Electric-Dipole–Quadrupole Interference of Overlapping Autoionizing Levels in Photoelectron Energy Spectra

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We have measured the photon energy dependence of electric-dipole–quadrupole interference in cadmium between the odd parity $4d^9 5s^2 5p$ $J = 1$ and even parity $5p6p\,^3P_2$ autoionizing levels. The resonant interference structure is isolated by taking the difference between constant ionic state spectra at 45° with respect to the photon beam in the forward and backward directions. We find interference effects that are approximately 0.5% of the dipole cross section for photon energies of 13 eV, in good agreement with theory. We compare the results with those from $(e, 2e)$ experiments. [S0031-9007(98)06548-X]

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The electric-dipole approximation usually gives an excellent description of the absorption of a low energy photon by an atom [1]. This approximation follows from the first term in an expansion of the photon field $\exp(i\mathbf{k}\cdot\mathbf{r}) = 1 + i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2 + \cdots$, in the limit $\mathbf{k}\cdot\mathbf{r} \ll 1$. Here, $\mathbf{k}$ is the photon propagation vector, and $\mathbf{r}$ is the atomic electron position vector; in atomic units $k = \alpha\omega$, where $\alpha \approx \frac{1}{137}$ is the fine structure constant, and ω is the photon energy in Hartrees (27.2 eV). Taking a typical atomic size as 1 a.u., the dipole approximation is valid for $\omega \ll \frac{1}{\alpha}$, i.e., below photon energies of about 1 keV. At larger energies the breakdown of the dipole approximation, caused by the second term in the expansion, may be observed in photoelectron angular distributions [2]. Whereas the largest nondipole term in the photoabsorption cross section scales as $(\alpha\omega)^2$, the photoelectron angular distribution contains an interference cross term that scales as $\alpha\omega$.

In this paper we report the first observation of interference between dipole and quadrupole amplitudes for the photoexcitation of autoionizing levels of different parity. Furthermore, for the cadmium target used, these levels correspond to extremely low photon energies (<15 eV) for which the nondipole effect is a fraction of 1% of the dominant dipole amplitude. Such tiny effects may be detected because of the rapid variation of the interference amplitude as the photon energy is swept through an autoionizing resonance; simultaneously sweeping the electron detector energy in order to collect the photoelectrons associated with the $\mathrm{Cd}^+ 5s\,^2S_{1/2}$ ion yields a constant ionic state (CIS) spectrum containing resonant dipole-quadrupole interference features.

Previous experiments have been carried out at much higher photon energies which give rise to correspondingly larger nondipole effects. Recent photoionization studies at photon energies >3 keV have carried out the first systematic measurements of photoelectron angular distributions that isolate nondipole effects [3,4]. Interferences were observed, for example, in the direct ionization of Ar $1s$, between the electric dipole $(s \rightarrow p)$ and electric quadrupole $(s \rightarrow d)$ processes. A careful choice of detection geometry enabled nondipole effects to be measured as deviations of up to 20% from an isotropic angular distribution. Nondipole effects have also been seen in the angular distribution of Ne valence photoelectrons at the relatively low energy of 250 eV [5].

The form of the photoelectron angular distribution has been given by Cooper [6]. For ionization out of s subshells for atoms having pure $^1S_0$ atomic ground states, only electric-dipole and quadrupole processes need to be considered. With light incident in the $+x$ direction and linear polarization along the z axis, the differential cross section of photoelectrons can be written in terms of spherical polar coordinates as

$$\frac{d\sigma(\omega,\theta,\phi)}{d\Omega} = \frac{\sigma_1(\omega)}{4\pi}[1 + \beta(\omega)P_2(\cos\theta)] + \frac{\sigma_{12}(\omega)}{4\pi}\sin\theta\cos^2\theta\cos\phi\,. \quad (1)$$

Here σ_1 is the dipole cross section, β is the photoelectron asymmetry parameter, and P_2 is a second order Legendre polynomial. The dipole-quadrupole interference is described by the parameter σ_{12}, which has the units of a cross section but may be positive or negative (Cooper uses a different parameter $\gamma = \sigma_{12}/\sigma_1$, and the general case is discussed in detail by Shaw *et al.* [7]). The angular form of the interference term follows directly from the product of a dipole (z) and a quadrupole (xz) matrix element. For nonresonant ionization all these quantities are slowly varying functions of ω.

