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Photoelectron angular distributions beyond the dipole approximation

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Abstract

We report the measurement of non-dipolar asymmetry parameters for the angular distributions of argon 1s, krypton 2s, and krypton 2p photoemission within 2-3 keV above their respective thresholds. Pronounced asymmetries with respect to the direction of photon propagation are present even at low electron kinetic energies. The energy dependence of the asymmetry is Z- and subshell-specific and causes the direction of preferred electron emission to change sign at least once in each of the cases studied. Towards higher energies the asymmetry increases and the photoelectron emission pattern is forward-skewed for all three cases. The measured asymmetry parameters are in good agreement with recent predictions from non-relativistic calculations which include the interference between electric-dipole and electric-quadrupole transition amplitudes in the photoabsorption process.

I. Introduction

The interaction of low-energy to soft x-ray photons with matter has largely been studied within the framework of the dipole approximation. This approximation is used when the photon's wavelength can be regarded large in comparison to the atomic dimensions. Consequently, the photon momentum, being proportional to inverse of the wavelength, is considered small and the dependence on the photon momentum is neglected. The photoelectron angular distribution in dipole approximation therefore remains unchanged if the direction of photon propagation is reversed. An extensive body of both theoretical and experimental work is concerned with the physical information that can be extracted from angular distributions in cases where the dipole approximation is valid (cf. the reviews [1, 2]).

With increasing energy the forward-backward symmetry in the angular distributions disappears. The first measurements of photoelectron angular distributions in the 1920s, using high-energy x-rays, displayed pronounced forward peaking of the distributions [3, 4]. It was shown that this could be related to the momentum of the absorbed radiation, however not in such a way, as one might assume, that the emitted electrons are simply kicked forward by the photon momentum [5]. The dependence on the photon momentum is retained when the photon wave's exponential is approximated by the first two terms, $e^{ik \cdot r} \sim 1 + k \cdot r$, rather than only

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by the unit term. This expansion of the exponential has a close correspondence to the multipole decomposition of the photon-atom interaction: the unit term leads to the long-wavelength limit of electric-dipole (E1) interaction, and the term linear in kr is related to magnetic-dipole (M1) and electric-quadrupole (E2) interactions. It is those additional contributions which are responsible for the observed forward-backward asymmetry in the angular distributions. In the early calculations, based on a hydrogenic model, this "retardation" effect was found to be proportional to v/c , in agreement with the experimental observations (cf. [6]).

Since the early papers relatively few theoretical and even fewer experimental studies have been reported on this subject. On the theoretical side, both relativistic and non-relativistic calculations were performed for a variety of cases using a more refined model [7, 8]. On the experimental side, however, progress in this field had been hampered by the restriction to the limited spectrum and intensity obtained from the x-ray sources used (cf. [9]; for a listing of experiments before 1978, see [10]). With the availability of intense and tunable x-ray radiation at high-energy synchrotron radiation facilities, renewed interest for the topic has emerged. Recently, theoretical predictions of non-dipolar angular distributions have been reported which differ significantly from the simpler retardation result, particularly for low photoelectron energies [11, 12, 13]. Stimulated by these findings, we performed an experiment to measure the angular distributions of photoelectrons from the Ar-*K* and Kr-*L* shells within 2-3 keV of the respective thresholds. In this brief report we present a summary of the experiment and the results. For details on the experimental procedure and the data treatment the reader may refer to the recent publications [14, 15]. Similar results for the Ne-*L* shell have been obtained in a recent experiment [16].

II. Photoelectron angular distributions

The photoelectron angular distribution, described by the differential cross section $d\sigma/d\Omega$, is proportional to the square of the matrix element for photon-induced transitions between the initial state ψ_i and the final state ψ_f

$$\frac{d\sigma}{d\Omega} = f |\langle \psi_f | \exp(i\mathbf{k} \cdot \mathbf{r}) \hat{\epsilon} \cdot \mathbf{p} | \psi_i \rangle|^2. \quad (1)$$

