Three-photon excitation of autoionizing states of atomic xenon between the $^2P^\circ_{3/2}$ and $^2P^\circ_{1/2}$ fine-structure thresholds

S. T. Pratt, P. M. Dehmer, and J. L. Dehmer
Argonne National Laboratory, Argonne, Illinois 60439
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The nonresonant, three-photon ionization spectrum of atomic Xe in the region between the Xe^+ $^2P^\circ_{3/2}$ and $^2P^\circ_{1/2}$ fine-structure limits is reported. Using linearly polarized light, four autoionizing Rydberg series are observed converging to the Xe^+ $^2P^\circ_{1/2}$ limit, corresponding to $(^2P^\circ_{1/2})ns'[\frac{1}{2}]^\circ_1$, $(2P^\circ_{1/2})nd'[\frac{3}{2}]^\circ_1$, $(^2P^\circ_{1/2})nd'[\frac{5}{2}]^\circ_3$, and $(^2P^\circ_{1/2})ng'[\frac{7}{2}]^\circ_3$; as expected, using circularly polarized light only the $J=3$ series are observed. These results are in contrast to earlier experimental work in which no resonant structure was observed. Photoelectron angular distributions are reported for the $(^2P^\circ_{1/2})9s'[\frac{1}{2}]^\circ_1$ and the $(^2P^\circ_{1/2})7d'[\frac{3}{2}]^\circ_3$ autoionizing resonances. The results are compared with the recent theoretical calculations by P. Gangopadhyay *et al.* [Phys. Rev. A **34**, 2998 (1986)].

I. INTRODUCTION

Recently, Gangopadhyay *et al.*[1] reported calculations of two- and three-photon ionization spectra of Xe in the energy region between the Xe^+ $^2P^\circ_{3/2}$ and $^2P^\circ_{1/2}$ fine-structure thresholds. Both the two- and three-photon calculations show strong resonances corresponding to autoionizing Rydberg series converging to the $^2P^\circ_{1/2}$ limit. In particular, the theoretical three-photon ionization spectrum shows structure corresponding to $J=1$ and $J=3$ Rydberg series. However, a recent experimental study of the three-photon ionization of Xe by Feldmann *et al.*[2] found no such resonance structure in the total ionization cross section in this region, although their photoelectron angular distributions did show a strong variation around a predicted autoionizing resonance at $3h\nu=13.134$ eV.

The lack of structure in the experimental three-photon ionization spectrum is somewhat surprising. The single-photon absorption[3] and ionization[4] spectra of ground-state $Xe(^1S_0)$ in the region between the Xe^+ fine-structure thresholds display the well-known $(^2P^\circ_{1/2})ns'$ and $(^2P^\circ_{1/2})nd'$ $J=1$ Rydberg series converging to the $^2P^\circ_{1/2}$ threshold. These series are also allowed in the electric dipole approximation for three-photon absorption, although the relative intensities may be different than the one-photon intensities. Additional Rydberg series with $J=3$ are also expected in the three-photon spectrum. For example, Wang and Knight[5] have recently observed the $(^2P^\circ_{1/2})ns'$ and nd' Rydberg series with $J\neq 1$ using two-step laser excitation of a Xe metastable beam; one of the reported series is $(^2P^\circ_{1/2})nd'$ series with $J=3$. Thus, one expects to see a number of Rydberg series in the three-photon ionization spectrum of Xe between the Xe^+ $^2P^\circ_{3/2}$ and $^2P^\circ_{1/2}$ fine-structure thresholds, and for this reason we have reexamined the spectrum in this region. Contrary to the previous measurements, four autoionizing Rydberg series are observed using linearly polarized light, corresponding to the $(^2P^\circ_{1/2})ns'[\frac{1}{2}]^\circ_1$, $(^2P^\circ_{1/2})nd'[\frac{3}{2}]^\circ_1$, $(^2P^\circ_{1/2})nd'[\frac{5}{2}]^\circ_3$, and $(^2P^\circ_{1/2})ng'[\frac{7}{2}]^\circ_3$ Rydberg series. Here, the notation $(^2P^\circ_{j_c})nl'[K]^\circ_J$ corresponds to $j_c l$ coupling,[6] in which the angular momentum of the ion core j_c, is coupled to the orbital angular momentum of the Rydberg electron l, to give K, which is then coupled to the Rydberg electron's spin to give J. In what follows the notation will be abbreviated $nl'[K]^\circ_J$, with the prime denoting the $^2P^\circ_{1/2}$ ion core. As expected, with circularly polarized light only the $J=3$ levels are observed.

