

Circular dichroism in photoelectron angular distributions from adsorbed atoms

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The theory of circular dichroism in the photoelectron angular distributions (CDAD) of oriented linear molecules is applied to the photoionization of adsorbed atoms. CDAD is shown to offer much greater detail about the atom than is available from standard angle-resolved photoionization studies. For oriented atomic orbitals, CDAD is shown to arise solely from interference between the $l \rightarrow l+1$ and $l \rightarrow l-1$ photoionization channels. In addition, for both adsorbed atoms and oriented molecules, CDAD is shown to arise entirely from the non-plane-wave nature of the final state. A simple calculation of CDAD from an oxygen-atom p orbital is given.

INTRODUCTION

Circular dichroism is a phenomenon in which the response of a system to left and right circularly polarized light is different. In a recent report,¹ we showed that circular dichroism in the photoelectron angular distributions (CDAD) from oriented linear molecules exists in the electric dipole approximation. In the present work, we point out that CDAD can be used to study atoms adsorbed on surfaces. While previous workers have discussed CDAD from molecules,² only one other worker has considered CDAD from atoms in the single-photon case. Parzyński³ showed that CDAD exists for strongly polarized alkali atoms in the presence of a magnetic field only when spin-orbit coupling is important. Here we show that CDAD exists from adsorbed atoms in the absence of any spin-orbit interaction. In addition, we show that CDAD from both adsorbed atoms and oriented linear molecules arises solely from the non-plane-wave nature of the final state.

When an atom is adsorbed on a surface, the orbitals other than s orbitals are no longer necessarily degenerate.⁴⁻⁶ For the case of an atom adsorbed at a fourfold site on the surface, the energy of the p_z orbital (perpendicular to the surface) will, in general, be different from that of the p_x, p_y pair. This p_z orbital is then an example of an atomic orbital of fixed spatial orientation. Grimley,⁵ Herbst,⁶ and Goldberg, Fadley, and Kono⁷ have considered angle-resolved photoelectron spectroscopy (ARPES) from oriented atomic p orbitals. In the present work, we will examine CDAD in the same spirit. The magnitude of the effect is illustrated by a simple calculation for an oriented oxygen p orbital.

THEORY

The formalism for CDAD has been developed in Ref. 1. For convenience, we consider the one-electron case. The final form for the difference in the differential cross section for left and right circularly polarized light D_{L-R} is

$$D_{L-R} = \frac{16\pi^2 E}{c\sqrt{3}} \langle 11-1 | 10 \rangle \sum_{L=0}^{2l_{\max}} (2L+1)^{-1/2} \sum_{\substack{l, m, \mu \\ l', m', \mu'}} (-1)^{m+\mu} [(2l+1)(2l'+1)]^{1/2} \\ \times \langle l'00 | L0 \rangle \langle l' - m m' | L-1 \rangle \langle 11 - \mu \mu' | 11 \rangle \\ \times \text{Im}(I_{lm\mu} I_{l'm'\mu'}^*) \text{Im}[Y_{L-1}(\theta_k, \phi_k) Y_{11}(\theta_p, \phi_p)] , \quad (1)$$

where E is the photon energy, c is the speed of light, and $I_{lm\mu}$ is the dynamical coefficient defined in Ref. 1 containing the radial matrix element. The angles (θ_p, ϕ_p) , (θ_k, ϕ_k) are the photon-propagation and electron-collection directions, respectively, measured relative to the atomic z axis. For an atom adsorbed on a surface we define this axis to be perpendicular to the surface plane.

Four important features of CDAD from oriented atomic orbitals follow from Eq. (1). The first three have been discussed in Ref. 1 and will therefore just be stated:

(i) CDAD is due only to interference terms between degenerate photoelectron continua differing by ± 1 in their m values ($\Delta m = m' - m = \pm 1$).

(ii) CDAD vanishes if \hat{k} , \hat{p} , and the axis of the atomic orbital are coplanar.

(iii) CDAD does not exist in the reflection plane perpendicular to the axis of the atomic orbital.

The fourth feature is unique to CDAD from adsorbed atoms.

