the $4d^95s5p \rightarrow 4d^{10}5s$ manifold of Xe^{7+}.

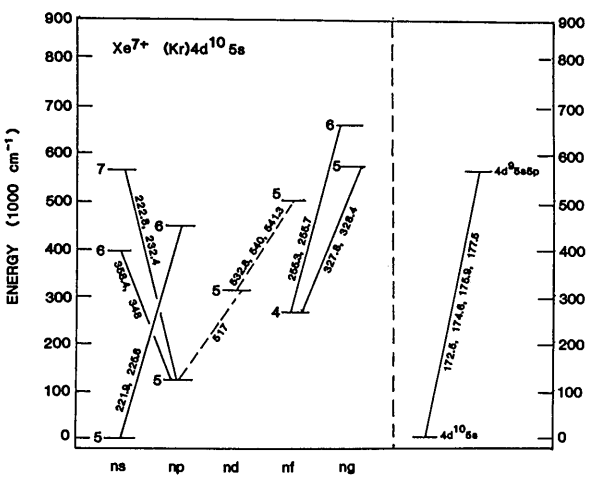

Fig. 5. Partial Grotrian diagram of Xe^{7+} indicating the experimentally observed transitions. Excited states involving excitation of either the 5*s* electron or a 4*d* electron are evident. Dashed lines, not observed.

a pedestal of ~5-psec duration, with an estimated energy of ~1 mJ, accompanying the short ~0.5-psec feature. The patterns of fluorescence observed with these two types of pulse were essentially identical. However, the radiation in the pedestal, with an intensity of $\sim 10^{-2}$–10^{-3} of the main pulse, should have produced a significant change in the distribution and quantity of clustered atoms. In the case of Kr, for example, comparison with the earlier work[39] on Kr_2 indicates that a considerable fraction (50%) of the Kr clusters would be singly ionized by the low-level radiation preceding the main subpicosecond feature. For these reasons, we do not believe that the experimental evidence points to a significant role for clustering in these studies.

A portion of the spectrum obtained from Xe is illustrated in Fig. 4. The tick marks on the wavelength scale indicate the positions of the transitions that compose the $4d^9 5s5p \rightarrow 4d^{10}5s$ manifold[20] of Xe^{7+}. In addition, Fig. 5 illustrates in a Grotrian diagram the observed and identified transitions from Xe^{7+}. An interesting feature is immediately apparent. The identified transitions in the spectrum of Xe^{7+} clearly indicate the presence of two fundamentally different electronic configurations. One involves transitions occurring from excitation of the 5s electron, whereas the other entails excitation of the 4d shell, giving rise to a configuration of the form $4d^9 5s5p$. This latter result should not come as a complete surprise, since ionization of the 4d shell was clearly seen[3,5,6] in the studies of ion formation. The corresponding 3d excitation in Kr^{7+}, however, has not been identified, although a $3d^9 4p \rightarrow 3d^{10}$ (11.5-nm) transition characteristic of Kr^{8+} is observed.

4. DISCUSSION OF RESULTS

A. Mechanism for Fluorescence Production

The currently available data do not unambiguously specify the mechanisms leading to the excitation of the radiating ionic levels. At least three different possibilities exist. They are (a) a direct atomic mechanism that leads to an excited ionic state, (b) recombination, and (c) collisional excitation by energetic electrons in the gas-jet plasma. For the former, reaction (1) is more clearly written to read as

$$\begin{array}{l} N\gamma + X \rightarrow (X^{q+})^* + qe^- \\ \qquad\qquad \downarrow \\ \qquad\qquad \rightarrow X^{q+} + \gamma', \end{array} \tag{3}$$

or, if a short-lived intermediate state that autoionizes to the final excited ionic level is involved, the process can be represented as

$$\begin{array}{l} N\gamma + X \rightarrow (X^{q_1+})^{**} + q_1 e^- \\ \qquad\qquad\quad \downarrow \\ \qquad\qquad\quad \rightarrow (X^{q+})^* + (q - q_1)e^- \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad \rightarrow X^{q+} + \gamma'. \end{array} \tag{4}$$

In principle, the two paths given by processes (3) and (4) are distinguishable for a given $(X^{q+})^*$ level by the distribution of energy among the q electrons that are released. These processes are prompt in the sense that they are generally expected to occur on a subpicosecond time scale. We consider it unlikely that processes of the general type

$$N\gamma + X^{q+} \rightarrow (X^{q+})^* \tag{5}$$

play any significant role, since that would require an accidental coincidence of the level structure, within the relevant linewidths, with harmonics of the 248-nm radiation.