In addition to the three-photon ionization spectrum, the photoelectron angular distributions have also been determined for the $9s'[\frac{1}{2}]^\circ_1$ and the $7d'[\frac{3}{2}]^\circ_3$ autoionizing resonances using linear polarized light. The angular distributions can be compared with the predictions of Gangopadhyay *et al.*[1] It is also instructive to compare the angular distribution for the $9s'[\frac{1}{2}]^\circ_1$ resonance with earlier results obtained using single-photon ionization.[7–9]

II. EXPERIMENTAL PROCEDURE

The experimental apparatus consists of a hemispherical electrostatic electron energy analyzer, a time-of-flight mass spectrometer, and a Nd:YAG-pumped (where YAG represents yttrium aluminum garnet) dye-laser system.[10] The dye-laser output is frequency doubled and approximately 0.5 mJ of the resulting uv light is separated from the fundamental using dichroic filters and is focused by a 150-mm lens into the interaction region. The Xe gas is introduced via an effusive jet and the chamber pressure is maintained at $\sim 6\times 10^{-5}$ Torr, with ~ 10–100 times higher pressure in the interaction region. The three-photon ionization spectrum was obtained by scanning the laser wavelength while monitoring the Xe^+ ion signal with the mass spectrometer. The uv light could be circularly polarized using a Babinet-Soleil compensator tuned as a $\frac{1}{4}$-wave plate at the appropriate wavelength.

Photoelectron spectra were also recorded at the wavelengths of features of interest. For all photon energies examined, only one photoelectron peak was observed, corresponding to the production of Xe^+ $^2P^\circ_{3/2}$. No evidence

for above-threshold ionization, that is, ionization by a larger number of photons than is required energetically (in this case four or more), was observed at the laser powers employed in the present study. Photoelectron angular distributions were recorded by tuning the electron spectrometer to the Xe^+ $^2P^\circ_{3/2}$ photoelectron peak and monitoring the electron signal as the laser polarization axis was rotated using a double Fresnel rhomb. The data were not corrected for the finite acceptance angle ($\sim 3°$) of the electron spectrometer.

III. RESULTS AND DISCUSSION

A. General considerations

Before presenting the experimental data, it is worth reviewing the applicable selection rules in the electric dipole approximation for three-photon transitions from the $^1S_0$ ground state to Rydberg series converging to the Xe^+ $^2P^\circ_{1/2}$ limit. From the selection rule on parity, the orbital angular momentum of the Rydberg electron must be even, and from the selection rule on the total angular momentum $\Delta J \leq 3$. In addition, for three-photon transitions from the $^1S_0$ ground state using linearly polarized light it can be shown that the final-state angular momentum must be odd,[11] and therefore J must equal either 1 or 3. Thus, in $j_c l$ coupling, the only allowed Rydberg series converging to the $^2P^\circ_{1/2}$ limit are $ns'[\frac{1}{2}]^\circ_1$, $nd'[\frac{3}{2}]^\circ_1$, $nd'[\frac{5}{2}]^\circ_3$, and $ng'[\frac{7}{2}]^\circ_3$. For right-hand circularly polarized light $\Delta M = +1$ for each photon,[12] and because the initial state is $^1S_0$, ΔJ must be $+1$ as well. Thus, with circularly polarized light only the $J=3$ series are allowed by three-photon excitation. The two $J=1$ series correspond to those observed in the single-photon absorption and ionization spectra,[3,4] and the $nd'[\frac{5}{2}]^\circ_3$ series has been observed recently by Wang and Knight.[5] To our knowledge, the $ng'[\frac{7}{2}]^\circ_3$ series has not been observed previously.

