

Atomic Quadrupolar Photoemission Asymmetry Parameters from a Solid State Measurement

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A method for measuring the asymmetry parameter γ arising from dipole-quadrupole interference in core-level photoemission is proposed which is based on condensed thin films and exploits the influence of this asymmetry in photoemission monitoring of x-ray standing wave field absorption. The high density of material in this method offers some advantages over a conventional gas-phase measurement. Results are presented for C, O, and F $1s$ photoemission at photon energies around 3 keV. The combined nondipole asymmetry factor $(\delta + \gamma/3)$ for non- s -states can be determined in a similar way.

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The dipole approximation has been widely used to interpret photoemission from atoms, molecules, and solids for many years and was commonly regarded as being appropriate except for x-ray excitation with photon energies greater than 10–20 keV. However, recent theoretical [1] and experimental data [2,3] for photoemission from inert gas atoms have shown that both quadrupole and magnetic dipole effects can substantially influence the *angular dependence* of such photoemission at much lower photon energies, and in some cases very close to threshold. We have shown [4] that this effect can be important for at least one application of photoemission in surface science, that of photoemission detection in x-ray standing wave (XSW) determinations of surface structure. Proper interpretation of these experiments requires a knowledge of the nondipole asymmetry parameters, and the materials of interest cover the whole periodic table, including many atoms, such as C, N, O, which are well removed from the inert gases, the only systems for which published data (experimental or theoretical) currently exist.

We have therefore devised a new method to measure these parameters which exploit the sensitivity of the standing wave experiment to this effect. This method is rather straightforward, exploiting samples that are in the form of condensed matter and thus have a density many orders of magnitude (typically 10^{10} times) larger than the gas phase traditionally used for such measurements. Specifically, we use deposited films, containing the element of interest, which are structurally incoherent with the underlying crystalline substrate in which the x-ray standing waves are established. Here, we illustrate our approach with the results of measurements of quadrupolar asymmetry parameters for photoemission from the C, O, and F $1s$ states (nominal binding energies 284, 543, and 697 eV) at photon energies around 3 keV. While our results are all for emission from s states, a minor modification of our method

is applicable to initial states of higher orbital angular momentum.

Electric quadrupolar and magnetic dipole contributions to photoemission from an atomic core level interfere with the electric dipole component, introducing an asymmetry for emission at an angle θ to the photon polarization vector \mathbf{A} depending on whether the emission direction has a positive or negative component relative to the direction of travel of the incident photon, i.e., whether electron emission is “forwards” or “backwards” relative to the photon propagation direction. The resulting angular derivative of the total cross section, $d\sigma/d\Omega$, can be parametrized in the form [1]

$$d\sigma/d\Omega = (\sigma/4\pi)[1 + (\beta/2)(3\cos^2\theta - 1) + (\delta + \gamma\cos^2\theta)\sin\theta\cos\varphi], \quad (1)$$

where β is the usual dipolar asymmetry parameter, δ and γ are the additional asymmetry factors associated with electric dipole-quadrupole and electric-magnetic dipole interference, and φ is the angle between the photon propagation direction and the projection of the electron wave vector in the plane perpendicular to \mathbf{A} . The factor $\cos\varphi$ is thus +1 or -1 for forward or backward emission, respectively. Figure 1 shows this angular distribution for the case of $\beta = 2$, $\delta = 0$, and $\gamma = 1$, close to the values in our measurements (see below); also shown (dashed line) for comparison is the pure dipole case ($\delta = 0$ and $\gamma = 0$) with no forward/backward asymmetry.

In the x-ray standing wave technique [5–7] for surface structure determination, an x-ray Bragg reflection condition is established in the crystal sample, and the interference of the incident and scattered x rays produces a standing wave field with a periodicity equal to that of the scatterer planes. By scanning through the Bragg condition in x-ray wavelength, the phase of this standing wave