Here, $\hat{\epsilon}$ is the polarization vector of the photon, $\hbar\mathbf{k}$ the photon momentum, and \mathbf{r} and \mathbf{p} are the position and momentum operators of the electron. The quantity f represents the combined cofactors in this expression. For simplicity, the matrix element in the following will be abbreviated by the symbol $\langle \mathcal{O} \rangle$. Employing a decomposition of the interaction with the photon in terms of electric and magnetic multipoles (cf. [17]), the transition matrix element is replaced by a sum of individual multipole transition matrix elements, $\langle \mathcal{O} \rangle = \sum_{\pi,j} \langle \pi j \rangle$. Here, the multipole transition elements are characterized by their parity π and order j . In terms of the multipole decomposition, the differential cross section breaks down into a sum of individual multipole interactions $|\langle \pi j \rangle|^2$ and cross terms of combinations $\langle \pi j \rangle \langle \pi' j' \rangle^*$ where $\pi' \neq \pi$ and/or $j' \neq j$. As a result of the angular properties of the multipole components, this sum, e.g. for unpolarized radiation [18], transforms according to

$$\frac{d\sigma}{d\Omega} = f \sum_{\pi,\pi',j,j'} \langle \pi j \rangle \langle \pi' j' \rangle^* = \frac{\sigma}{4\pi} \sum_L B_L P_L(\cos \Theta). \quad (2)$$

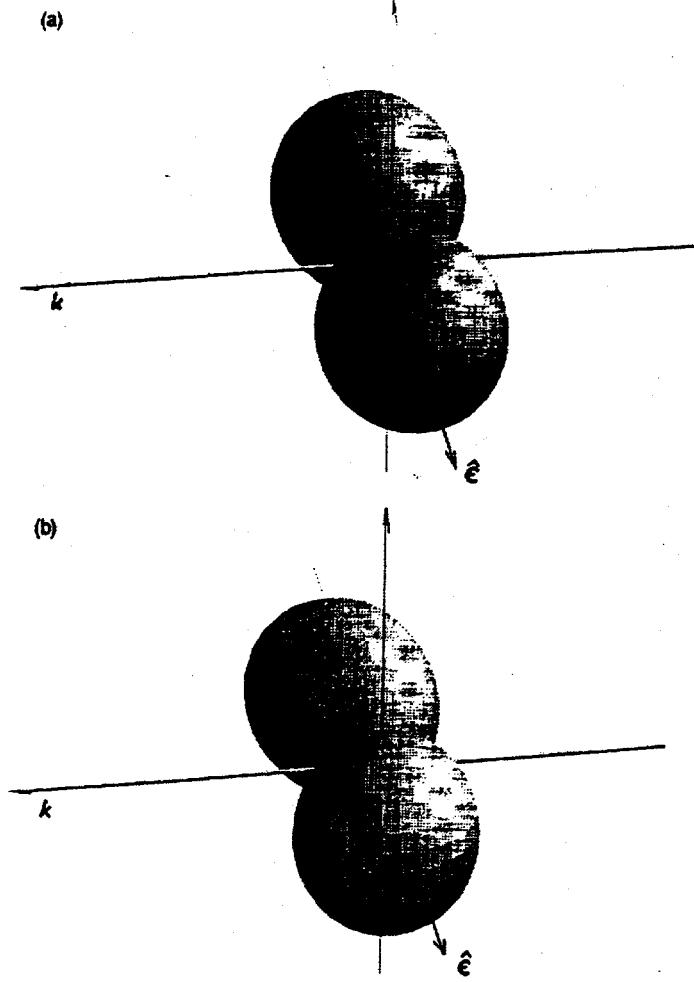


Figure 1: The angular distribution of photoelectrons from an s subshell. (a) dipole approximation (pure E1 interaction); (b) including the E1-E2 non-dipolar contribution.

In this expression the angle Θ represents the emission angle of the photoelectron with respect to the photon beam. The angular integrations in a term $\langle \pi j \rangle \langle \pi' j' \rangle^*$ contribute Legendre Polynomials P_L of orders $|j - j'| \leq L \leq j + j'$, and these orders L are exclusively *even* for $\pi' = \pi$ and exclusively *odd* for $\pi' \neq \pi$. In the same manner, the corresponding radial integrations contribute to the respective coefficients B_L [11]. The B_L are normalized such that $B_0 = 1$ and $\sigma = f \sum_{\pi,j} |\langle \pi j \rangle|^2$.