B. The three-photon ionization spectrum

Figure 1 shows the three-photon ionization spectrum of Xe obtained using linear polarized light between 2791.00 and 2800.75 Å. Two members of three different Rydberg series are clearly discernible; these correspond to the sharp $ns'[\frac{1}{2}]^\circ_1$ and $nd'[\frac{5}{2}]^\circ_3$ series, and the broad $nd'[\frac{3}{2}]^\circ_1$ series. As will be demonstrated below, in this spectral range the intense $ns'[\frac{1}{2}]^\circ_1$ peaks obscure the members of the fourth allowed series, $ng'[\frac{7}{2}]^\circ_3$. The section of the spectrum shown in Fig. 1 is representative of the three-photon spectrum between 2920 Å ($3h\nu = 12.74$ eV) and the $^2P^\circ_{1/2}$ threshold at 2768.26 Å ($3h\nu = 13.436$ eV). In particular, the portion of the three-photon ionization spectrum between 2850 and 2810 Å, in which Feldmann *et al.*[2] observed no resonant structure, displays structure completely analogous to that of Fig. 1, but corresponding to lower principal quantum numbers (for example, the $n = 10, 11, 12$ members of the $ns'[\frac{1}{2}]^\circ_1$ series are observed at 2848.9, 2827.0, and 2812.9 Å, respectively). The explanation for the differences in the two observations is not clear to us at this time. The structure in the present spectrum is quite regular; however, due to the modest resolution of the dye laser (~ 0.3 cm^{-1}) and the high order of the process (six dye-laser photons), the series are only resolved to $n \sim 20$.

The appearance of the three-photon ionization spectrum is not determined solely by the structure at the three-photon energy. The transition amplitude for three-photon excitation is given by[1]

$$M_{fg} = \sum_{a_1, a_2} \frac{\langle f | \mathbf{r}\cdot\boldsymbol{\epsilon} | a_2 \rangle \langle a_2 | \mathbf{r}\cdot\boldsymbol{\epsilon} | a_1 \rangle \langle a_1 | \mathbf{r}\cdot\boldsymbol{\epsilon} | g \rangle}{(E_{a_2} - E_g - 2h\nu)(E_{a_1} - E_g - h\nu)} , \quad (1)$$

where $\boldsymbol{\epsilon}$ is the unit polarization vector of the light, the a_i's represent all possible intermediate levels allowed by selection rules, E_i is the energy of the ith level and $h\nu$ is the photon energy. It is clear from Eq. (1) that, as the laser wavelength is scanned, the three-photon transition amplitude will change as different energy levels contribute more or less to the summation over states at the one- and two-photon energies. In addition, the interference between different terms in the summation must be considered when the amplitude M_{fg} is squared to obtain the transition probability. However, in the present case the one- and two-photon energies are always over 4 and 1 eV away from the nearest allowed levels, respectively.[13] Thus, the important terms in Eq. (1) are not expected to vary dramatically in the wavelength region of the present study. This allows one to rationalize the observed regularity of the Rydberg structure and indicates that interference effects do not dramatically distort the observed spectrum.