Recombination[41,42] and collisional excitation[43–48] for the conditions of this experiment are estimated to occur at a much slower rate. For $q \cong 10$, a plasma characterized by a thermal energy of ~35 eV and an electron density of $\rho_e \sim 3 \times 10^{18}$ cm^{-3}, the recombination time[42] is estimated to be approximately 600 psec. Future experiments utilizing an x-ray streak camera are currently being prepared that will be able to distinguish between the fast process of direct excitation and the much slower processes of recombination and collisional excitation.

B. Fluorescence Cross Section

It is of interest to determine, on the basis of the experimental data, what the equivalent cross section σ_F for fluorescence is, assuming that the radiating excited states are generated by the direct processes (3) and (4). It is also valuable to inquire into the nature of the electronic motions that could give rise to a direct mechanism. This point is examined in Subsection 4.D below. An estimate of the value of σ_F can be derived by comparison of the signal strength for fluorescence with that observed for harmonic generation. Specific cases for Kr and Xe are given in Table 4. From a comparison of the ion data, which give values[3,5,6] for the cross sections for energy transfer $\langle \sigma_{N\gamma} \rangle_{av}$, the harmonic data, which establish σ_N, and the fluorescent emission giving σ_F, we find as a general statement for the class of materials studied that the ordering of these quantities is given by

$$\langle \sigma_{N\gamma} \rangle_{av} > \sigma_F > \sigma_N \qquad (N > 7) \tag{6}$$

and that

$$\frac{\sigma_F}{\langle \sigma_{N\gamma} \rangle_{av}} \sim 1 \times 10^{-4} \tag{7}$$

for Xe.

C. Anomaly Observed in the Kr Fluorescence

Figure 6 illustrates a section of the observed spectrum for Kr. An accompanying Grotrian diagram for Kr^{7+} is illustrated in Fig. 7. The lines assigned to Kr^{7+} in the 18–21-nm region give information related to the recombination rate and the specificity of excited-state population. Both points are related to the observation of the $5d \rightarrow 4p$ multiplet near 20 nm, a transition that is anomalously weakened by an

Table 4. Tabulation of Approximate Values of Observed Cross Sections σ_N for Fluorescence, Assuming That Excitation Occurs by the Direct Process (3) or (4)

Material	σ_F (cm^2)	Species	Transition	Wavelength (nm)
Kr	$\sim 8 \times 10^{-25}$	Kr^{7+}	$5p \rightarrow 4s$	18.2
Xe	$\sim 6 \times 10^{-25}$	Xe^{7+}	$4d^9 5s5p \rightarrow 4d^{10}5s$	17.7

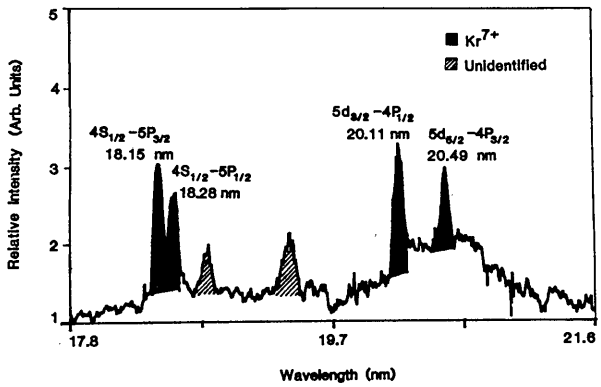

Fig. 6. Kr^{7+} spectrum illustrating the presence of both the ~20-nm $5d \rightarrow 4p$ transitions and the $5p \rightarrow 4s$ lines at ~18.2 nm.