For a single autoionizing resonance with angular momentum ℓ that couples to a single continuum, the amplitude of the final continuum state can be written [8]

$$A_\ell \sim \mathcal{M}_\ell \frac{q_\ell + \varepsilon_\ell}{\varepsilon_\ell + i} e^{i\delta_\ell}, \quad (2)$$

where $\varepsilon_\ell = (\omega - \omega_\ell)/(\Gamma_\ell/2)$ is the energy relative to the resonance position ω_ℓ in units of half the resonance width Γ_ℓ. The nonresonant ionization magnitude and phase are $\mathcal{M}_\ell$ and δ_ℓ, and the Fano q parameter is a measure of the enhancement of the resonant over the nonresonant process. For two overlapping autoionizing resonances of opposite parity, excited by dipole and quadrupole transitions, the interference is given by $\sigma_{12} \propto (A_1^* A_2 + A_1 A_2^*)$, which is a rapidly varying function in the neighborhood of each resonance.

The photoabsorption [9] and CIS [10] spectra of cadmium, for photon energies between 11.5 and 13.5 eV (ejected-electron energies $E = 2.5 \rightarrow 4.5$ eV; ionization potential 8.994 eV), are dominated by the intense and broad spectral lines of the odd parity $4d^9 5s^2 5p$ $J = 1$ autoionizing levels. These levels are excited from the even parity $4d^{10} 5s^2$ $J = 0$ ground state by the strong single electron $4d \rightarrow 5p$ dipole transition and autoionize into the $5sEp\,^{1,3}P_1$ continua. A number of narrow features in the spectrum are due to $5pn\ell$ $J = 1$ odd parity levels [11]. This energy range also contains the even parity $5p6p$ $J = 2$ autoionizing levels embedded in the $5sEd$ $J = 2$ continuum.

Recent Cd $(e,2e)$ experiments that are the electron-scattering analog of nondipole photoionization have demonstrated interferences between the even and odd parity levels due to electron-impact quadrupole and dipole processes, respectively. Details of the experimental techniques and calculations, which involve a generalization of Eq. (2), are given in Refs. [12,13]. Of interest here is a sharp feature in the interference spectrum close to $E = 4$ eV which was ascribed to $5p6p\,^3P_2$; for momentum transfer $K \approx 0.2$ a.u. this feature is about 10% of the dipole cross section. Good agreement between theory and experiment requires an accurate determination of the relative phases of multipole amplitudes. An important difference between photoprocesses and charged particle scattering is that in the former the relative dipole-quadrupole phase contains a simple $\frac{\pi}{2}$ contribution given by the expansion of the photon field, whereas in the latter there are the additional phase shifts of charged particles scattered by atomic and ionic potentials. Thus, as well as being of interest in its own right, the measurement of electric-dipole–quadrupole interference in photoelectron emission provides reference phase information for the analysis of $(e,2e)$ experiments. Note that this is a rare occurrence of a photon experiment imitating an electron scattering experiment; it is more usual to use a high energy electron beam to simulate the dipole selection rules of photoabsorption experiments.

We have carried out a calculation to predict the equivalent photoelectron dipole-quadrupole interference effect in cadmium; this is shown in Fig. 1 for the autoionizing levels listed in Table I. Also shown is the dipole cross section σ_1 normalized to the experimental photoabsorption cross section [9]. Note that, although the maximum in the interference term σ_{12} of about 0.5 Mb is quite respectable in absolute terms, it is tiny relative to the very large dipole cross section. In order to measure this term experimentally, we use the properties of the angular terms in Eq. (1): the angular part of the dipole term is unaffected, but the interference term changes sign for reflection through the origin, $(\theta, \phi) \rightarrow (\pi - \theta, \phi + \pi)$. Thus the *sum* of CIS spectra for opposite photoelectron directions yields the pure dipole cross section, and the *difference* between the spectra isolates the interference term.

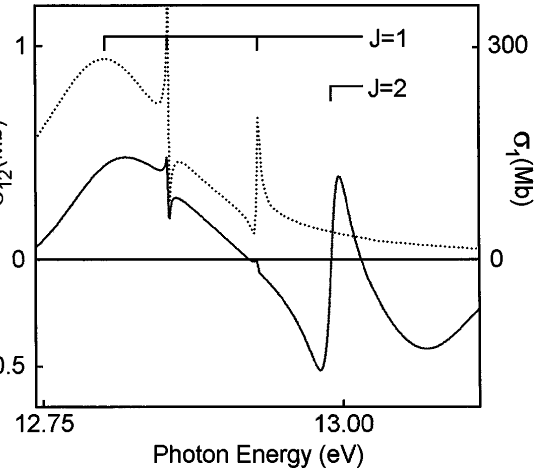

FIG. 1. Calculated photoelectron dipole cross section σ_1 (dotted line), and dipole-quadrupole interference σ_{12} (solid line), due to Cd $4d^9 5s^2 5p$ $J = 1$ and $5p6p\,^3P_2$ autoionizing levels.

