Experimental Verification of Quadrupole-Dipole Interference in Spin-Resolved Photoionization

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We have measured the spin polarization of Xe $(4p)^{-1}$ photoelectrons after ionization with circularly polarized light at photon energies close to the ionization threshold where a resonant enhancement of quadrupole transitions has recently been predicted. At a reaction angle of 90° a nonvanishing longitudinal spin polarization component of about 4% clearly indicates a quadrupole contribution to the photoexcitation. This is the first experimental evidence for the influence of nondipole transitions on the photoionization process at excitation energies much below 1 keV in an observable other than the intensity angular distribution.

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At photon energies below 1 keV the electric-dipole approximation is usually adopted for the description of atomic photoionization processes [1]. Since in this case the corresponding wavelength is much larger than the Bohr radius, higher-order multipoles are assumed to be negligible for the transition from bound states into the continuum. On the other hand, the improvement of available sources for ionizing radiation along with the continuous sophistication of detection techniques allows—and indeed requires—an ever more refined characterization of the photoionization process. Recent studies of the forward-backward asymmetry in the angular intensity distribution of photoelectrons have revealed evidence of significant nondipole effects at photon energies of only a few hundred eV [2–6] and demonstrated that phenomena, previously considered too subtle to be relevant, have now to be taken into account. Apart from the differential cross section, a comprehensive description of the ionization process also has to consider the three components of the spin polarization vector of the photoelectron. In selected cases measurement of this additional information may even serve for a quantum mechanically complete characterization of the process [7]. Recent theoretical works [8–11] considered the influence of nondipole contributions to the photoelectron spin polarization. While in general such higher-order terms were found to be small, Cherepkov and Semenov [10] predicted a pronounced electric-dipole electric-quadrupole interference for photoionization from the xenon $4p$ shell at photon energies as low as 170 eV. The origin of this extraordinarily strong nondipolar spin polarization of as much as 15% [12] was attributed to a resonant phenomenon [11] closely resembling the well-known shape resonances in the cross section, e.g., for Xe $4d$ photoionization around 100 eV photon energy. According to these authors, in close similarity with the dipole case the transition probability can be enhanced by a double-well shape of the effective potential appearing in near-threshold transitions to an outgoing εf wave.

In this Letter, we report on the experimental verification of this theoretical prediction. Because of the loss of intensity of about 3 orders of magnitude connected with spin polarization analysis, the small cross section of the studied transition and the superposition of faint nondipole with generally stronger dipole contributions, an experimental implementation represents a particular challenge. In the following we will therefore prelude the presentation of results with a discussion of the experimental preconditions, the measurement strategy, as well as the calibrating and referencing procedures that were found to be necessary in order to correct for spectral background and apparative asymmetries.

Data were acquired during two independent beam times at the BESSY storage ring, Berlin, in May and October 2001 with the same apparatus but using different beam lines and different measurement procedures as described below. The experimental setup, described in detail in [13], is sketched in Fig. 1 together with the coordinate frame used for definition of the spin polarization vector. Circularly polarized ionizing radiation with a degree of circular polarization close to 1 was provided by the

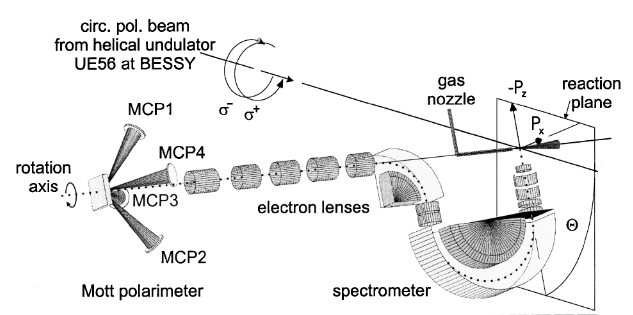

FIG. 1. Experimental setup. At $\Theta = 90°$ two orthogonal spin polarization components in the reaction plane are measured simultaneously. In this case, $P_x = P_{\rm transf}$ and $P_z = P_{\rm long}$ as referred to in the text.