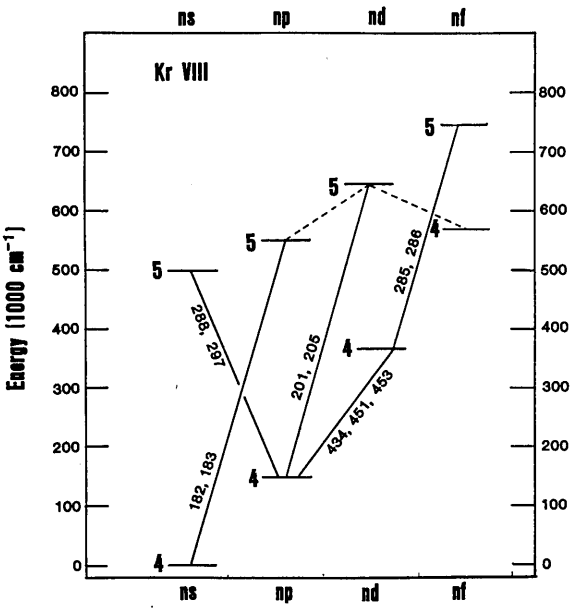

Fig. 7. Grotrian diagram for the $n = 4$ and $n = 5$ levels of Kr^{7+} illustrating the observed transitions below 50 nm. The transitions indicated by the dashed lines determine the $5d$ lifetime.

accidental cancellation in the dipole matrix element.[24,25,29] Analysis of the available information in the literature[24,25,49,50] indicates that the $5d$ levels have a radiative lifetime of ~200 psec, a value determined by the radiative rates for transitions near 110 nm ($5d$–$5p$) and 128 nm ($5d$–$4f$) (the dashed lines in Fig. 7). Since the $5d \rightarrow 4p$ transition is relatively slow[25] ($\sim 3.4 \times 10^7$ sec^{-1}), the fractional yield into that branch is very low, with a value of less than $\sim 10^{-2}$. This feature has been used to account for the absence of these 20-nm lines in an earlier beam-foil study.[24] They were also not observed in an experiment involving a linear theta pinch.[51] In comparison with the weak ~20-nm emission from the $5d$ state, the $5p$ level of Kr^{7+} radiates strongly on the $5p \rightarrow 4s$ doublet near 18.2 nm, with a fractional yield of ~0.5. The lifetime[25] of the $5p$ state is ~150 psec.

Given the great difference in radiative strengths, it is significant that the $5p \rightarrow 4s$ doublet and the $5d \rightarrow 4p$ lines appear with nearly equal strengths, as illustrated in Fig. 6. We have considered the possible influence of trapping on the intensity of the $5p \rightarrow 4s$ features and conclude, on the basis of our observation that the intensity ratio is unchanged with variation of the plasma scale length, that trapping is not a significant factor.

Three important conclusions may be inferred from the Kr spectrum. They are (a) that a mechanism involving considerable selectivity is operating in the production or destruction of the $5d$ state; (b) that the $5d$ level is populated to a magnitude approximately fiftyfold greater than the $5p$ state, a fact that, scaling from the cross section given in Table 4 for the $5p$ state, gives an effective cross section for excitation $\sigma_F(5d) \sim 4 \times 10^{-23}$ cm^2; and (c) on the basis of the overall intensity of these transitions, that substantial quenching by recombination on a time scale of ~200 psec is unlikely. The last-named point, dealing with recombination, is consistent with the estimate[42] of this rate given in Subsection 4.A above.

D. Xenon Spectrum

The experiments examining ion production[3,5,6] and fluorescence both indicate the excitation and ionization of a $4d$ electron in Xe. We now explore several atomic phenomena that may be related to this observation. Normally, with irradiation at 248 nm, the $4d$ inner-electron would be shielded from the external field[52,53] by the outer $5s$ and $5p$ subshells. Therefore direct coupling of the radiation field to the $4d$ shell is not expected to be of significance in the neutral atom. However, it is possible for such an inner-shell excitation to occur by an indirect process[52,54,55] involving a multielectron interaction. For Xe it is well established, particularly from photoionization studies involving multiple-electron ejection,[56–61] that the $5p$, $5s$, and $4d$ shells exhibit substantial intershell coupling[62] and behave collectively in a fashion resembling a single supershell.[63] Significantly, similar multielectron characteristics were recently revealed[64] in studies of electron impact ionization of Xe^{6+} ions. In the case under study,[64] this feature was exhibited in the overall process

$$e^- + Xe^{6+} \rightarrow Xe^{9+} + 4e^-, \quad (8)$$

which, in the energy range between 400 and 600 eV, perforce must involve a multiple-target-electron mechanism. We remark that some corresponding information on processes of photoexcitation in Kr is also available.[65]

