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Beyond the Dipole Approximation: Angular-Distribution Effects in the 1s Photoemission from Small Molecules

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Beyond the Dipole Approximation: Angular Distribution Effects in the 1s Photoemission from Small Molecules

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Abstract. Over the past two decades, the dipole approximation has facilitated a basic understanding of the photoionization process in atoms and molecules. Recent experiments on the 1s inner shells of small molecules at relatively low photon energies (≤ 1000 eV) show strong nondipole effects. They are significant and measurable at energies close to threshold, in conflict with a common assumption that the dipole approximation is valid for photon energies below 1 keV.

INTRODUCTION

The electric-dipole (E1) approximation [1], applied to photoionization, leads to the well-known expression for the differential cross section [2],

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{2} (3 \cos^2 \theta - 1) \right] \quad (1)$$

which describes the angular distribution of photoelectrons from a randomly oriented sample created by 100% linearly polarized light. Here, σ is the partial photoionization cross section, and θ is the angle between the vector of the outgoing electron and the vector of linear polarization. The parameter β completely describes the angular distribution of photoelectrons, within the dipole approximation. In this approximation, all higher-order interactions, such as electric-quadrupole (E2) and magnetic-dipole (M1), are neglected. This assumption is justified by the argument that the strengths of the E2 and M1 interactions relative to electric-dipole effects are approximately equal to the ratio of the photoelectron's velocity to the speed of light [3], a ratio which is small except at very high energies.

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Over the past two decades, the dipole approximation has facilitated a basic understanding of the photoionization process in atoms and molecules [2], as well as the application of photoelectron spectroscopy to a wide variety of condensed-phase systems. The first hint of deviations from the dipole approximation was provided by Krause [4] in measurements using unpolarized x-rays [5]. A small deviation from the expected dipolar angular distribution at photon energies between 1 and 2 keV was observed and attributed to the influence of **E2** and **M1** interactions. These lowest-order, non-electric-dipole corrections to the dipole approximation lead to so-called *nondipole* effects in the angular distributions of photoelectrons, described by [6]

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

for 100% linearly polarized light. The nondipole angular-distribution parameters γ and δ are attributable to interference terms between electric-dipole and electric-quadrupole interactions. Figure 1 describes the geometry and the angles θ and ϕ .

Figure 1. Geometry applicable to photoelectron angular-distribution measurements using polarized light. θ is the polar angle between the photon polarization vector ϵ and the momentum vector $\mathbf{p}$ of the photoelectron. ϕ is the azimuthal angle defined by the photon propagation vector $\mathbf{k}$ and the projection of $\mathbf{p}$ into the x-z plane.

More-recent measurements [7,8], focussing on noble-gas core levels (Ar *K* and Kr *L*) and photon energies above 2 keV, have begun to investigate nondipole effects in photoelectron angular distributions in more detail. In contrast, the present experiment concentrates on the N_2 *N1s* and CO *C1s* inner shells at relatively low photon energies (300 to 700 eV). Nondipole effects are observed to be large and highly energy dependent in this region, especially close to core-level thresholds, in conflict with a common assumption in applications of photoelectron spectroscopy; namely, that the dipole approximation is valid for photon energies below 1 keV. The potential significance of these findings is nicely illustrated by comparison of the present results for the N_2 and the CO γ_{1s} parameters with theories for atomic nitrogen and atomic carbon [9], where the influence of nondipole effects are expected to be much smaller.

Figure 2. Experimental schematic of the electron time-of-flight system. Light from the ALS storage ring passes through beamline optics into a differential-pumping section. The chamber and analyzers can rotate around the photon beam for more accurate electron angular-distribution measurements.

EXPERIMENT

The experiments were performed on undulator beamline 8.0, [10], which covers the 100-1500 eV photon-energy range. The monochromator entrance slit was set to 70 μm and the exit slit to 100 μm yielding very high flux, because high photon resolution was not needed. During the measurements the ALS operated at 1.9 GeV in two-bunch mode with a photon pulse every 328 ns. Four time-of-flight (TOF) electron analyzers, equipped with microchannel plates for electron detection, collect spectra simultaneously at different angles. The total electron flight paths are 437.5 mm, and the analyzers have a full cone acceptance angle of 5.4° .