The comparison of the experimental spectrum with the theoretical three-photon cross section of Gangopadhyay *et al.* (Fig. 2 of Ref. 1) requires some care. The calculation was not intended to provide precise energy levels, and it is not surprising that there is some discrepancy between the theoretical and experimental resonance positions. No labels other than the total angular momentum J are given to the resonances in the theoretical spectrum. Because the ng partial waves were not included in the theoretical calculations,[1] the $ng'[\frac{7}{2}]^\circ_3$ resonances will not be present in the theoretical cross section. Therefore, the most intense series, labeled $J=3$, must correspond to the $nd'[\frac{5}{2}]^\circ_3$ series. One of the two remaining allowed series should be the extremely broad $nd'[\frac{3}{2}]^\circ_1$ series. This series may be responsible for the broad dips in the theoretical spectrum. Finally, the weak but relatively sharp $J=1$ peaks (at ~ 12.6, 12.9, and 13.08 eV in the theoretical spectrum) should correspond to members of the $ns'[\frac{1}{2}]^\circ_1$ series.

It is seen from Fig. 1 that the most intense features in the experimental spectrum correspond to the $ns'[\frac{1}{2}]^\circ_1$ Rydberg series, while in the theoretical spectrum the $nd'[\frac{5}{2}]^\circ_3$ series is most intense. In fact, the theoretical $J=3$ series shows enhancements of 2 orders of magnitude above the direct ionization continuum. While this could be explained if the linewidths of the $nd'[\frac{5}{2}]^\circ_3$ series members were much narrower than the laser bandwidth, the experimentally determined $nd'[\frac{5}{2}]^\circ_3$ linewidths[5] are actually significantly larger than those of the $ns'[\frac{1}{2}]^\circ_1$ series.

The theoretical three-photon cross section of Gangopadhyay *et al.*[1] also displays considerably more irregulari-

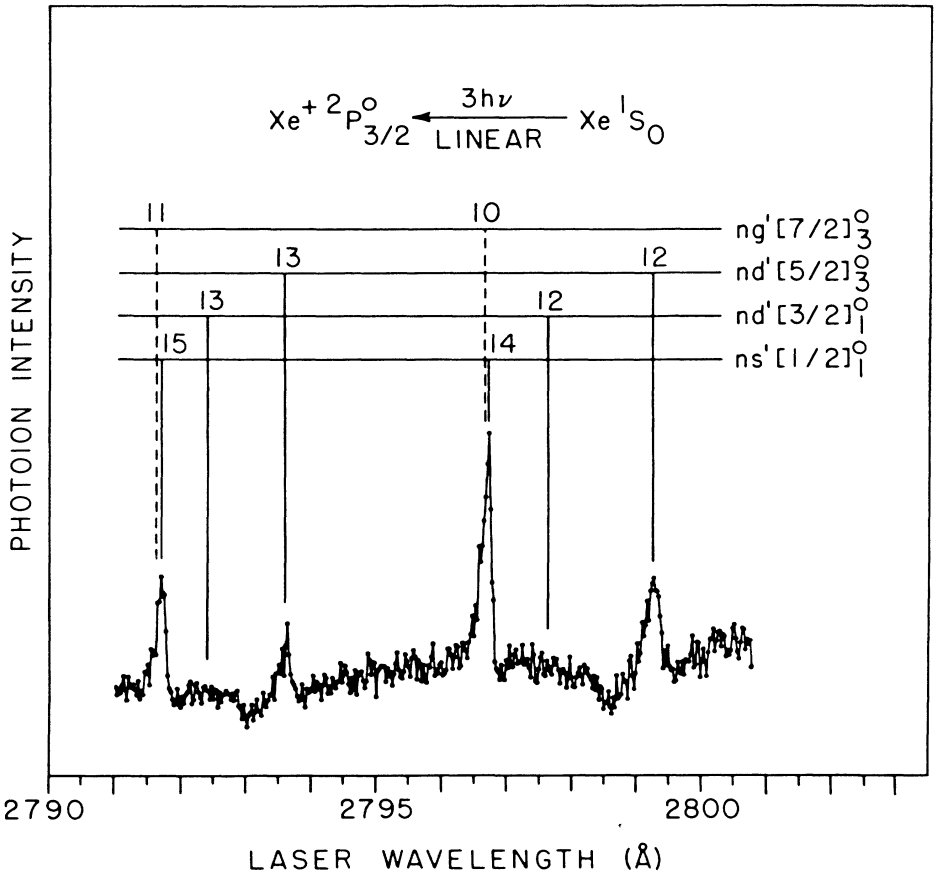

FIG. 1. The three-photon ionization spectrum of atomic Xe between 2800.75 and 2791.00 Å obtained using linearly polarized light.