Eq.(2) gives a convenient way of parameterizing the differential cross section with a set of angular distribution parameters B_L . The sum in L extends no further than to $2j$, with j being the highest contributing multipole order. In general the angular distribution is well described by a small number of terms, because the multipole amplitudes decrease rapidly with increasing order. The M1 and E2 interactions are smaller than the E1 interaction by a factor of $Z\alpha$, and higher multipoles are further suppressed by higher powers of $Z\alpha$. The M1

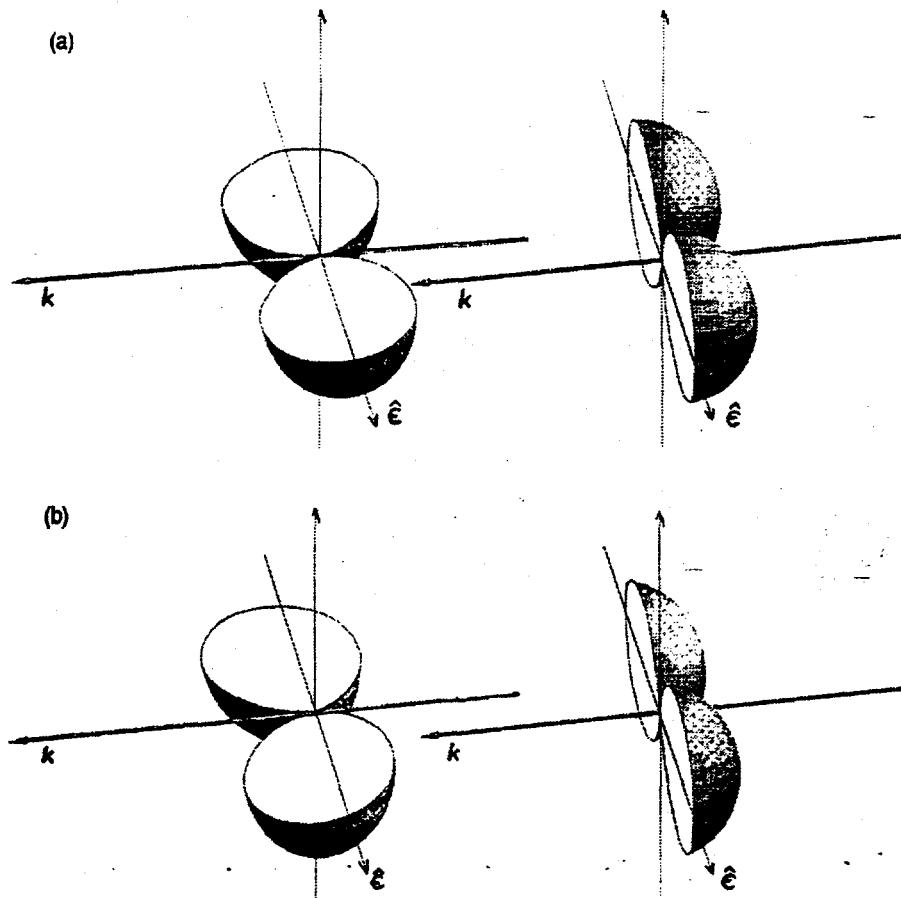


Figure 2: Vertical and horizontal cuts through the angular distributions depicted in Fig.1. (a) dipole approximation (pure E1 interaction); (b) including the E1-E2 non-dipolar contribution.

interaction acts only on the angular and spin part, but not on the spatial part of the electron's wavefunction, and thus, depending on the theoretical model, either vanishes or contributes very little. Consequently, the next-higher level of approximation to the dipole approximation includes the even-parity electric-quadrupole interaction up to terms of order $Z\alpha$ [7, 12, 13]. The parameterization of the angular distribution extends up to $L = 3$ and involves three angular distribution parameters B_1, B_2, B_3 .