The interaction region is formed by an effusive gas jet intersecting the photon beam which has a diameter of less than 1 mm. Energy resolution of the TOF analyzers with a focus size of 1 mm is 1% of the electron kinetic energy. Each spectrum was collected for about 600 s. The gas samples were obtained either commercially (CO) or directly from ambient air (N_2). A mixture of the sample with xenon was used sometimes because Xe has an abundance of Auger lines below 100 eV kinetic energy, which provide excellent internal calibration for each spectrum.

RESULTS

Figure 3 shows two superimposed spectra, both taken at the magic angle $\theta=54.7^\circ$, but at different ϕ angles. The spectra were measured close to the $\text{C}1s$ threshold (296 eV) and are scaled to the area of the Xe NOO Auger lines and the obvious intensity differences between the CO $\text{C}1s$ peaks in the two spectra are due entirely to nondipole

Figure 3. Photoelectron spectra of a CO-Xe mixture measured at a photon energy of 320 eV. One spectrum was taken with the dipole magic-angle analyzer and the other spectrum with the nondipole analyzer. The spectra are normalized to the Xe NOO Auger lines. The intensity differences in the CO C1s lines between the two analyzers is due entirely to nondipole effects.

effects because both spectra are at the magic angle where the β parameter has no influence.

For the dipole magic-angle analyzer the differential cross section in Eq. (2) reduces to the partial cross section; E2 and M1 effects vanish in the $\phi=90^\circ$ plane even if relativistic effects are included [11]. For the nondipole analyzer,

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 + \sqrt{\frac{2}{27}} (3\delta + \gamma) \right] = \frac{\sigma}{4\pi} \left[1 + \sqrt{\frac{2}{27}} \zeta \right] \quad (3)$$

which simplifies further for s subshells [6,12] in the non-relativistic approach where δ vanishes. We are using $\zeta=3\delta+\gamma$ for measurements that don't resolve the δ and γ parameters of the angular distributions. In the case of molecular effects it is not clear if the δ parameter for s -shells vanishes near threshold.

With our experimental geometry, it is possible to measure the ζ parameter for s subshells directly, if the degree of linear polarization is known, by using the two magic angle analyzers. The data points for CO and N₂ in Figures 4 and 5 show strong nondipole contributions with maxima of $\zeta=1.2$.

The difference between CO and N₂ lies in the position of the maxima. For N₂ the maximum is about 60 eV above the N₂ 1s ionization threshold much higher than the maximum of the dipole shape resonance at about 420 eV. The maximum of the ζ parameter for the CO C1s is close to the maximum of the dipole shape resonance at 305 eV.

Figure 4. Electron angular anisotropy parameter ζ for the CO C1s photoline from threshold to $h\nu=500$ eV. The theoretical curve for atomic carbon is from Lajohn and Pratt [9].

A qualitative explanation for the behavior of ζ can be obtained from the following model. Just as molecular β values can change rapidly with photon energy for large differences in polarization components for ionization along and perpendicular to a molecular axis (due to a resonance, for example), so also ζ values can behave similarly but with greater sensitivity to the difference in polarization components because of the higher power of the transition moment coordinate involved. Thus, the observed molecular ζ effects may be universal.

Figure 5. Electron angular anisotropy parameter ζ for the N₂ 1s photoline from threshold to $h\nu=700$ eV. The theoretical curve for atomic nitrogen is from Lajohn and Pratt [9].

Figure 6. Electron angular anisotropy parameter β for the N_2 $1s$ photoline from threshold to $h\nu = 450$ eV. Measurements by Kempgens [14] and Lindle [15] did not take non-dipolar effects into account and deviate from our measurements.

The variations of β (and ζ) with photon energy in atoms are due to the interference of different partial waves ($p \rightarrow s$ and d , for example) whereas in molecules this can be due to the interference of the polarization components ($1s \rightarrow p\sigma$ and $p\pi$ in N_2 , for example).

One consequence of these strong molecular nondipole effects near threshold is the possibility of influences on previous measurements of β -parameters, as demonstrated in Fig. 6. If the β -parameter is not measured in the plane perpendicular to the direction of the light (and linear polarized light) the intensities used to determine β are influenced by the forward/backward intensities of ζ . These intensities reduce or increase the β values as shown in Fig. 6 for Kempgens and Lindle. Larger values of ζ lead to larger deviations in β .

The present results illustrate that any photoemission experiment, whether on gases, solids, or surfaces, can be influenced by nondipole effects at relatively low photon energies, pointing to a general need for caution in interpreting angle-resolved photoemission data.

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