(iv) CDAD from oriented atomic orbitals arises solely from interference between the $l'' \rightarrow l''+1$ and $l'' \rightarrow l''-1$ photoionization channels. This result arises from a combination of factors. First, a transition from an initial state l'' can only result in a final state $l'' \pm 1$ by the dipole selection rule. As shown in Eq. (1), CDAD is a result of interference terms $\text{Im}(I_{lm\mu} I_{l'm'\mu'}^*)$, where l and l' represent orbital angular moments of the final states. Because the imaginary part of the product of the two dynamical coefficients is proportional to $\sin(\delta_l - \delta_{l'})$ where $\delta_l, \delta_{l'}$ are the partial-wave phase shifts of the continuum wave functions, CDAD

will vanish for $l=l'$. As a result, only interference terms for which $l \neq l'$ will contribute to CDAD; for an initial l'' , CDAD will arise solely from the interference of the $l'' \rightarrow l''+1$ and $l'' \rightarrow l''-1$ photoionization channels. This rule does not apply to oriented linear molecules, since in that case the phase shifts depend on both l and m and the initial states are not described by a well-defined l'' . Note that ARPES studies with linearly polarized light supply information about the cosine of the phase-shift difference. In this respect, CDAD nicely complements ARPES studies.

Finally, we comment on the feature that CDAD will not exist for plane-wave final states. A plane-wave final state has no "memory" of the symmetry of the initial state or the polarization of the incoming photon. That CDAD vanishes for this reason can be derived simply as follows: The double differential cross section D is

$$D \propto |\langle f | \mathbf{A} \cdot \mathbf{p} | i \rangle|^2, \quad (2)$$

where $\mathbf{A} = \hat{\epsilon} A_0 e^{i\mathbf{q} \cdot \mathbf{r}} \approx A_0 \hat{\epsilon}$ in the electric dipole approximation and $\mathbf{p} = -i\hbar \nabla$. $\hat{\epsilon}$ is the unit polarization vector of the photon. The initial state is unimportant for now and may be that of an adsorbed atom or an oriented linear molecule. If the final state is a plane wave,⁵ then $|f\rangle = e^{i\mathbf{k} \cdot \mathbf{r}}$ (ignoring normalization) and operating with ∇ on $|f\rangle$,

$$|\langle f | \mathbf{A} \cdot \mathbf{p} | i \rangle|^2 = |\hat{\epsilon} \cdot \mathbf{k}|^2 |\langle e^{i\mathbf{k} \cdot \mathbf{r}} | i \rangle|^2. \quad (3)$$

From this expression one can see immediately that for plane-wave final state CDAD does not exist in the electric dipole approximation, since $|\hat{\epsilon} \cdot \mathbf{k}|^2$ is identical for left and right circularly polarized light. For non-plane-wave final states, however, Eq. (2) cannot be factored into the simple form of Eq. (3), and the differential cross section for left and right circularly polarized light will not necessarily be equal. Thus, CDAD is a direct consequence of the non-plane-wave nature of the final state.

CDAD FROM p ORBITALS

Consider the adsorption of an atom to a surface at a four-fold site. In this case, the p_z orbital of the adatom is no longer degenerate in energy with the p_x, p_y pair.⁴⁻⁶ Photoionization from this p_z orbital occurs through the following pathways:

$$\begin{aligned} P_z &\rightarrow ks(00) \\ &\rightarrow kd(20) \\ &\rightarrow kd(21) \\ &\rightarrow kd(2-1), \end{aligned}$$

where the numbers in the parentheses are the (lm) values for the continuum states. The expression for ARPES (Ref. 1) then consists of the following combinations of dynamical coefficients [recalling that $I_{lm\mu} = I_{l-m-\mu}$ and symbolically representing the combination $I_{lm\mu} I_{l'm'\mu}^*$ as $(lm) \times (l'm')$]:

$$\begin{aligned} &(00) \times (00) \quad (00) \times (20) \\ &(20) \times (20) \quad (00) \times (21) \\ &(21) \times (21) \quad (20) \times (21). \end{aligned}$$

Thus, although the degeneracy between the p_z orbital and the p_x, p_y pair has been broken by the interaction with the

surface, ARPES still contains contributions from many terms.

Now consider the terms which contribute to CDAD. From the features of CDAD discussed earlier, only one of the above terms contributes,

$$(00) \times (21).$$

CDAD from an adatom p_z orbital contains information solely about interference between the $p_z \rightarrow ks(00)$ and $p_z \rightarrow kd(21)$ [or $kd(2-1)$ channels]. This information is masked in ARPES.