helical undulators UE56/2 (May) and UE56/1 (October), respectively. An electrostatic electron energy analyzer of the simulated spherical field type accepts emitted photoelectrons at a selectable angle Θ with respect to the light propagation direction. Guided by an electrostatic lens system, the photoelectrons are subsequently spin analyzed with respect to two orthogonal components P_x and P_z in a spherical retarding Mott polarimeter. Disentanglement of pure dipole contributions and dipole-quadrupole interference terms was achieved by choosing a reaction angle Θ perpendicular to the photon beam where the two simultaneously measured spin polarization components [14] become the transferred spin polarization $P_{\rm transf} = P_x(\Theta = 90°)$ and the longitudinal spin polarization $P_{\rm long} = P_z(\Theta = 90°)$, respectively.

For this case the expressions given in [10] reduce to

$$P_{\rm transf} = \pm\frac{A + \alpha/2}{1 + \beta/4}, \qquad (1)$$

connecting the transferred polarization with the dynamical dipole parameters A, α, and β describing the integral spin polarization, its angular distribution, and the asymmetry in the intensity distribution, respectively [15], and

$$P_{\rm long} = \pm\frac{1/2(\sqrt{6}\,B_{211} - 3B_{231})}{1 + \beta/4}, \qquad (2)$$

containing parameters B_{211} and B_{231} expressing the interference between electric-dipole and electric-quadrupole matrix elements. The 90° geometry is therefore particularly sensitive to nondipole effects as they will show up only in the longitudinal component $P_{\rm long}$ while direct dipole contributions are completely suppressed. A finite acceptance angle (approximately 2° half angle) of the spectrometer will only slightly reduce the measured spin polarization for this component because it is symmetrical with respect to $\Theta = 90°$. Note that for this angle no nondipole correction for the angular intensity distribution [denominator of (1) and (2)] has to be taken into account. Because $P_{\rm transf}$ as well as $P_{\rm long}$ change sign with the light helicity, a periodic reversal of the photon spin was used for efficient correction of apparative asymmetries, e.g., different sensitivity of the four electron detectors. However, this procedure does not correct artificial spin polarization asymmetries introduced by a rotation of the spin polarization vector in space. Even very small residual magnetic fields on the μT level can lead to a significant projection of the strong transferred (P_x)—to the longitudinal (P_z)—component during the travel of photoelectrons from the ionization region to the spin detector.

In addition to μ-metal shielding we therefore carefully compensated magnetic fields with Helmholtz coils by referring to the Xe $-$ $4d_{3/2}$ photoline for which an extremely small nondipole effect is expected [11]. To this end for each investigated kinetic energy of the Xe $-$ $4p^{-1}$ photoelectrons the photon energy was first tuned so as to obtain the same kinetic energy for the Xe $-$ $(4d_{3/2})^{-1}$ electrons [Fig. 2(c)]. The current through the Helmholtz coils was then adjusted such that the asymmetry for the P_z component vanished. The electron intensity spectra for the Xe $-$ $4p$ threshold region in Fig. 2 show that due to the small $4p$ cross section a pronounced spectral background from NOO Auger lines, multiple ionization, and cascade processes has to be taken into account. Only for distinct photon energies is the $4p$ line sufficiently separated from other resonances.

For these points two different approaches were used for subtraction of spectral background: in May 2001 we acquired spin polarization data on top of the resonance and off-resonance at 1–2 eV higher kinetic energies; in October 2001 the photon energy was instead lowered by 2 eV, thereby providing access to the spectral background at constant kinetic energy [Figs. 2(a) and 2(b)]. The measured background spin polarization indicates a vanishing component $P_{\rm long}$ in accordance with the expectation that Auger and higher-order processes should exhibit extremely small nondipole effects. The background-corrected experi-