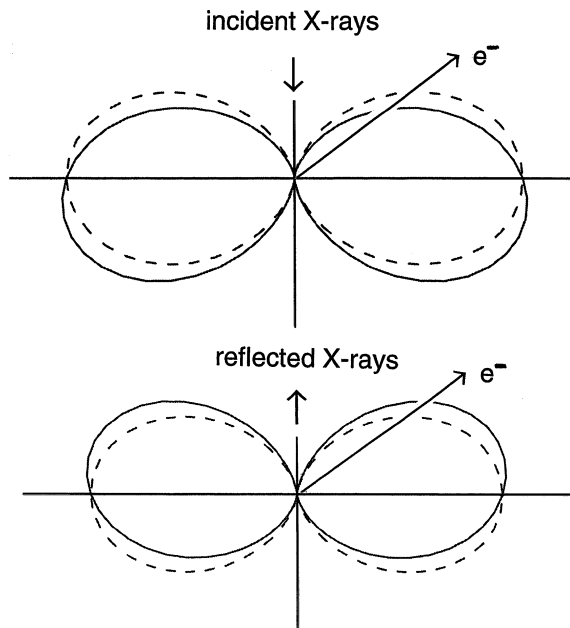


FIG. 1. Polar diagrams showing the influence of quadrupolar asymmetry in photoemission in measurements of the signal induced by the incident and Bragg-reflected x rays in a normal incidence XSW experiment. The curves plotted as full lines correspond to asymmetry parameter values of $\beta = 2$, $\delta = 0$, and $\gamma = 1$, similar to the cases measured here. The dashed line shows the situation when the dipole approximation is valid ($\delta = 0$ and $\gamma = 0$). For the reflected x rays, an arbitrary value for the reflectivity of 0.9 has been used. The figure also illustrates the experimental geometry for the (111) reflection with the surface aligned along the abscissa facing upwards, and the photoemission signal collected along the direction marked e^- .

field shifts in a systematic fashion, and the x-ray absorption profile of an adsorbed atom on the surface is characteristic of its layer spacing relative to the scatterer planes. For low atomic number adsorbates, or in cases in which chemical-state resolution is required, photoemission from the adsorbed atom is the preferred method of monitoring the x-ray absorption. An electron energy analyzer placed

outside the crystal surface is typically in a geometry such that the photoemission from the incident x rays are measured in a backwards direction; whereas that from the reflected x rays is measured in the forwards direction (see Fig. 1). If there is a forward/backward asymmetry in the photoemission, the detected photoemission signal does not then monitor the true x-ray standing wave absorption. If the atomic asymmetry factors are known, however, we have shown that the true absorption profile can be extracted [4]. Alternatively, if the true structure is known, or if a true x-ray absorption profile can be measured (e.g., by monitoring the intensity of an Auger electron emission signal), then the photoemission XSW profile can be used to determine the asymmetry parameters.

Although this general approach offers a route to measurement of the nondipole asymmetry factors, situations in which photoemission monitoring of x-ray absorption profiles is preferred are generally those in which no suitable alternative method of monitoring is available. Detailed prior knowledge of the relevant surface structural parameters is also commonly not possible. A solution is to exploit the case in which the x-ray absorbing atoms are in a structure which is sufficiently disordered that there is no coherence in the atomic positions relative to the substrate scatterer periodicity. In this case, the relevant (trivial) structural parameters *are* known, and the extraction of the nondipole asymmetry parameters is especially straightforward.

Our XSW experiments use normal incidence to the scatterer planes, a geometry which greatly lowers the demands of crystalline perfection and allows standard metal single crystals to be used [7,8]; this geometry also ensures that the \mathbf{A} vectors of the incident and reflected x rays are coincident, and that the incident and reflected photon propagation directions are collinear (but opposite). We define a forward/backward asymmetry parameter for our experiment, Q , such that the ratio of the photoemission signal detected in the forward direction to that detected in the backward direction is $(1 + Q)/(1 - Q)$. Relative to Eq. (1), we then have

$$\frac{(1 + Q)}{(1 - Q)} = \frac{[1 + (\beta/2)(3 \cos^2\theta - 1) + (\delta + \gamma \cos^2\theta) \sin\theta]}{[1 + (\beta/2)(3 \cos^2\theta - 1) - (\delta + \gamma \cos^2\theta) \sin\theta]} \quad (2)$$

For the specific problem addressed here of emission from $1s$ states, $\beta = 2$ and $\delta = 0$ [1], so

$$\frac{(1 + Q)}{(1 - Q)} = \frac{[3 + \gamma \sin\theta]}{[3 - \gamma \sin\theta]}$$

and thus $Q = \gamma \sin\theta/3$. In our experiments, the angle θ between the detector and the x-ray \mathbf{A} vector was 50° , so $Q = 0.26\gamma$.

For the special case in which interference of the incident and reflected x-ray beams is not detected because the absorbing atoms are incoherent relative to the substrate periodicity in which the standing wave is established (as in

the case of a disordered film), one obtains the following for the detected angle-resolved photoemission signal:

$$d\sigma/d\Omega \propto [1 + R(1 + Q)/(1 - Q)],$$

and the photoemission absorption profile has the same shape as the x-ray reflectivity R but is enhanced in modulation amplitude for the usual case of a positive value of Q .