These intershell couplings provide a basis for the excitation of atomic inner-shell electrons through a radiative interaction with the outer-shell electrons. To explore this point, we consider the known single-quantum double-ionization process[59,61] in Xe

$$\gamma + Xe(4d^{10}5s^25p^6) \rightarrow Xe^{2+}(4d^95s^25p^5) + 2e^-, \quad (9)$$

which has an estimated[60] threshold energy of ~90 eV. This direct two-electron process, which produces a continuous distribution of electron energies in the final state and which represents a significant fraction of the total absorption,[60,61] specifically demonstrates the correlated removal of a $5p$ electron with one from the $4d$ shell. Therefore, by analogy, this would appear to admit the possibility of nonlinear processes of the type

$$N\gamma + Xe(4d^{10}5s^25p^6) \rightarrow Xe^{2+}(4d^95s^25p^5) + 2e^- \quad (10)$$

for the neutral atom and corresponding channels of the form

$$N\gamma + Xe^{3+}(4d^{10}5s^25p^3) \rightarrow Xe^{5+}(4d^95s^25p^2) + 2e^- \quad (11)$$

for ions, in which the choice of Xe^{3+} simply serves as an example. In this picture, owing to the strong intershell coupling, it should be possible to produce the same exit channels if sufficient energy is available from the intense ultraviolet field. For the single-quantum reaction (9) this energy requirement is met by having a frequency sufficiently high that the quantum energy $\hbar\omega$ exceeds the appropriate ionization threshold. For the multiquantum processes (10) and (11) the energy needed is furnished by having an intensity great enough that the energy of nonlinear coupling to the atom or ion surpasses the corresponding threshold value. Processes (9) and (10) are fundamentally similar in the sense *that additional channels arise* when the main physical parameter governing the reaction, either frequency in the former or intensity in the latter, is sufficiently large.

Since 5*s* and 5*p* electrons in such processes are expected to behave similarly,[60] a particular example of process (11) is

$$N\gamma + Xe^{5+}(4d^{10}5s^25p) \rightarrow Xe^{7+}(4d^95s5p) + 2e^-. \quad (12)$$

This reaction yields the specific excited state generating the 17.7-nm radiation shown in Fig. 4 and listed in Table 4. Hence the existence of multielectron processes, which arise as a consequence of the strong intershell coupling, lead naturally, by a nonlinear analog, to the excitation of the experimentally observed radiating level. Furthermore, the fact that an intra-atomic coupling of this nature can occur in ions is strongly indicated by its presence in the electron-impact multiple ionization demonstrated,[64] for example, by process (8). On this basis, there appears, in principle, no reason to exclude reactions[64] similar to processes (9)–(12) that have more than two electrons in the final state.

The importance of multielectron interactions can be summarized in the following manner. For Xe in the 4*d* region[66,67] as well as the lanthanides,[68] it is well known that the single-particle picture of single-quantum photoionization fails to provide even a qualitative understanding of the data.[62,69,70] The strongly correlated character of the electronic motions is a fundamental aspect of the reaction. Process (9), which leads to double ionization with a continuous distribution of electron energies in the final state,[60,61] represents one aspect of this intra-atomic coupling. In addition, it is now found that multiply ionizing electron collisions[64] involving ionized Xe, such as those observed in reaction (8), totally fail to be described within the single-particle framework. Given the common link of intra-atomic coupling for processes (8)–(12), it would appear likely, at least for Xe and probably for many heavy elements, that mechanisms producing multiquantum ionization and associated atomic excitation with intense fields will require a theoretical formulation that includes electron correlation[6,71] as a fundamental element.

5. CONCLUSIONS

The availability of extraordinarily bright femtosecond ultraviolet sources is permitting the study of a wide range of new nonlinear phenomena. Measurements of the radiation produced by the high field interaction with the rare gases with subpicosecond 248-nm radiation at an intensity $\sim 10^{16}$ W/cm^2 have revealed the presence of both copious harmonic production and fluorescence. All the noble gases produced harmonic radiation, and the highest harmonic observed was the seventeenth (14.6 nm) in Ne. Strong fluorescence below 50 nm was seen only in Ar, Kr, and Xe, with the shortest wavelengths observed being below 12 nm. Radiation was detected from inner-shell excited states, specifically, transitions involving the $4d^95s5p \rightarrow 4d^{10}5s$ manifold at ~17.7 nm in Xe^{7+}. In addition, fluorescence observed from Kr^{7+} on the $5d \rightarrow 4d$ lines indicates the generation of anomalously large populations in the 5*d* level.