The angular distributions for pure E1 interaction and for E1 with additional E1-E2 interference are juxtaposed in Fig.1 (a) and (b) for the case of ionization in an s subshell with linearly polarized x-rays. It is clear that the E1 interaction is still the dominant feature in the angular distributions depicted in (b), which represents the strongest non-dipolar asymmetry that has been observed in our experiment. The degree of the asymmetry can be better appreciated in the cuts through the distribution shown in Fig.2. On the left, parts (a) and (b) each contain the cuts in the plane spanned by \mathbf{k} and $\hat{\epsilon}$, and on the right the cuts in the plane perpendicular to \mathbf{k} are shown. The non-dipolar angular distribution is strongly asymmetric in the plane of

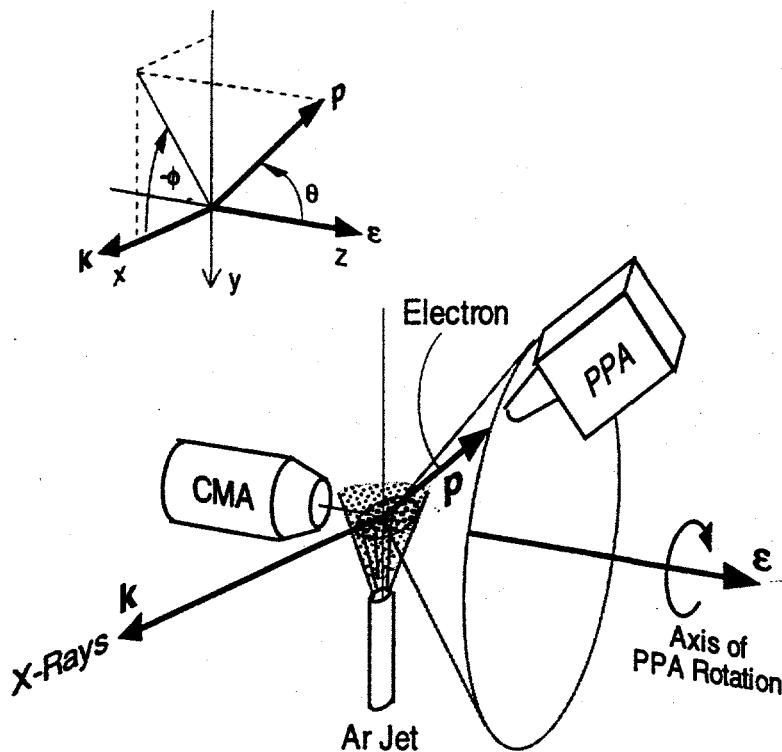


Figure 3: The set-up of the experiment and the coordinate frame used in the representation of the angular distribution, Eq.(3). See text.

the photon beam. In the plane perpendicular to the photon beam there is no difference between the dipolar and the non-dipolar angular distributions.

III. Experiment

The idea pursued in the experiment was to probe the angular distribution by rotating an electron spectrometer on a circle around the polarization direction $\hat{\epsilon}$. Pure dipolar interaction results in an isotropic signal on this circle, and the non-dipole effect causes an asymmetry between the forward and backward directed semicircles.

The experiment was performed using the monochromatized and highly linearly polarized x-ray beam from beamline X-24A at the National Synchrotron Light Source and an apparatus designed for angle-resolved electron spectrometry. A schematic of the experimental set-up is shown in Fig.3. The interaction region is defined by the intersection of the collimated x-ray beam and the target gas emanating from an effusive jet. A parallel-plate analyzer (PPA) is mounted such that it can be rotated on a cone with opening angle $\theta = 54.7^\circ$. A stationary cylindrical mirror analyzer (CMA) and a downstream $p-i-n$ diode (not shown in the Fig.3) were used to monitor the target density and the photon flux during the experiment. The photoelectron intensity was recorded with the PPA-angle setting varied in 15° increments over

a full 360° range. The dwell time per angle was 60–120 s, and several such angular scans were added up for each x-ray energy.

The angular distribution measured with this geometry is more conveniently represented in the system of coordinates shown in the inset of Fig.3. In conjunction with this coordinate frame we employ an alternative parameterization to Eq.(2) and adopt the terminology for linear polarization used in Ref. [13]:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left(1 + \beta P_2(\cos \theta) + (\gamma \cos^2 \theta + \delta) \sin \theta \cos \phi \right). \quad (3)$$

The parameters β , γ , δ and the ones used in the introduction, B_1 , B_2 , B_3 , are connected by the relations

$$\beta = -2B_2; \quad \gamma = -5B_3; \quad \delta = B_1 + B_3. \quad (4)$$

The parameter β describes the angular anisotropy of the E1 interaction, and γ and δ govern the non-dipolar part of the angular distribution. Positive/negative values of γ and δ signify a forward/backward-directed angular distribution.