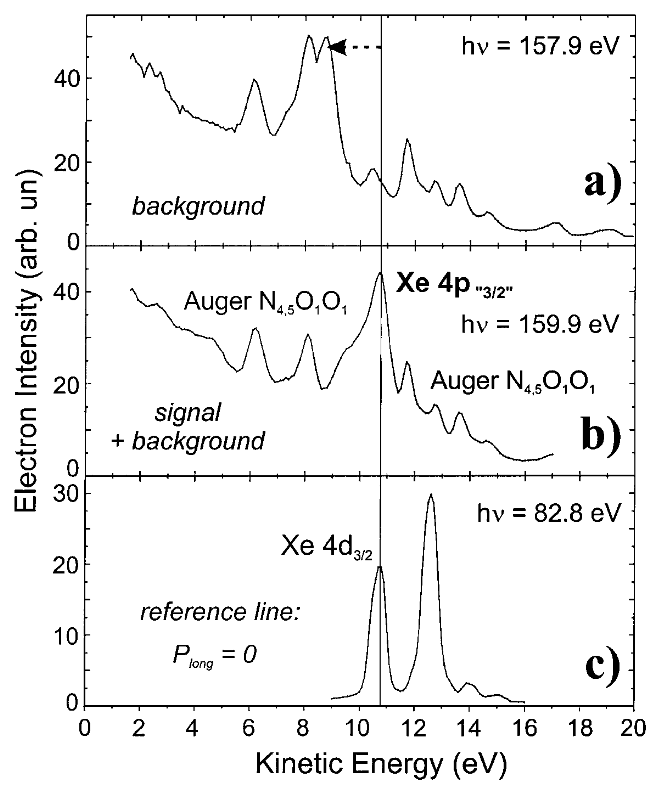

FIG. 2. Intensity spectra in the Xe $-$ $4p$ threshold region. Subtraction of spectral background is accomplished by shifting the Xe $4p_{"3/2"}$ photoline (b) to lower kinetic energies (a) while keeping the spectrometer bandpass fixed. (c) The Xe $-$ $4d_{3/2}$ photoline is shifted to the same energetic position for control of residual magnetic fields (see text).

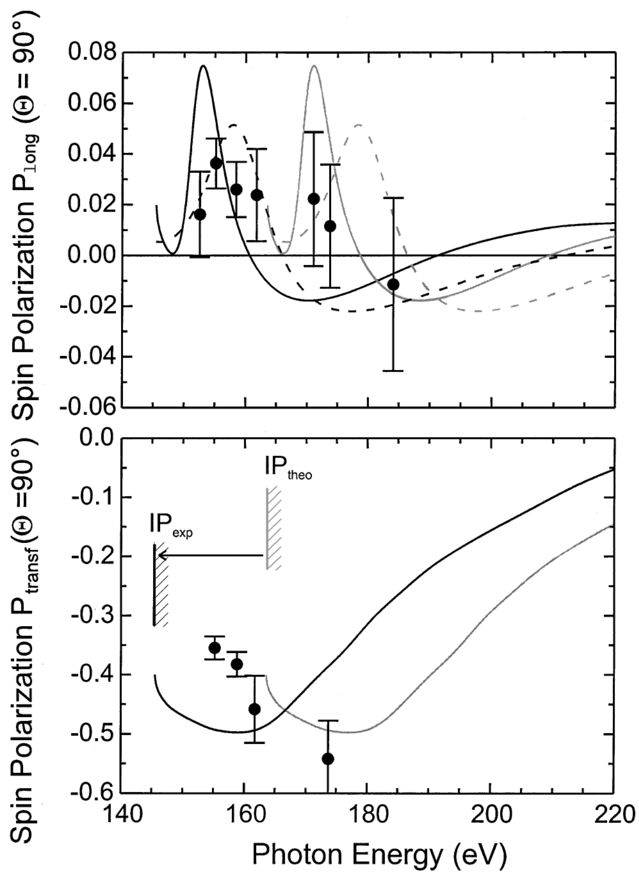

FIG. 3. Spin polarization of Xe $(4p_{“3/2”})^{-1}$ photoelectrons. Upper panel: longitudinal component sensitive to quadrupole contribution; lower panel: transferred component. Gray solid curves: RPAE [10]; gray dashed curve: adopted from IPA [16]; black curves are shifted according to the difference between theoretical and experimental ionization thresholds.