The experimental findings of these studies, in combination with experimental results of other work on inner-shell processes involving both mechanisms of photoionization and electron-collision ionization, give evidence for a role of electron correlations in a direct nonlinear multiquantum process of inner-shell excitation. If such a mechanism involving multielectron channels is present, it is expected to be a general property of the heavier atoms in the periodic table and, perhaps, a prominent characteristic of actinide species such as U.

ACKNOWLEDGMENTS

The authors wish to acknowledge fruitful discussions with T. Graber, M. H. R. Hutchinson, D. C. Gregory, R. P. Madden, A. Szöke, D. Levy, U. Becker, and H. P. Kelly. The technical assistance of R. Bernico, T. Pack, R. Slagle, and J. Wright is also warmly acknowledged. This research was supported by the U.S. Office of Naval Research, the U.S. Air Force Office of Scientific Research, the Innovative Science and Technology/Strategic Defense Initiative Organization (IST/SDIO) and directed by the Naval Research Laboratory, the U.S. Department of Energy, the Lawrence Livermore National Laboratory, the National Science Foundation, the Defense Advanced Research Projects Agency, and the Los Alamos National Laboratory.

REFERENCES

1. T. S. Luk, U. Johann, H. Egger, H. Pummer, and C. K. Rhodes, Phys. Rev. A **32**, 214 (1985).
2. U. Johann, T. S. Luk, I. A. McIntyre, A. McPherson, A. P. Schwarzenbach, K. Boyer, and C. K. Rhodes, "Multiphoton ionization in intense ultraviolet laser fields," in *Proceedings of the Topical Meeting on Short Wavelength Coherent Radiation*, J. Bokor and D. Attwood, eds. (American Institute of Physics, New York, to be published).
3. C. K. Rhodes, "Ordered many-electron motions in atoms and x-ray lasers," in *Proceedings of the NATO Advanced Study Institute on Giant Resonances in Atoms, Molecules, and Solids*, J.-P. Connerade, J. M. Esteva, and R. C. Karnatak, eds. (Plenum, New York, to be published).
4. U. Johann, T. S. Luk, H. Egger, and C. K. Rhodes, Phys. Rev. A **34**, 1084 (1986).
5. U. Johann, T. S. Luk, I. A. McIntyre, A. McPherson, A. P. Schwarzenbach, K. Boyer, and C. K. Rhodes, "Multi-quantum processes at high field strengths," in *Proceedings of the Topical Meeting on Short Wavelength Coherent Radiation*, J. Bokor and D. Attwood, eds. (American Institute of Physics, New York, to be published).
6. C. K. Rhodes, "Physical processes at high field strengths," Phys. Scr. (to be published).
7. A. McPherson, T. S. Luk, M. H. R. Hutchinson, H. Jara, U. Johann, I. A. McIntyre, A. P. Schwarzenbach, K. Boyer, and C.

K. Rhodes, "VUV fluorescence and harmonic generation with intense picosecond 248 nm KrF* radiation," presented at the Society of Photo-Optical Instrumentation Engineers Symposium on Fiber Optics, Optoelectronics and Laser Applications, Cambridge, Massachusetts, September 1986.