The angular dependence of CDAD from adatom p orbitals may be derived simply. Due to the Clebsch-Gordon coefficient $\langle ll'00|LO\rangle$, CDAD exists only for $L=2$. The angular dependence is then $\sin(2\theta_k) \sin\theta_p \sin(\phi_p - \phi_k)$. For the collection plane at right angles to the incident plane ($\phi_p - \phi_k = 90^\circ$) CDAD will be maximized and will depend on the collection angle θ_k as $\sin(2\theta_k)$. (Both the incident and collection plane are assumed to include the z axis defined previously.)

In Fig. 1, we show the ARPES and CDAD spectra at 21.2 eV for photoionization from an oriented p orbital (along the z axis) of an oxygen atom. The radial matrix elements and phase shifts for the continuum functions were obtained from Ref. 7. The collection plane is at right angles to the incident plane. Note that the CDAD spectrum has the expected $\sin(2\theta_k)$ dependence. The magnitude of the spectrum is roughly half that of the ARPES spectra. This result follows from the fact that, in general, the $p \rightarrow kd$ transition is more intense than the $p \rightarrow ks$ transition,^{7,8} and while the magnitude of the ARPES spectra depends roughly on $|\langle p|\mu|kd\rangle|^2$, the CDAD spectrum depends on the interference term $|\langle p|\mu|kd\rangle| |\langle p|\mu|ks\rangle|$.

What about CDAD from the p_x, p_y pair? CDAD from this pair will be the same magnitude as CDAD from the p_z orbital but opposite in sign. This result follows from the fact that, when taken together, the three unperturbed p orbitals form a spherical initial state. CDAD from the three

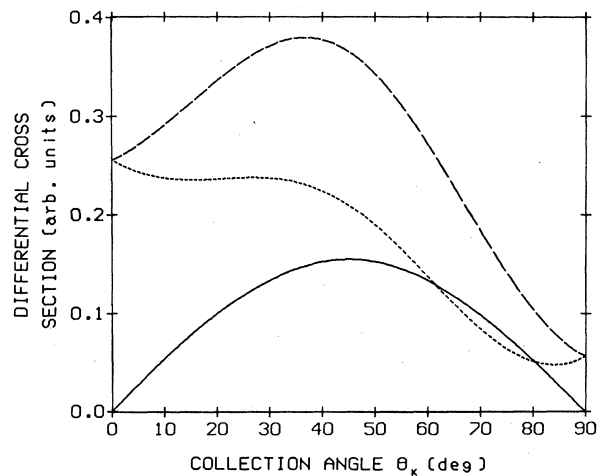


FIG. 1. Differential cross section vs the collection angle θ_k for left and right circularly polarized light and CDAD. Left (—), right (---), CDAD (left-right) (—). Photon-propagation direction is $(\theta_p, \phi_p) = (135^\circ, 0^\circ)$ and electron collection is in the plane $\phi_k = 90^\circ$. Photon energy is 21.2 eV.

orbitals together must thus vanish.

Admittedly, exploring CDAD from adsorbed atoms by using unperturbed, oriented atomic orbitals is a crude first step. Nevertheless, that CDAD does exist from these atomic orbitals is an interesting and useful fact. Bonding of the adatom to the surface can be considered along the lines of Gadzuk's treatment⁹ for studying ARPES from adsorbed atoms. In this way, CDAD can be used to probe the orbitals of the surface atoms involved in bonding. In addition, we have only examined CDAD from *p* orbitals; the present treatment can easily be extended to *d* orbitals, etc.

In conclusion, we have shown that CDAD arises from atoms adsorbed on surfaces and that CDAD offers more detailed information than is provided by standard ARPES studies. CDAD from oriented atomic orbitals arises solely

from interference between the $l \rightarrow l+1$ and $l \rightarrow l-1$ photoionization channels. For both adsorbed atoms and oriented linear molecules CDAD has been shown to arise solely from the non-plane-wave nature of the final state. Finally, because standard ARPES studies provide information about the cosine of the phase-shift differences, while CDAD provides information about the sine of these differences, CDAD studies should nicely complement ARPES studies.

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