If we are able to grow incoherent overlayers containing the element of interest on a crystalline substrate, a comparison of the intensity variation of the photoemission and the reflectivity as one scans through the Bragg condition provides a direct measure of Q , and, for photoemission

from a $1s$ core level, a direct measure of γ . Ideally, this involves growing an amorphous film on the crystalline substrate, but in reality the requirements are much less stringent than this. Even if the film is crystalline, providing that the interlayer spacing of the film is different from that of the substrate in the same direction, the signal from several layers will add to produce a signal which is largely incoherent providing the sampling depth is sufficient (a requirement favored by photoelectron kinetic energies above about 1 keV, as in the present case). The simplest normal-incidence XSW experiment involves Bragg scattering from the scatterer planes parallel to the surface, but ordering in a film grown on this surface will be most pronounced perpendicular to the surface; the effects of this layering can be overcome by using a different Bragg condition which exploits scatterer planes inclined to the surface. Indeed, a comparison of data obtained from scatterer planes parallel to, and inclined to, the surface provides a convenient additional means of checking the degree of structural coherence of the deposited film.

In order to illustrate the utility of this approach, and to obtain asymmetry parameters relevant to the interpretation of our XSW surface structural studies, we have measured the quadrupole-dipole interference asymmetry parameter, γ , for the $1s$ photoemission from O and F at the photon energy of 2975 eV corresponding to the normal-incidence (111) Bragg condition of Cu, together with a similar measurement for C $1s$ at the energy of 3046 eV corresponding to the same condition for Ni. The experiments were conducted using Cu(111) and Ni(111) substrates with incident (synchrotron radiation) x rays from the Daresbury SRS and Grenoble ESRF sources, respectively. The samples, initially prepared by x-ray Laue alignment, spark machining, and mechanical polishing, were mounted in conventional ultrahigh vacuum surface science end-stations and cleaned *in situ* by the usual combination of argon ion bombardment and annealing cycles. Surface cleanliness and order were established by Auger electron spectroscopy and low energy electron diffraction, although we note that for the present purpose some degree of disorder of the surface may be a positive advantage. More important is the good crystalline order in the subsurface region of the substrate, and this was checked by measuring substrate XSW absorption profiles from the clean surfaces. For the O $1s$ measurements, multilayer films of water (H_2O) were grown onto the Cu(111) surface cooled to approximately 140 K, while similar films of perfluorohexane (C_6F_{14}) and benzene (C_6H_6) were used for the F $1s$ and C $1s$ measurements, respectively. XSW profiles were recorded using normal incidence to the (111) planes parallel to the surface, and to the $(\bar{1}11)$ planes inclined at 70.5° to the surface.

The general methodology for the analysis of the data was the same as that developed for our XSW surface structural studies [7]. In particular, the nonstructural fitting parameters for the XSW data, the exact photon energy calibration, and the energy resolution, were obtained by fitting

XSW obtained from the substrate, in the present case comprising both reflectivity measurements using photodiodes at x-ray incidence approximately 1° off normal and substrate absorption profiles measured from the intensity of the substrate *LMM* Auger electron emission. The adsorbate $1s$ photoemission signals were then fitted using the full form of the XSW equation (including Q) [9] to check that the coherent fractions needed really were close to zero. Examples of these data sets, for H_2O and C_6F_{14} overlayers on Cu(111), are shown in Fig. 2. Notice that the O and F $1s$ intensity variations through the XSW region mirror the shape of the reflectivity measurement, but show a much stronger modulation. These can be fitted by values of Q of 0.27 ± 0.01 and 0.25 ± 0.01 , for O and F, respectively, corresponding to values for γ of 1.04 ± 0.04 and 0.96 ± 0.04 . The corresponding value of γ for C $1s$ was 0.92 ± 0.08 . These values were consistent for both the (111) and $(\bar{1}11)$ XSW measurements confirming the incoherence of the films; further confirmation for the C_6F_{14} film comes from the F *KLL* Auger data which do not show backward/forward asymmetry [see Fig. 2(c)]. The published theoretical value for $1s$ photoemission from Ne, adjacent to F in the period table, at this photon energy is 0.95 [1], essentially identical to our measured value for F. Very recent (unpublished [10]) calculations for O and F $1s$ at a photon energy of 3 keV gave values of 1.03 and