8. T. S. Luk, A. McPherson, H. Jara, U. Johann, I. A. McIntyre, A. P. Schwarzenbach, K. Boyer, and C. K. Rhodes, "Experimental study of harmonic generation with picosecond 248 nm radiation," in *Ultrafast Phenomena V*, G. R. Fleming and A. E. Siegman, eds. (Springer-Verlag, Berlin, to be published).
9. A. P. Schwarzenbach, T. S. Luk, I. A. McIntyre, U. Johann, A. McPherson, K. Boyer, and C. K. Rhodes, Opt. Lett. **11,** 499 (1986).
10. M. H. R. Hutchinson, I. A. McIntyre, G. W. Gibson, and C. K. Rhodes, "Measurement of 248 nm subpicosecond pulse radiations by two-photon fluorescence of xenon dimers," Opt. Lett. (to be published).
11. N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).
12. S. E. Harris, Phys. Rev. Lett. **31,** 341 (1973).
13. J. Bokor, P. H. Bucksbaum, and R. R. Freeman, Opt. Lett. **8,** 217 (1983).
14. K. Codling, R. P. Madden, and D. L. Ederer, Phys. Rev. **155,** 26 (1967).
15. R. L. Kelly and L. J. Palumbo, "Atomic and ionic emission lines below 2000 angstroms," Naval Res. Lab. Rep. 7599 (U.S. Government Printing Office, Washington, D.C., 1983).
16. J. Sugar and V. Kaufman, Phys. Scr. **26,** 419 (1982).
17. J. R. Roberts, E. J. Krystautas, and J. Sugar, J. Opt. Soc. Am. **69,** 1620 (1979).
18. V. Kaufman and J. Sugar, J. Opt. Soc. Am. B **1,** 38 (1984).
19. E. J. Krystautas, J. Sugar, and J. R. Roberts, J. Opt. Soc. Am. **69,** 1726 (1980).
20. J. Blackburn, P. K. Carroll, J. Costello, and G. O'Sullivan, J. Opt. Soc. Am. **73,** 1325 (1983).
21. K. Codling and R. P. Madden, Phys. Rev. A **4,** 2261 (1971).
22. D. L. Ederer, Phys. Rev. A **4,** 2263 (1971).
23. V. Kaufman and J. Sugar, Phys. Scr. **24,** 738 (1981).
24. A. E. Livingston, L. J. Curtis, R. M. Schectman, and H. G. Berry, Phys. Rev. A **21,** 771 (1980).
25. K.-T. Chang and Y.-K. Kim, At. Data Nucl. Data Tables **22,** 547 (1978).
26. E. H. Pinnington, W. Ansbacher, and J. A. Kernahan, J. Opt. Soc. Am. B **1,** 30 (1984).
27. M. Druetta and J. P. Buchet, J. Opt. Soc. Am. **66,** 433 (1976).
28. D. J. G. Irwin, J. A. Kernahan, E. H. Pinnington, and A. E. Livingston, J. Opt. Soc. Am. **66,** 1396 (1976).
29. L. J. Curtis and D. G. Ellis, J. Phys. B **11,** L543 (1978).
30. L. A. Jones and E. Källne, J. Quant. Spectrosc. Radiat. Transfer **30,** 317 (1983).
31. R. P. Madden, D. L. Ederer, and K. Codling, Phys. Rev. **177,** 136 (1969).
32. S. Bashkin and J. O. Stoner, Jr., *Atomic Energy Level and Grotrian Diagrams* (North-Holland, Amsterdam, 1975–1982), Vols. 1–4 and addenda.
33. B. C. Fawcett, A. Ridgeley, and G. E. Bromage, Phys. Scr. **18,** 315 (1978).
34. M.-C. Buchet-Poulizac, J.-P. Buchet, and P. Ceyzeriat, Nucl. Instrum. Methods **202,** 13 (1982).
35. N. J. Peacock, R. J. Speer, and M. G. Hobby, J. Phys. B **2,** 798 (1969).
36. C. W. Clark, M. G. Littman, R. Miles, T. J. McIlrath, C. H. Skinner, S. Suckewer, and E. Valeo, J. Opt. Soc. Am. B **3,** 321 (1986).
37. A. Szöke, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550 (personal communication).
38. U. Buck and H. Meyer, J. Chem. Phys. **84,** 4854 (1986); D. R. Worsnop, S. J. Buelow, and D. R. Herserbach, J. Phys. Chem. **88,** 4506 (1984); U. Buck, H. Meyer, and H. Pauly, in *Flow in Real Fluids*, G. B. A. Meier and F. Obermeier, eds. (Springer-Verlag, Berlin, 1985), p. 170; U. Buck and H. Meyer, Phys. Rev. Lett. **52,** 109 (1984); A. Van Deursan, A. Van Lumig, and J. Reuss, Int. J. Mass. Spectrom. Ion Phys. **18,** 129 (1975); U. Buek and A. Meyer, Ber. Bunsenges. Phys. Chem. **88,** 254 (1984).
39. M. Rothschild, W. Gornik, J. Zavelovich, and C. K. Rhodes, J. Chem. Phys. **75,** 3794 (1981).
