

Circular Dichroism in the Angular Distribution of Photoelectrons from Oriented CO Molecules

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Theoretical predictions of a new phenomenon arising in photoelectron emission from oriented molecules by circularly polarized light have been experimentally verified for CO. For a special geometry photoelectron-intensity differences occur upon reversal of photon helicity. The measured asymmetries (up to 80%) show good agreement with an *ab initio* calculation at photon energies between 20 and 40 eV. Theoretically, the new manifestation of circular dichroism is already obtained in the pure electric dipole approximation without inclusion of spin-orbit interaction.

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In recent years several theoretical investigations¹⁻⁵ have predicted circular dichroism (CD) in photoemission, a phenomenon leading to different photoelectron intensities when the ionizing light is either left- or right-circularly polarized. Regarding its outward appearance, this effect shows complete analogy to the "classical" CD in *photoabsorption*,⁶ well known for optically active molecules without a plane or center of symmetry. Classical CD is described by an interference of electric and magnetic dipole transitions. Consequently, the measured asymmetries are relatively weak.⁷

For obvious reasons, CD with chiral molecules should be visible in *photoemission* as well. Ritchie¹ first pointed out that nonchiral molecules also might show a circular dichroism in the angular distribution (CDAD) of photoelectrons if they are fixed in space (we will call this spatially oriented). Cherepkov² found that for all fixed molecules CDAD occurs in the electric dipole approximation. Proceeding from this important result he predicted that CDAD asymmetries are of the same order of magnitude as the differential cross section itself and hence should be easily observable in a photoemission experiment.

A numerical model calculation of CDAD in photoemission from the 4σ orbital of spatially oriented CO was performed by Dubs, Dixit, and McKoy.³ The calculation showed pronounced CDAD features with huge maxima of almost 100% asymmetry. It is the purpose of our Letter to report the experimental verification of the general predictions of this new effect and to present a quantitative comparison between *ab initio* theory and experiment.

Possible ways to obtain a molecular orientation or alignment in a photoemission experiment are the use of an external electrostatic hexapole field⁸ or optical pumping to an excited state with polarized laser light.⁹ The first technique especially is rather involved and yields only relatively low target densities and an incomplete orientation. In resonant two-photon photoionization of NO molecules a CDAD due to partial alignment of the intermediate state has been reported recently.⁹ We

chose to fix CO molecules by adsorption on a single-crystal metal surface, which yields a perfectly oriented ensemble of molecules with the carbon end pointing towards the metal.¹⁰ Thus it is possible to obtain a very high target density, about 2 orders of magnitude higher than in the gas phase, resulting in huge photoelectron intensities. Of course, a certain disadvantage of this method is that the mutual interaction of the molecules and their bonding to the surface must be taken into account.

Nonchiral molecules can only show CDAD in photoemission if the experimental arrangement has a definite chirality.¹⁻⁵ It is the proper choice of electron collection and photon propagation direction which breaks the symmetry of the target and gives rise to dichroic effects. A schematic drawing of our experimental arrangement is shown in Fig. 1. The axes of the uniformly oriented CO molecules form an angle of 50° with the incoming light beam. The direction of observation is denoted by \mathbf{k}_e , i.e., the momentum of the electron. Note the different azimuthal planes of photon incidence and photoelectron collection.

As a circularly polarized light source for photon ener-

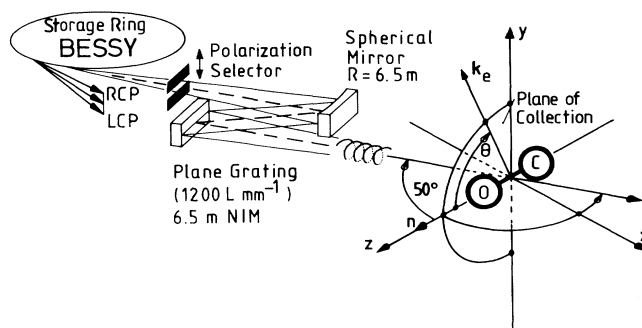


FIG. 1. Schematic drawing of the experimental geometry at the 6.5-m normal-incidence monochromator (NIM) at BESSY. Molecular axis \mathbf{n} and incoming light beam span a plane perpendicular to the plane of photoelectron collection, by \mathbf{n} and the photoelectron momentum \mathbf{k}_e .

gies up to 40 eV we used the synchrotron radiation from the 6.5-m normal-incidence monochromator¹¹ at the storage ring BESSY in Berlin. As indicated in Fig. 1, an upper and a lower beam stop at the entrance of the monochromator can be driven up or down to select the degree and helicity of polarization. The two beam stops define a horizontal slit of variable width. If the slit lies in the plane of the storage ring, linearly polarized light is obtained, if it lies above or below, right- or left-circularly polarized light is transmitted (RCP or LCP, respectively). The monochromator consists of a spherical mirror and a plane grating. Its maximum intensity at $h\nu=30$ eV is 8×10^{11} photons/sec (for a 500-mA stored beam), the circular polarization was set to 92% and the bandwidth was 0.5 nm. The photoelectrons were collected at a variable polar angle θ , energy analyzed by an electron spectrometer, and detected by a Channeltron multiplier. The spectrometer was a simulated hemispherical condenser with an angular acceptance cone of $\pm 3^\circ$ and an overall energy resolution (electrons and photons) of better than 200 meV. Magnetic fields were compensated to less than $0.1 \mu\text{T}$ by three pairs of Helmholtz coils in addition to two layers of Mumetal foil.