The angle θ of the experimental set-up was chosen to be the so-called “magic angle”, $\theta_m = 54.7^\circ$, which is the zero of $P_2(\cos \theta)$, to remove the influence of the dipolar anisotropy parameter β on the measurement. The photoelectron intensity as a function of the azimuthal angle ϕ can then be expressed as

$$I(\theta_m, \phi) = I_0 \left(1 + \sqrt{\frac{2}{27}}(\gamma + 3\delta) \cos \phi \right). \quad (5)$$

It is clear that one can only determine a combined quantity $\gamma + 3\delta$ with this experimental geometry.

There are two instrumental effects which cause the actually observed angular distribution to deviate from the form given Eq.(5). In this brief report these will only be summarized; for a detailed description of these effects and their incorporation in the data evaluation procedure, see Ref. [15].

The first effect pertains to the inherent anisotropy of the set-up depicted in Fig.3. It is caused by the oblong source volume formed by the ~ 1 mm-diameter x-ray beam traversing the target gas. In order to assess this anisotropy, we measured the angular response of a variety of Auger electrons with different kinetic energies: Ar-*LMM*, N-*KVV* from N₂, O-*KVV* from CO₂, Xe-*MNN*, Ne-*KLL*, Kr-*LMM*, Ar-*KLL*. Within the description of the two-step model, Auger electrons emitted in *KLL* transitions are emitted isotropically [19], and any non-dipole terms related to the mixing of different parities, e.g. $\langle E1 \rangle \langle E2 \rangle$, vanish, rendering the remaining non-dipole contributions negligible [20]. As a result, all of the measured Auger transitions should emit isotropically on the cone with opening angle equal to the magic angle. The recorded intensity variation of Auger electrons therefore represents a good measure of the instrumental anisotropy.

The second effect to cause a deviation from Eq.(5) is caused by non-complete linear polarization of the x-rays (here, $P_{\perp} \approx 0.95$) and by any misalignment of the experiment's rotation axis with respect to the polarization vector of the x-rays [15, 21]. Even a small tilt λ between the rotation axis and the polarization vector \hat{e} (here, $\lambda \approx 1^\circ$) creates an asymmetry between

the upper ($0^\circ < \phi \leq 180^\circ$) and lower ($180^\circ < \phi \leq 360^\circ$) semicircles. The dependence on λ can be essentially removed by averaging data points at azimuthal angles ϕ and $-\phi$. This procedure gives the same result as would have been obtained for a measurement with perfect alignment of the rotation axis, but with a slightly reduced degree of linear polarization, $P' = P_\perp \cos 2\lambda$. The experimental angular distribution for partially linearly polarized x-rays, after correcting for the instrumental anisotropy and averaging between the upper and lower semicircles, has the form

$$I_{P'}^{\text{av}}(\theta_m, \phi) = I_0 \left[1 + \sqrt{\frac{2}{27}}(\gamma + 3\delta) \cos \phi - \frac{(1 - P')\beta}{4} \cos 2\phi - \frac{(1 - P')\gamma}{3\sqrt{6}} \cos \phi \cos 2\phi \right]. \quad (6)$$

When using Eq.(6) as fitting function, a reasonable choice of four fitting parameters is I_0 , $[\gamma + 3\delta]$, $[(1 - P')\beta]$, $[(1 - P')\gamma]$, since their associated angular terms are distinctly different. In particular, the polarization-dependent terms in Eq.(6) vanish at the angles $\phi = 45^\circ, 135^\circ, 225^\circ, 315^\circ$. Just as in the case of complete linear polarization, a combined non-dipole quantity $\gamma + 3\delta$ is readily obtained from such a fit without knowing the quantities P' or β . Furthermore, if the dipolar anisotropy parameter β is known, a fairly accurate determination of P' can be made. Conversely, however, the higher the degree of linear polarization and the smaller the tilt angle λ (i.e. the closer the quantity P' approaches unity), the less accurate become any evaluations of either β or γ from the fit parameters $[(1 - P')\beta]$ and $[(1 - P')\gamma]$, respectively.