mental results from the two campaigns were found to coincide well within the experimental uncertainty; the data for P_{long} presented in Fig. 3 were therefore obtained from a weighted average for such points where the kinetic energy differed by less than 0.8 eV. At photon energies some 10 eV above the ionization threshold the measured data clearly indicate a significant nondipole contribution in this spin polarization component. The predicted resonant character of the phenomenon is supported as revealed by comparison with theoretical curves adopted from a RPAE (random phase approximation with exchange) [10] and an IPA (independent particle approximation) [16] calculation. Since the original curves rely on theoretical values for the ionization potentials, in Fig. 3 also curves shifted according to the experimental ionization threshold, $IP_{exp} = 145.5$ eV, are shown.

The apparent overestimation of the magnitude of the effect by the theoretical models deserves some discussion: It is well established that the $4p$ photoionization in xenon is strongly affected by electron correlations [17]. Interaction with double excitations of the $4d$ subshell causes the $(4p_{“1/2”})^{-1}$ peak to completely disappear and the $(4p_{“3/2”})^{-1}$ peak to be asymmetrically smeared out [18]. An assignment of the studied photoline to $(4p_{“3/2”})^{-1}$ is supported by our measurement of the transferred spin polarization component P_{transf}, presented in Fig. 3, with values being compatible in sign and magnitude only with a $j = 3/2$ character. The theoretical consideration of these correlations represents a particular challenge and is—to our knowledge—not included in the current predictions [10,16]. However, the theoretical curves in Fig. 3 are based on calculations for a $(4p_{1/2})^{-1}$ ($j = 1/2$) photoionization process [19]. Following the general statement that—within a nonrelativistic approximation—any spin polarization should vanish if one integrates over both fine structure components in the final state, the polarization of the desired $j = 3/2$ component can be deduced from the $j = 1/2$ one by weighting with the relative electron intensities. Suppression of the $(4p_{1/2})^{-1}$ photoline in the spectra prohibits a determination of the branching ratio; in Fig. 3 we therefore used the statistical weight of the magnetic substates $I_{3/2}/I_{1/2} = 2$ and correspondingly multiplied the original theoretical spin polarization curves for $(4p_{1/2})^{-1}$ by -0.5 in order to obtain theoretical curves for the $(4p_{3/2})^{-1}$ case.

Still, the observed discrepancy in the magnitude of P_{long} cannot be explained by assuming a larger branching ratio because the corresponding value for P_{transf} of the $(4p_{1/2})^{-1}$ ionization process would then exceed unity [already P_{transf} ($j = 3/2$) is measured to be -0.5]. While the measured magnitude of the nondipole effect is closer to the IPA prediction, no conclusive statement in favor of one theoretical approach can be made with respect to the resonance position or width. In any case, for P_{long} the theoretical curves become more applicable when shifted according to the experimental ionization threshold (black curves in Fig. 3).

In conclusion, by measurement of the longitudinal spin polarization component of the Xe $(4p_{“3/2”})^{-1}$ photoline we were able to identify a significant contribution due to electric-dipole-quadrupole interference terms. The result supports the theoretically expected resonant behavior near the ionization threshold with a smaller magnitude than predicted. This first experimental verification of quadrupole contributions to observables other than the intensity angular distribution underlines that higher-order multipoles must be considered for a comprehensive description of photoionization when resonant phenomena govern the process. Also for the magnetic dichroism a very recent calculation [20] predicts detectable nondipole contributions in the Cooper minimum of sodium atoms. Since shape resonances and Cooper minima are found in a number of atomic systems, further experimental corroboration of nondipole effects in various observables of photoionization is to be expected.

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