ty than the experimental spectrum. For example, in the theoretical spectrum the $J=3$ series member at ~ 12.8 eV shows a strong dip on its high-energy side, while the next $J=3$ member at ~ 13.0 eV shows dips to equal magnitude to lower and higher energy, and the member at ~ 13.14 eV shows a sharp dip on its low-energy side and only a smaller dip to higher energy. By contrast, the experimental spectrum displays quite regular structure. Although it is clear from the discussion that discrepancies between the experimental and theoretical three-photon spectra do exist, it should be remembered that the calculations represent the first attempt at understanding multiphoton ionization via autoionizing levels in this complex system.

The linewidths for the $ns'[1]^{\circ}_{1/2}$ and $nd'[\frac{5}{2}]^{\circ}_{3}$ Rydberg series are in reasonable agreement with those of Wang and Knight.[5] Although the statistics make an analysis of the linewidths of the broad $nd'[\frac{3}{2}]^{\circ}_{1}$ series rather difficult, some qualitative remarks can be made on the lineshapes. In particular, the $nd'[\frac{3}{2}]^{\circ}_{1}$ Rydberg states show positive Fano q parameters[14] in three-photon (and one-photon[3,4]) excitation from the ground state, and negative q parameters in single-photon excitation from the $6p'[\frac{3}{2}]^{\circ}_{1}$ level,[5] that is, the peaks are asymmetric in opposite senses for the two different excitation pathways. Such a dependence of the line profile on the excitation pathway has been observed previously and is discussed in detail by Ganz *et al.*[15]

The lower half of Fig. 2 shows the portion of the linearly polarized, three-photon ionization spectrum that contains the $9s'[\frac{1}{2}]^{\circ}_{1}$ resonance. The small peak to higher energy corresponds to the lowest member ($n=5$) of the $ng'[\frac{7}{2}]^{\circ}_{3}$ Rydberg series. This is demonstrated in the upper half of Fig. 2 by using circularly polarized light, which eliminates the $9s'[\frac{1}{2}]^{\circ}_{1}$ peak through the $\Delta J=3$ selection rule. The two spectra are plotted to show the approximate relative intensities for the two different laser polarizations. Higher members of the $ng'[\frac{7}{2}]^{\circ}_{3}$ series, which are overlapped by the more intense $ns'[\frac{1}{2}]^{\circ}_{1}$ series, can be uncovered by recording the entire spectrum using circularly polarized light. As expected for a high-l, nonpenetrating Rydberg series, the quantum defect of the ng' series is extremely small, having a value $\mu \sim 0.01$. Unfortunately, the wavelength resolution is low and the wavelength calibration too poor for the $ng'[\frac{7}{2}]^{\circ}_{3}$ series to provide a more accurate determination of the $^2P^{\circ}_{1/2}$ limit than is already available.[3] Similarly, it is also not feasible to use the present determination of the $ng'[\frac{7}{2}]^{\circ}_{3}$ series to provide accurate information on the polarizability and quadrupole moment of the $^2P^{\circ}_{1/2}$ ion core.[16]