The substrate was a Pd(111) crystal which was cleaned by repeated cycles of argon-ion sputtering, heating in oxygen to remove carbon contaminations, and flashing to about 1100 K. The clean surface was characterized by LEED. CO was dosed to the crystal until saturation coverage at room temperature. The base pressure during measurement was in the 10^{-10} -mbar range.

Figure 2 shows typical spectra of CO on Pd(111) for left- and right-circularly polarized light, taken at a photon energy of $h\nu=30.7$ eV and an emission angle of $\theta=40^\circ$. As denoted in this figure, the adsorbate-induced structures correspond to CO 4σ and 5σ and in the shoulder of the latter peak Co 1π .¹⁰ These adsorbate features

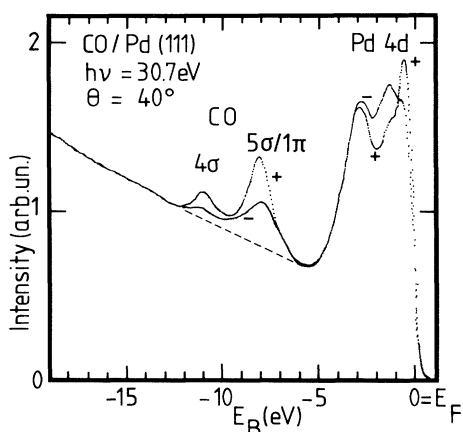


FIG. 2. Typical photoelectron spectra of CO on Pd(111) illustrating CDAD. + and - denote right- and left-handed circularly polarized light, respectively. The binding-energy scale refers to the Fermi energy E_F of the substrate crystal. Dashed lines, see text.

are riding on the typical smooth background of secondary electrons (dashed line) from the Pd $4d$ -band photoemission close to the Fermi energy E_F . The photoelectron intensities of CO 4σ and $5\sigma, 1\pi$ indeed show the predicted substantial difference for the two photon helicities. The secondary electrons do not show this dependence because they have been scattered in the crystal several times and have lost their former angular distribution before they reached the surface. The CDAD features in the Pd $4d$ bands (near E_F) will be discussed elsewhere.

Data acquisition was done by a microcomputer which accumulated the spectra in the multichannel scaling mode with a 50-meV energy increment. All spectra were normalized to the intensity of the vacuum-ultraviolet radiation from the storage ring. For comparison with theory, we define a CDAD asymmetry as

$$A_{\text{CDAD}}(\theta) = [I^+(\theta) - I^-(\theta)] / [I^+(\theta) + I^-(\theta)], \quad (1)$$

where $I^+(\theta)$ [$I^-(\theta)$] denotes the photoelectron intensity for right- (left-) circularly polarized light. In this definition it is not necessary to measure absolute cross sections, which is experimentally problematic. The CDAD data shown below represent the peak heights above an assumed linear background (dashed line), which yielded the same results as the peak areas within the experimental uncertainties. The linear background underlying the adsorbate peaks is reasonable because the clean Pd spectrum shows this featureless linear background too. Since theory³ assumed 100% photon polarization and an angle of incidence of 45° (experimentally $92 \pm 2\%$ and $50 \pm 1^\circ$, respectively), a small correction factor entered into the figures.

Figure 3 shows the CDAD signal as a function of θ for photoemission from CO 4σ at different photon energies together with the theoretical calculation (solid curve³). The experiment clearly confirms the general prediction² that CDAD is for all energies of the same order of magnitude as the differential cross section itself. There is reasonable agreement with the numerical calculation³ concerning the general behavior of the angular and energy dependences; only at higher collection angles do substantial deviations become apparent. Because of its symmetry properties, CDAD is an odd function of the emission angle θ . The asymmetries rise with increasing photon energy until around $h\nu=30.7$ eV a maximum of 80% (theoretically almost 100%) is reached. At higher energies a marked drop appears around $\theta=55^\circ$ as a consequence of a shape resonance¹⁰ centered around $h\nu=36$ eV, which governs CO 4σ photoemission in this region.