For illustrative examples of raw data sets obtained in the angular scans, of the correction for the instrumental anisotropies, and of the corresponding fitting curves, see Refs. [14, 15].

IV. Results

The collected results of non-dipolar anisotropy parameters for Ar-1s, Kr-2s, and Kr-2p photoionization are displayed in Fig.4. The experimental data points are plotted as open symbols with error bars, and theoretical predictions from Refs. [12] and [13] are given for comparison as dashed and solid lines, respectively. For the level of approximation used in these calculations, i.e. including terms $\langle E1 \rangle \langle E2 \rangle$, the quantity δ vanishes for ionization from an s subshell. The results for Ar 1s and Kr 2s are therefore given in terms of the non-dipole anisotropy parameter γ , whereas the results of Kr 2p are given as the combined quantity $\gamma + 3\delta$.

The agreement between the theoretical non-relativistic central-field calculations and the experimental data is very good in all three cases. The experiment confirms the prediction that the non-dipolar asymmetry neither approaches zero towards threshold nor is exclusively positive, as it would be expected on the basis of the simple retardation picture [6]. This difference is caused by the mutual screening of the electrons and would be absent in a simple hydrogenic model (cf. [7, 12]).

The energy dependences of γ differ considerably for the Ar 1s and Kr 2s cases (top and middle panels in Fig.4). Ultimately, this difference is caused by the different shapes and nodal structure of the wavefunctions in the initial states. The non-dipole asymmetry parameter γ for