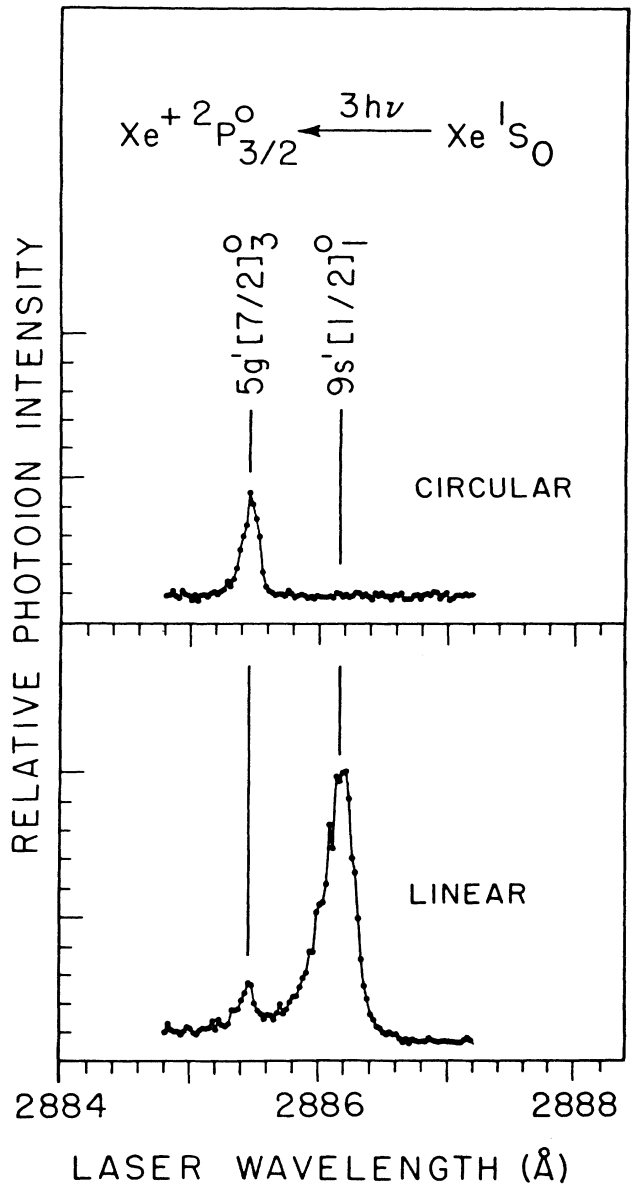

FIG. 2. The three-photon ionization spectra of atomic Xe around the $(^2P^\circ_{1/2})9s'[\frac{1}{2}]^\circ_1$ autoionizing resonance obtained using linearly polarized light (lower half) and circularly polarized light (upper half). The spectra are plotted so that the relative peak heights in the two spectra reflect the approximate relative intensities of the peaks.

C. Photoelectron angular distributions

The photoelectron angular distributions for three-photon ionization of atomic Xe via the $9s'[\frac{1}{2}]^\circ_1$ and $7d'[\frac{5}{2}]^\circ_3$ autoionizing levels are shown in Fig. 3. The photoelectron angular distributions for three-photon ionization from the $^1S_0$ ground state using linearly polarized light must have the functional form[17,18]

$$I(\theta) \propto \sum_{i=0}^{3} A_i \cos^{2i}\theta \ . \tag{2}$$

Here, I is the photoelectron intensity, θ is the angle between the polarization axis of the light and the detector, and the A_i are asymmetry coefficients. Figure 3 also shows the best fits of the experimental data to the functional form of Eq. (2) as well as best fits to the form

$$I(\theta) \propto A_0 + A_2 \cos^2\theta \ . \tag{3}$$

The latter is appropriate for single-photon ionization of an unaligned sample or for ionization when the final angular momentum is restricted to $J=1$. Although the $9s'[\frac{1}{2}]^\circ_1$ autoionizing level fulfills the latter condition, it is clear that neither of the angular distributions in Fig. 3 can be satisfactorily fit with the functional form of Eq. (3). The nonresonant ionization background at the wavelength of the $9s'[\frac{1}{2}]^\circ_1$ autoionizing resonance is substantial, and the higher-order terms necessary to fit the angular distribution at this wavelength must arise from direct three-photon ionization into the $J=3$ continua.