The general form of the photoelectron spectrometer is similar to that used in previous Cd experiments [10]. For the present work two electrostatic analyzers were used to collect simultaneous CIS spectra 180° apart. The whole apparatus was oriented so that the photoelectron detection plane was the horizontal plane containing the light propagation direction and polarization axis, as shown in Fig. 2. From practical considerations, the spectrometer was operated with fixed detection angles corresponding to $(\theta, \phi) = (45°, 0)$ and $(135°, 180°)$. Labeling the CIS spectra $I^+(\omega)$ and $I^-(\omega)$, respectively, the sum and difference of the CIS spectra are given by

$$I^+ + I^- \sim 2\sigma_1(\omega)\left[1 + \frac{1}{4}\,\beta(\omega)\right], \qquad (3)$$

TABLE I. Cadmium autoionizing levels above the ground state neutral, labeled by their largest LS component. The ionization potential is 8.99 eV. Energies and widths of $J = 1$ are from Refs. [9,10]. The $J = 2$ width is from an *ab initio* HFR calculation and its energy is from an improved analysis of the $(e,2e)$ data of Ref. [13].

			Energy (eV)	Width (eV)
$J = 1$	$4d^9 5s^2 5p$	^1P	12.805	0.140
		^3D	12.930	0.003
	$5p5d$	^3D	12.856	0.003
$J = 2$	$5p6p$	^3P	12.992	0.023

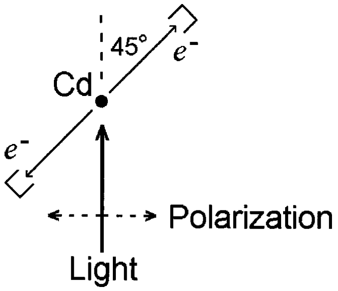

FIG. 2. Schematic of the coplanar experimental arrangement showing the relationship of the two photoelectron detectors to the linearly polarized light.

$$I^+ - I^- \sim \frac{1}{\sqrt{2}}\,\sigma_{12}(\omega)\,. \tag{4}$$

Figure 1 contains two types of interference features. The first type is due to $J = 1$ autoionization and $J = 2$ direct ionization $5s \rightarrow Ed$. Since these features are coincident with the dominant $J = 1$ resonances their reliable observation depends critically on the correct experimental normalization of the two CIS spectra before subtraction; the relative intensities need to be known to better than 0.1%. On the other hand, the second type of interference feature in Fig. 1 is due to the sharp $J = 2$ resonance and smoothly varying wing of the $J = 1$ autoionizing resonance (direct $J = 1$ photoionization is negligible in this region). Here the detection of dipole-quadrupole interference does not depend critically on the correct relative calibration of the two CIS spectra provided that we restrict ourselves to the $J = 2$ resonance region; slightly inaccurate normalization merely adds a smoothly varying offset.

The experiment took place at the storage ring Aladdin at the University of Wisconsin Synchrotron Radiation Center on the Aluminum Seya Namioka beam line. The polarization of the radiation was better than 95% and no correction to our analysis was deemed necessary. The full width at half maximum (FWHM) of the photon beam used was (14 ± 2) meV, measured using the Xe $5p \rightarrow 8s$ resonance at 12.575 eV, and assumed to be constant over the energy range $12.6 \rightarrow 13.1$ eV of our Cd experiment. This relatively poor photon beam resolution was chosen in order to maximize the photoelectron intensity. Since the ground state of Cd^+ is separated from its first excited state by 5.4 eV, the electrostatic analyzers also could be operated at low energy resolution in order to maximize the signal. Photoelectron spectra at selected wavelengths were collected before and after each CIS spectrum; these were used primarily to correct secondary-electron background. The channeltron's "dark count" (<0.5 Hz) was monitored between experimental runs to ensure that there was no spurious, and possibly nonrandom, contribution to the spectra. An effusive quasibeam was produced by heating metallic cadmium in a tantalum oven to a temperature close to the melting point of 330 °C. Each charge was sufficient to obtain three CIS spectra, after which the oven had to be refilled.

Nearly 40 pairs of CIS spectra were measured. These were combined to produce a single pair with approximately one million counts in the ${}^1P_1$ maximum. The CIS spectral pair (corrected for secondary electron counts) were normalized to each other by taking the average of their point-by-point ratio as the normalization factor; details of this procedure will be given in a later publication. Experimental effects were considered that could give rise to spurious differences in the CIS pair. Stray electric fields can cause Stark mixing of the opposite parity autoionizing levels [14]; in the present experiment stray fields were <0.1 V/cm ($<10^{-10}$ a.u.) and have negligible effect. The relative energy scales and resolution (FWHM) of the two spectra can be slightly shifted because of asymmetric instrument functions of the two electrostatic analyzers, and cadmium deposition on the entrance slits of the analyzers can change the effective detection angle (θ, ϕ) of photoelectrons. It was found that applying exploratory corrections for these effects could account for differences between the CIS spectra close to the $J = 1$ maxima but had little effect on structure in the region of the $J = 2$ resonance. In our final analysis the relative energy scales were corrected by 0.1 meV and the effective relative resolutions by 2 meV.

