Circular dichroism in X-ray photoemission from Pd(111) and CO/Pd(111)

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Abstract. It is shown experimentally that in the soft X-ray region a large circular dichroism in the photoelectron angular distribution (CDAD) exists for both valence orbitals and core levels of CO molecules adsorbed on Pd(111). From theoretical consideration it follows that in the case of a spherically symmetric ground state wave function, like the 1σ and 2σ orbitals of CO, CDAD appears due to the lack of spherical symmetry in the final state. For carbon K-shell experimental results are compared to model calculations. Investigations at the Pd core levels proved that CDAD does also arise in X-ray photoemission from non-magnetic crystals.

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1 Introduction

The phenomenon of Circular Dichroism in the Angular Distribution of photoelectrons (CDAD) has been theoretically and experimentally investigated during the last years. CDAD is the difference between photoelectron currents ejected by left and right circularly polarized radiation at a definite angle. It can be considered as a kind of optical activity. The first theoretical prediction of CDAD for molecules fixed-in-space was done by Ritchie [1]. He investigated photoionization of diatomic molecules for the particular geometry of the experiment when the incoming light is parallel to the molecular axis. For this geometry, CDAD is a consequence of the interference between electric-dipole and magnetic-dipole terms and is small, of the order of the fine structure constant α, just like the usual optical activity [2]. Some years later Cherepkov [3] showed that for the “chiral” geometry, with the incoming photon beam, the molecular axis, and the direction of the outgoing electrons being not coplanar, CDAD from diatomic molecules already appears in the electric-dipole approximation and therefore does not contain any small parameter.

The first numerical calculations, carried out by Dubs et al. [4] for a spatially fixed CO molecule, showed a huge CDAD effect with asymmetry values of nearly 100%. They have also shown that CDAD exists for aligned or oriented molecules in the gas phase. Appling et al. [5, 7] verified the existence of the predicted phenomenon for NO molecules being aligned by laser excitation. For spatially fixed molecules, such as CO, NO, C6H6, and CH3I, Westphal et al. [6, 8] observed large CDAD effects. In these experiments, the molecules were oriented by adsorption on single crystal surfaces yielding at the same time a high target density as well as a nearly perfect orientation. For photon energies below ℏν = 40 eV, the experimental results [6] for the valence orbitals of CO/Pd(111) confirmed first theoretical ab-initio calculations [4]. This limit in the photon energy range was given by the normal-incidence optics of the 6.5 m NIM monochromator at the storage ring BESSY in Berlin. CDAD results for single crystal surfaces such as graphite(0001) and palladium(111) were obtained by Schönhense et al. [9, 10].

In all previous investigations of CDAD, the outer shells of molecules have been ionized. In this paper we show for the first time that even for K shells the CDAD effect remains as large as for the outer shells. In principle, CDAD only appears if the object is not spherically symmetric. The carbon and oxygen K shells of CO molecules remain to a good approximation spherically symmetric. It means that CDAD from K shells appears mainly due to the absence of spherical symmetry in the final state, that is due to the anisotropic environment of the emitter atom. The availability of circularly polarized synchrotron radiation in the soft X-ray region using the SX 700/3 monochromator of BESSY opened up the possibility to study CDAD directly at the carbon and oxygen K shells of CO molecules fixed on a single crystal surface. First results have been presented in [11].
2 Theory

In classical optics, circular dichroism is defined as the difference in absorption of left and right circularly polarized light [2]. By analogy, a difference between photoelectron fluxes ejected by left and right circularly polarized light at a definite angle is called circular dichroism in the angular distribution of photoelectrons [1]. The equations describing CDAD from oriented linear molecules have been presented elsewhere [3,4,8,12], therefore we will give here only a short description with the emphasis on the particular case of K shell photoionization.

The process of photoionization of fixed-in-space molecules is characterized by three vectors, namely, by the vector \( \mathbf{n} \) in the direction of the molecular axis, the vector \( \mathbf{k} \) in the direction of outgoing electrons (all three vectors have unit length). Suppose that the laboratory vector \( \mathbf{n} \) defines the laboratory Z axis. Then the angular frame is defined by the molecular orientation, so that the three vectors \( \mathbf{n}, \mathbf{k}, \mathbf{q} \) have in (3) the interference of partial waves with projections \( m \) of the angular momentum differing by 1, \( \Delta m = \pm 1 \) [4], we have in (3) the interference of \( \mathbf{pe} \) and \( \mathbf{pe} \) waves.

The complex dipole matrix element can be presented in the form

\[
\langle \mathbf{pm} | d_m | 0 \rangle = d_m \cdot e^{i \delta_m}
\]

(4)

where \( d_m \) is its real part and \( \delta_m (\delta_e \text{ or } \delta_s) \) is the phase shift. Then

\[
A_{2-1}^{11} = \frac{3\sqrt{2}}{\sqrt{5}} \frac{x \sin(\delta_e - \delta_s)}{2 + x^2}
\]

(5)

where \( x = d_e/d_s \). For a spherically symmetric final state \( \delta_e = \delta_s \) and CDAD vanishes, while the spherical symmetry of the initial state alone does not lead to the absence of CDAD.

For the theoretical estimation of CDAD, the quasiatomic description of the CO molecule is used as it was proposed in [14, 15]. In this approach the photoionization cross section of the carbon K shell for an adsorbed CO molecule is presented as

\[
\sigma = \frac{1}{3} \sigma^a(1s) \cdot (M_e + 2M_s)
\]

(6)

where \( \sigma^a \) (1s) is the atomic carbon 1s photoionization cross section, and \( M_e \) and \( M_s \) are the values which describe the changes in the spectral variation of the atomic cross section due to the influence of surroundings. The influence of the substrate was completely neglected and only the scattering from the oxygen atom was included. The oxygen atom was described by a model Heine-Abarekrov potential which was expanded in multipoles relative to the center of the carbon atom, and terms up to the quadrupole one were retained. The plane wave expansion was used for the photoelectron wave function, and the admixture of higher \( \ell \) partial waves to the \( p \) wave was neglected. This simple model gives the phase shift difference \( \delta_e - \delta_s \) and the ratio of dipole matrix elements \( x \).

The goal of our model calculation was to show that CDAD can appear even from a spherically symmetric ground state, if in the final state the spherical symmetry is broken. In a more realistic model, one should start from the Hartree-Fock molecular wave functions as it was done in [4, 8] which include the scattering effect considered in our quasiatomic calculation. Then one should take into account also a backscattering from the surface [16] as well as nuclear degrees of freedom of adsorbed molecules.