Gangopadhyay *et al.*[1] have calculated photoelectron angular distributions following three-photon ionization for the resonances at 13.068 and 13.134 eV, which correspond to the $10s'[\frac{1}{2}]^\circ_1$ and $9d'[\frac{5}{2}]^\circ_3$ resonances, respectively. The $9s'[\frac{1}{2}]^\circ_1$ resonance was chosen in the experimental study because it is better resolved from the corresponding $ng'[\frac{7}{2}]^\circ_3$ level. In addition, the signal levels for the $9s'[\frac{1}{2}]^\circ_1$ and $7d'[\frac{5}{2}]^\circ_3$ resonances are considerably higher than for the corresponding $10s'[\frac{1}{2}]^\circ_1$ and $9d'[\frac{5}{2}]^\circ_3$ resonances. The differences in principal quantum numbers notwithstanding, a comparison of the angular distributions from states in the same Rydberg series is certainly appropriate.

Both of the theoretical angular distributions[1] show minima at $\theta=0°$ and $\pm 90°$ and maxima at $\sim \pm 45°$. The minima are most pronounced in the $J=3$ distribution, in which the intensities at both 0 and $\pm 90°$ are nearly zero; the $\pm 90°$ minima in the $J=1$ distribution are more pronounced than that at $\theta=0°$, but none of the minima are as deep as those in the $J=3$ distribution. In contrast, the experimental angular distributions are somewhat less dramatic in the degree of variations and show qualitative departures from theory. The $9s'[\frac{1}{2}]^\circ_1$ distribution shows a minimum at $\theta=0°$, with maxima at $\sim \pm 45°$ but with very little falloff between $\pm 45°$ and $\pm 90°$. The $7d'[\frac{5}{2}]^\circ_3$ distribution displays a broad, flat maximum between $\pm 20°$ with minima at $\pm 60°$ and secondary maxima at $\pm 90°$.

Due to the large contribution of the $J=3$ continua to the angular distribution recorded for the $9s'[\frac{1}{2}]^\circ_1$ resonance, it is difficult to compare this distribution with those obtained using single-photon ionization,[7–9] in which only the $J=1$ continua are probed. However, it is worth noting that the experimental single-photon angular distributions for the peaks of the $ns'[\frac{1}{2}]^\circ_1$ autoionizing resonances are more isotropic than those for the background continua.[8,9] In addition, the single-photon angular distributions are predicted to show sharp resonant structure as the excitation wavelength is scanned across the autoionizing resonances.[7] More detailed studies of the angular distributions for three-photon ionization are expected to reveal similar resonant structure.