40. M. Rothschild, J. Zavelovich, W. Gornik, and C. K. Rhodes, Opt. Commun. **39,** 316 (1981).
41. D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes*, D. R. Bates, ed. (Academic, New York, 1962), p. 245.
42. D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. R., Soc. London Ser. A **267,** 297 (1982); **270,** 155 (1962).
43. G. J. Pert, J. Phys. B **11,** 1105 (1978).
44. R. J. Dewhurst, G. J. Pert, and S. A. Ramsden, J. Phys. B **7,** 2281 (1974).
45. G. J. Pert, J. Phys. B **8,** 3069 (1975).
46. G. J. Pert, J. Phys. A **5,** 1221 (1972); **9,** 1797 (1976).
47. G. J. Pert, J. Phys. A **5,** 506 (1972).
48. R. U. Datla, H. J. Kunze, and D. Petrini, Phys. Rev. A **6,** 38 (1972).
49. E. H. Pinnington, R. W. Gosselin, J. A. O'Neill, J. A. Kernahan, K. E. Donnelly, and R. L. Brooks, Phys. Scr. **20,** 151 (1979).
50. E. J. Knystautas and R. Drouin, J. Quant. Spectrosc. Radiat. Transfer **17,** 551 (1977).
51. R. Engleman, Jr., D. B. Thomson, and D. A. Monaghan, "Vacuum ultraviolet emission from argon, krypton, and xenon in a radial-viewed theta pinch," Los Alamos National Laboratory Rep. LA-6275-MS (Los Alamos National Laboratory, Los Alamos, N.M., 1976).
52. G. Wendin, L. Jönsson, and A. L'Huillier, Phys. Rev. Lett. **56,** 1241 (1986); A. L'Huillier, L. Jönsson, and G. Wendin, Phys. Rev. A **33,** 3938 (1986).
53. L. I. Schiff, Phys. Rev. **132,** 2194 (1963).
54. K. Boyer and C. K. Rhodes, Phys. Rev. Lett. **54,** 1490 (1985).
55. A. Szöke and C. K. Rhodes, Phys. Rev. Lett. **56,** 720 (1986).
56. M. J. Van der Wiel and T. N. Chang, J. Phys. B **11,** L125 (1978).
57. M. Ya. Amusia, in *Advances in Atomic and Molecular Physics*, D. R. Bates and B. Bederson, eds. (Academic, New York, 1981), Vol. 17, p. 1.
58. 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).
59. H. Aksela, A. Aksela, G. M. Bancroft, K. A. Tan, and H. Pulkkinen, Phys. Rev. A **33,** 3867 (1986).
60. U. Becker, T. Prescher, E. Schmidt, B. Sonntag, and H.-E. Wetzel, Phys. Rev. A **33,** 3891 (1986).
61. U. Becker, R. Hölzel, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, "Zerfälle der Xe $4d \rightarrow np$ Anregungen: resonante Auger und Doppel-Auger-Prozesse," Bericht (BESSY, Berlin, 1984).
62. A. F. Starace, in *Fundamental Processes in Energetic Atomic Collisions*, H. O. Lutz, J. S. Briggs, and H. Kleinpoppen, eds. (Plenum, New York, 1983), p. 69; A. F. Starace, Handb. Phys. **31,** 1 (1982).
63. M. Ya. Amusia and N. A. Cherepkov, in *Case Studies in Atomic Physics 5*, E. W. McDaniel and M. R. McDowell, eds. (North-Holland, Amsterdam, 1975), p. 47.
64. A. M. Howald, D. C. Gregory, R. A. Phaneuf, D. H. Crandall, and M. S. Pindzola, Phys. Rev. Lett. **56,** 1675 (1986).
65. H. Aksela, S. Aksela, H. Pulkkinen, G. M. Bancroft, and K. H. Tan, Phys. Rev. A **33,** 3876 (1986).
66. G. Wendin, J. Phys. B **3,** 455, 466 (1970); **4,** 1080 (1971); **5,** 110 (1972); **6,** 42 (1973).
67. D. J. Kennedy and S. T. Manson, Phys. Rev. A **5,** 227 (1972); J. B. West, P. R. Woodruff, K. Codling, and R. G. Houlgate, J. Phys. B **9,** 407 (1976); G. R. Wight and M. J. Van der Wiel, J. Phys. B **10,** 601 (1977); D. M. P. Holland, K. Codling, J. B. West, and G. V. Marr, J. Phys. B **12,** 2465 (1979).
68. J. P. Connerade and D. H. Tracy, J. Phys. B **10,** L235 (1977).
69. G. Wendin, in *Photoionization and Other Probes of Many-Electron Interactions*, F. J. Wuilleumier, ed. (Plenum, New York, 1976), p. 61.
70. H. P. Kelly and S. L. Carter, Phys. Scr. **21,** 448 (1980).
71. A. F. Starace, "Electron correlation effects in nonresonant multiphoton ionization processes," Phys. Scr. (to be published).