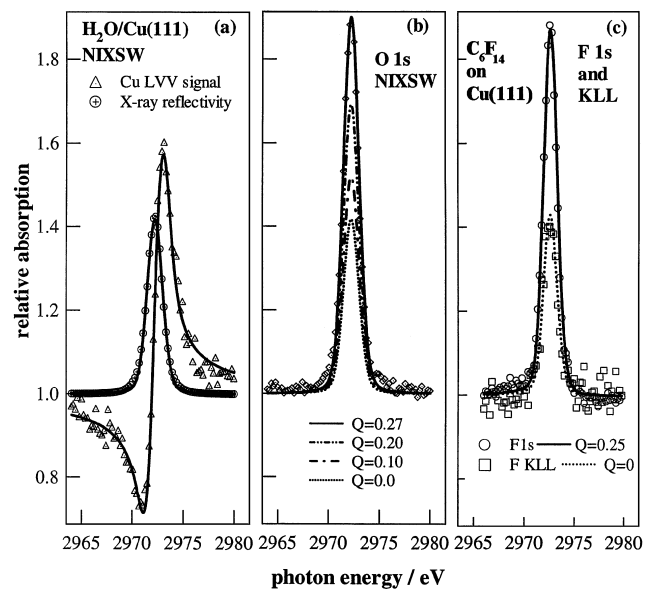


FIG. 2. Results of experiments to determine the quadrupolar asymmetry parameter for O $1s$ and F $1s$ at a photon energy of 2975 eV. In (a) are shown the x-ray reflectivity and Cu absorption profile (measured by the Cu *LMM* Auger electron yield) as the photon energy is scanned through the normal incidence (111) Bragg reflection condition. In (b) and (c) are the O $1s$ and F $1s$ photoemission intensities measured in the same range from incoherent overlayers. The lines are fits to the data as described in the text. (c) also shows the F *KLL*-monitored absorption profile which reproduces the reflectivity profile of (a).

1.05, the first of these, in particular, being an excellent agreement with our measured value.

While our primary motivation in conducting these experiments is to aid interpretation of our XSW surface structural studies, this approach to determining the quadrupole-dipole interference asymmetry parameter does offer some advantages over conventional gas phase measurements. In particular, the density of the sample (a multilayer solid film) is many (typically 10) orders of magnitude larger than in the gas phase, so the data collection times can be expected to be very much shorter. Of course, this is an advantage of any solid-state measurement, but usually the importance of elastic scattering of photoelectrons by atoms surrounding the emitter precludes the use of a solid sample for measurements of intrinsic angular effects in photoemission. In the present case, we exploit a technique which measures only the *difference* in the angular distribution of photons traveling in opposite directions; this measurement is almost totally unaffected by strong scattering, because its effect is identical for the photoemission derived from both the incident and reflected x-ray beams.

Of course, there are limitations to our approach. Here, we have used an experimental geometry of $\theta = 50^\circ$ for which the direct measurement of the quadrupole-derived asymmetry parameter, γ , is possible only when β and δ are known, as in the case of an initial s state. However, if one sets θ to the "magic angle" of 54.7° , then $(3 \cos^2 \theta - 1) = 0$ and Eq. (2) becomes independent of β , leading to $Q = 0.816(\delta + \gamma/3)$; one can thus measure directly, for states of any orbital angular momentum, the combined nondipole parameter $(\delta + \gamma/3)$, which has been recently measured for emission from the Ne $2p$ state in a gas-phase study [11]. In the measurements we have made, which exploit the experimental simplification provided by normal incidence to the Bragg scatterer planes, the measurement energy is restricted to the specific value for this Bragg condition. Even including normal incidence Bragg conditions from other scatterer planes in the same substrate [e.g., (200) in the present case], only a few discrete energies are accessed. One way to overcome this limitation is to use several different substrates with different interplanar spacings. A more versatile solution is to move away from the normal incidence condition. This typically requires the use of more perfect crystals, but one could envisage using a silicon substrate crystal and then making measurements over a wide range of angles. The basic integrity of the method, and, in particular, its insensitivity to dipolar angular effects, is retained as long as one conducts the experiments in σ polarization [12]. Finally, we note that in our approach we specifically ignore any molecular or solid-state effects on the parameter γ , with so few experimental measurements of any kind, this seems a reasonable initial stance, and indeed this seems to

be supported by the good agreement between our results and those of recent calculations for free atoms. Ultimately, such effects may prove of interest, and in this case one may also wish to exploit the ability of a surface to produce preferred orientations of the molecular species in a way not possible in simple gas-phase measurements.

In conclusion, we have demonstrated that we can exploit the sensitivity of photoemission monitoring of x-ray standing waves in crystalline solids to measure in a rather simple way the quadrupole-dipole interference asymmetry factor for photoemission from core levels of s symmetry. The fact that the sample is in the form of a condensed film provides a very large advantage in cross section relative to conventional gas-phase measurements. The method can be used for almost any element, and, while our own studies were conducted at single photon energies, extension of the approach to a wider range of energies is possible. Specific values for C, O, and P $1s$ photoemission have been measured. Developments of this approach to cover a wider energy range, to study non- s -states and ultimately to study oriented molecular species, appear viable.

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