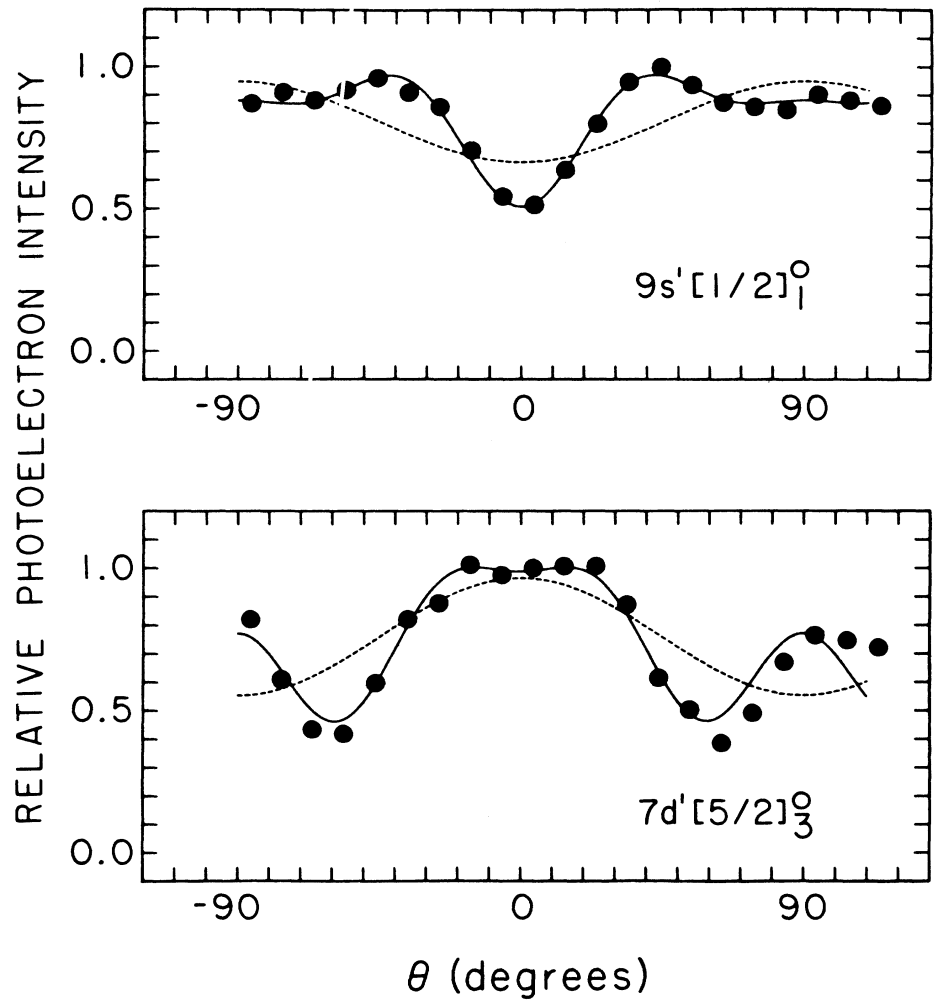

FIG. 3. Photoelectron angular distributions for three-photon ionization of atomic Xe via the $(^2P^\circ_{1/2})9s'[\frac{1}{2}]^\circ_1$ (upper frame) and the $(^2P^\circ_{1/2})7d'[\frac{5}{2}]^\circ_3$ (lower frame) autoionizing resonances. Data points are shown as solid circles. The dashed and solid lines are best fits to the functional forms $A_0+A_2\cos^2(\theta)$ and $A_0+A_2\cos^2(\theta)+A_4\cos^4(\theta)+A_6\cos^6(\theta)$, respectively.

IV. CONCLUSIONS

The three-photon ionization spectra of atomic Xe between the Xe^+ $^2P^\circ_{3/2}$ and $^2P^\circ_{1/2}$ ionization thresholds reveal four Rydberg series of autoionizing resonances, corresponding to the $ns'[\frac{1}{2}]^\circ_1$, $nd'[\frac{3}{2}]^\circ_1$, $nd'[\frac{5}{2}]^\circ_3$, and $ng'[\frac{7}{2}]^\circ_3$ series. These observations are in contrast to the results of Feldmann *et al.*,[2] who observed no resonance structure in an overlapping spectral region. The results are in qualitative agreement with the theoretical three-photon cross section of Gangopadhyay *et al.*,[1] which predicts resonance structure due to Rydberg series converging to the $^2P^\circ_{1/2}$ limit. However, quantitative agreement between experiment and theory is rather poor, indicating that substantial improvements in the theoretical calculations are called for. In particular, the inclusion of g ($l=4$) partial waves is clearly essential. Photoelectron angular distributions are reported for the $9s'[\frac{1}{2}]^\circ_1$ and $7d'[\frac{5}{2}]^\circ_3$ autoionizing resonances, and both exhibit very anisotropic behavior. More extensive angular distribution studies of three-photon ionization of Xe in this wavelength region are desirable in order to map out the variation of angular distributions within resonant profiles, analogous to those observed in single-photon ionization studies.[7–9]

ACKNOWLEDGMENTS

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