The behavior of the experimental data at large collection angles needs to be discussed. A source of systematic quantitative deviations from theory is the existence of the (electrostatic) surface barrier. For comparison with the calculation valid for *one isolated CO molecule fixed in space*, the angle of detection in the experiment had to

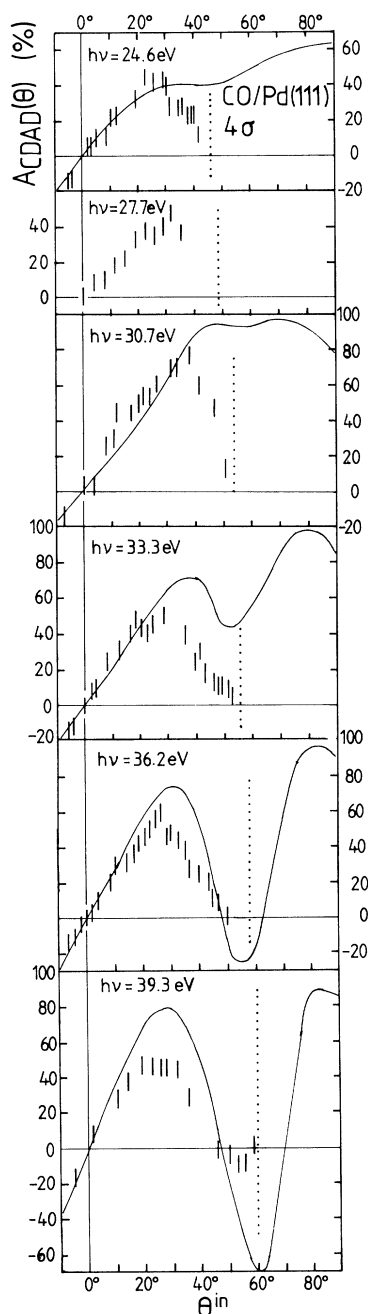


FIG. 3. Circular dichroism in the angular distribution (CDAD) for CO(4σ) on Pd(111) at different photon energies. The error bars represent the experimental uncertainty including counting statistics and reproducibility. Full lines show the theoretical calculation for isolated spatially fixed CO (Ref. 3). At the vertical dashed lines total internal reflection occurs at the surface barrier.

be corrected for the refraction of the outgoing photoelectrons at the surface barrier. This is done by assuming a region of constant potential between crystal surface and vacuum.¹² For CO we found a reduced inner potential

of -8 eV to account for this effect in a reasonable way. The vertical dashed lines denote the angle where total internal reflection starts. Obviously, already 15° below this angle a decrease of CDAD set in (cf. $h\nu = 24.6$ and 30.7 eV). Another systematic difference between theory and experiment is that the calculation³ was done for a gas-phase CO molecule with a 4σ ionization potential of 19.7 eV, whereas at the palladium surface the binding energy is reduced to 16.3 ± 0.3 eV due to screening of the ionic state. Further reasons for quantitative deviations are the mutual interaction of neighbor molecules and the chemical bond to the substrate. However, both influences are expected to be quite weak for 4σ , being the lone-pair orbital located at the oxygen atom.

From the theoretical treatments^{2,3,5} we recall some general properties of CDAD illuminating its physical origin. The occurrence of CDAD in photoemission is a consequence of the *interference of degenerate photoelectron continua differing in their m values by ± 1* . This can be seen in the theoretical expression of CDAD: It contains a sum over terms like $\text{Im}\{I_{l,m,\mu} I_{l',m',\mu'}^*\}$, where $I_{l,m,\mu}$ ($I_{l',m',\mu'}$) are the dynamical coefficients describing the transition to the two interfering photoelectron continua. The subscripts l,m (l',m') and μ (μ') denote the angular momentum quantum numbers and helicity subscripts, respectively. For photoemission from CO 4σ this expression simplifies because only the two reaction channels $4\sigma \rightarrow k\sigma$ and $4\sigma \rightarrow k\pi$ are allowed. The imaginary part is then proportional to the sine of the relative phase-shift difference.

The photon energy determines which of the two final-state channels, $4\sigma \rightarrow k\sigma$ or $4\sigma \rightarrow k\pi$, dominates. Normally, the cross section of the π channel is larger than that of the σ channel, except in the vicinity of $h\nu = 36$ eV, where the matrix element of the σ channel goes through a shape resonance.¹³ This resonance is known to be associated with the $l=3$ partial wave of the outgoing electron in the continuum. The interference of partial waves with angular parts Y_{30} and Y_{11} ($l=1,2,3$) is the origin of the marked drop of CDAD at energies above $h\nu = 33.3$ eV.

In conclusion, we have experimentally verified a circular dichroism in the angular distribution (CDAD) of photoelectrons for spatially oriented CO molecules adsorbed on a surface. The measured asymmetries reach high values of up to 80% confirming the general prediction² that CDAD occurs already in the pure electric-dipole approximation. The angular and energy dependences are in good agreement with a numerical *ab initio* calculation³ for the 4σ orbital. Although we have demonstrated CDAD by the example of CO, there is both theoretical and experimental evidence that the new phenomenon occurs for *all spatially oriented species* including aligned atoms,⁴ and even clean surfaces.

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