The experimental sum and difference spectra are shown in Figs. 3 and 4. Figure 3 covers the full experimental range, whereas the difference spectrum in Fig. 4 is limited to the region away from the $J = 1$ resonance maxima ($E_1 \rightarrow E_2$ in Fig. 3), for the reasons discussed above. Both the sum and difference spectra are given relative to the sum spectrum at 13 eV. The statistical uncertainties in the difference spectra are shown; those of the sum spectra have the same values. The normalization procedure results in a systematic uncertainty of the true experimental zero in Fig. 4 of at least ±0.005. The statistics are

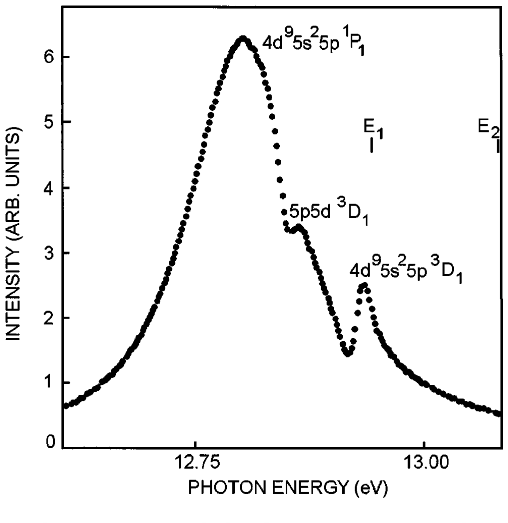

FIG. 3. The experimental dipole spectrum given by the sum of CIS spectra collected by the two electron detectors shown in Fig. 2. The ordinate is normalized to the value at 13 eV.

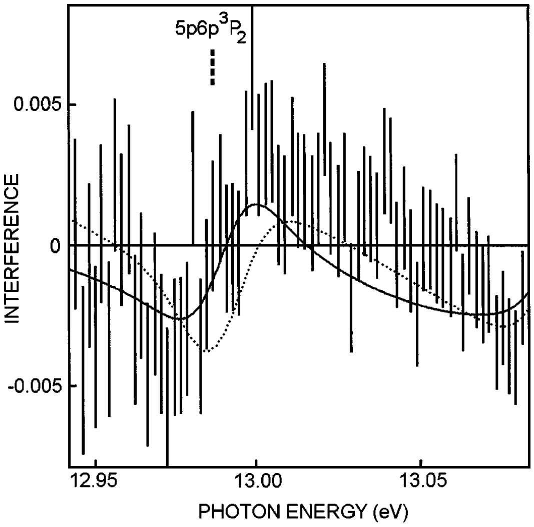

FIG. 4. The experimental dipole-quadrupole interference spectrum given by the difference of CIS spectra taken by the two electron detectors shown in Fig. 2. The energy range corresponds to $E_1 \rightarrow E_2$ in Fig. 3. The ordinate is normalized to the dipole spectrum at 13 eV. The solid curve is a calculation appropriate to photoionization, and the dotted curve is a calculation with the phase appropriate for electron scattering; see the text for details. Both calculations include the instrumental energy resolution of 14 meV.

adequate to reveal the dipole-quadrupole interference associated with $5p6p\,^3P_2$: there is a minimum at 12.97 eV followed by a maximum at 13 eV with an interference variation of approximately 0.006. (As a check the data were split into three groups of scans; a similar feature was seen in each group, albeit with the scatter associated with poorer statistics.) The solid curve in Fig. 4 is the calculated interference (Fig. 1) folded with a Gaussian of FWHM 14 meV; in general the agreement is very good with a similar variation of 0.005 across the resonance. The dotted curve is a similar calculation but uses the relative dipole-quadrupole phase found for electron scattering in the $(e, 2e)$ experiments. Thus the present photoionization experiment seems to confirm an expected 10 meV energy shift, due to a $\frac{\pi}{4}$ phase difference [13], between the two types of experiment.

Previous observations of nondipole effects have relied on photon energies sufficient to produce nondipole effects of at least a few percent in photoelectron angular distributions. It would be very difficult to observe deviations of less than 1% from a pure dipole angular distribution because instrumental uncertainties would preclude an absolute calibration of the angular instrument function to the required accuracy. Here we have used a different method to demonstrate that it is possible to observe nondipole effects at the extremely low energy $\omega\alpha \approx 0.004$, where the effects are about 0.5%. We did this by looking for a sharp dipole-quadrupole resonant feature against a large but smoothly varying dipole autoionization background. In addition we find that a comparison with complementary $(e, 2e)$ experiments enables the extraction of the phase shift due to charged particle impact ionization.

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