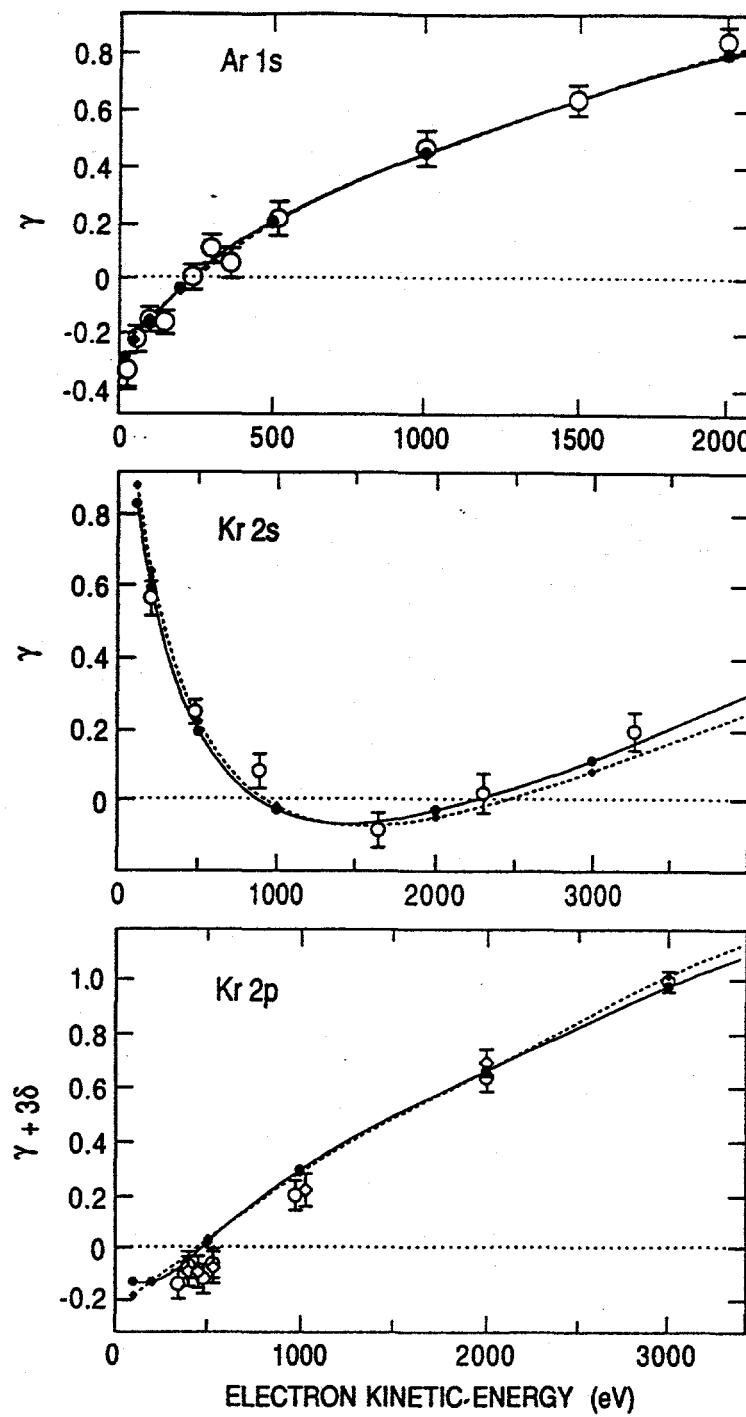


Figure 4: Energy dependence of the non-dipole angular distribution parameter γ for Ar 1s (top), Kr 2s (middle), and of the combined quantity $\gamma + 3\delta$ for Kr 2p; (bottom). Open circles/diamonds, experimental results; in the case of Kr 2p, the circles and diamonds refer to the $j = 1/2$ and $j = 3/2$ fine structure components. Dashed and solid lines, theoretical predictions from [12] and [13], respectively.

ionization from an ns subshell can be expressed as

$$\gamma = 3k \frac{Q(ns \rightarrow \epsilon d)}{D(ns \rightarrow \epsilon p)} \cos(\delta_{\epsilon d} - \delta_{\epsilon p}). \quad (7)$$

The quantities $Q(ns \rightarrow \epsilon d)$ and $D(ns \rightarrow \epsilon p)$ are the radial quadrupole and dipole matrix elements, and $\delta_{\epsilon d}$ and $\delta_{\epsilon p}$ are the phase shifts of the continuum partial waves for quadrupole and dipole transitions, respectively. The zeros in the energy dependences for Ar 1s and Kr 2s reflect the zeros of the quadrupole matrix element and of the cosine of the phase difference. From Eq.(7) it is also clear that a zero in the dipole transition amplitude would create extremely enhanced non-dipolar asymmetries.

The individual fine structure components, $j = 1/2, j = 3/2$, could be resolved in the experiment for Kr 2p for all but the highest energy point (bottom part of Fig.4). No difference in the energy dependence of $\gamma + 3\delta$ for the two fine structure components was detected. The agreement between prediction and experiment is not quite as good as for Ar 1s and Kr 2s. At the lower energies the experimental data points are slightly, yet systematically lower than both of the theoretical predictions. For Kr 2p, too, backward directed non-dipolar asymmetries are detected towards threshold and steadily rising positive values for increasing energies. Expressions similar to Eq.(7) for both γ and δ are given in Ref. [13]. Many more transition elements and phase differences have to be taken into account for the partial waves occurring in conjunction with the ionization from p or higher- ℓ subshells. It is an interesting observation that the two theoretical predictions agree closely in their result of $\gamma + 3\delta$, even though they obtain somewhat different results for γ and δ . For further tests of the theory, future experiments will have to make provisions that enable separate determinations of all three angular distribution parameters β, γ, δ .

V. Outlook

As intense tunable x-ray beams ranging from 1–100 keV in energy are currently becoming available at third-generation synchrotron radiation sources in Europe, USA, and Japan, the study of non-dipole effects and their inclusion in the interpretation of photoionization data will increasingly become part of data acquisition and analysis. The non-dipolar asymmetries reported in this paper, particularly in the cases of ionization from s subshells, are representative of rather straight-forward physical systems and hence the validity of non-relativistic central-field descriptions has to some extent been expected. Just as for determinations of the β parameter in the electric-dipole interaction, it is the less straight-forward situations, for example the non-dipolar asymmetries in the threshold region, in the regions of resonances [7] and of Cooper minima [22], which represent interesting subjects for future experimental and theoretical investigations. In addition, relativistic effects gain importance in studies with higher- Z elements and higher x-ray energies. The photoionization cross sections decrease significantly at higher photon energies and, consequently, experimental determinations of angular distributions become much more difficult. Nevertheless, further work is needed to explore the extent to which current theoretical descriptions are able to predict non-dipolar angular distributions in the regime of high Z and high x-ray energies, and the extent to which other multipole terms need to be taken into account in the photon-atom interaction.

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