Toward Valence-Level Photoelectron Distributions: Application to Oriented Diatomic Molecules and the Study of Shape Resonances

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INTRODUCTION

The near-term aim of this project is to develop the capability to interpret photoelectron diffraction intensities measured at low final-state energies for any system, including molecules, surfaces and interfaces. This will provide sensitivity to electronic bonding information and allow its extraction from experiment.

We use multiple scattering photoelectron diffraction theory to calculate the angular distribution of electrons photoemitted from core levels of fixed-in-space molecules of carbon monoxide (CO) at <u>low</u> final-state energies. These can be compared, for example, with data measured at the ALS by the COLTRIMS collaboration [1], as well as prior data [2].

METHOD

Non-spherical scattering potentials, needed for low photoelectron energies ($E < 50$ eV), are included in our formalism through non-diagonal scattering matrices; these fit directly into our recent approaches for multiple scattering theory originally based on spherical potentials [3, 4].

In addition, we have considered the effect of the final-state hole, and found this to be important as well. As an excellent test, we calculate the angular distribution of photoelectrons emitted from the K shells of C in oriented gas-phase CO molecules, as recently measured by several groups. Particularly important are the energies for which shape resonances appear in the continuum, with the angular distributions showing radical changes across such resonances.

EXAMPLES OF THEORETICAL RESULTS

Figure 1 shows the sensitivity that we can obtain to methods of treating the molecular potential that an emitted photoelectron feels. By fitting the calculation to experiment, it is thus possible to extract valuable information about the potential felt by the electron, and thereby about the electronic structure of the valence electrons.

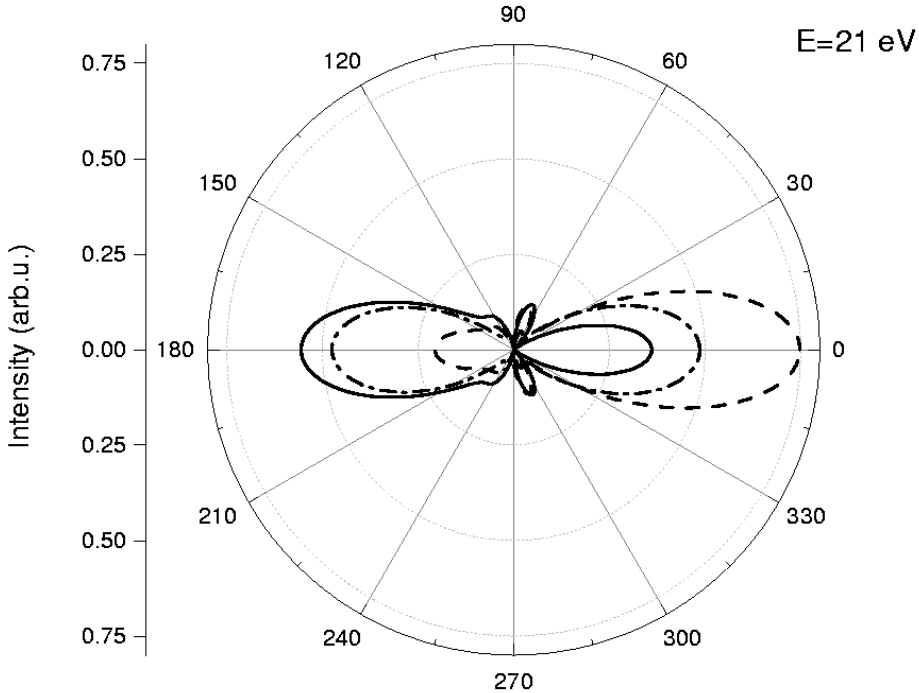

Fig. 1. Theoretical calculation of the angular distribution of electrons photoemitted from the K shell of C in CO. Three different models (defined in the text) are included: NSMS, solid line; MTMS, dash-dotted line; and AMS, dashed line. The potential corresponds to a CO molecule, with a radius of 1.8 atomic units. The carbon end of the molecule points toward 180°. The polarization of the light is parallel to the molecular axis.

Figure 1 compares the theoretical calculation of the angular distribution of photoelectrons emitted from the K shell of C in CO using our method (Non-Spherical Multiple Scattering, NSMS) with two other models based on spherical non-overlapping potentials. The results labeled as AMS (Atomic Multiple Scattering) have been obtained using two atomic spherical potentials calculated at the same level of approximation, with touching radii. The results labeled as MTMS (Muffin-Tin Multiple Scattering) use a similar model, but the origin of energies is shifted to avoid 'potential walls' surrounding the atoms. The kinetic energy of the electrons is shifted accordingly.

An interesting situation arises when the kinetic energy of the electron passes through a shape resonance of the molecule: then the angular distribution of photoelectrons changes drastically and rapidly. This increases the sensitivity to the scattering potential. This situation is illustrated in figure 2. The shape of the angular pattern is quite similar to experiment [1, 5].

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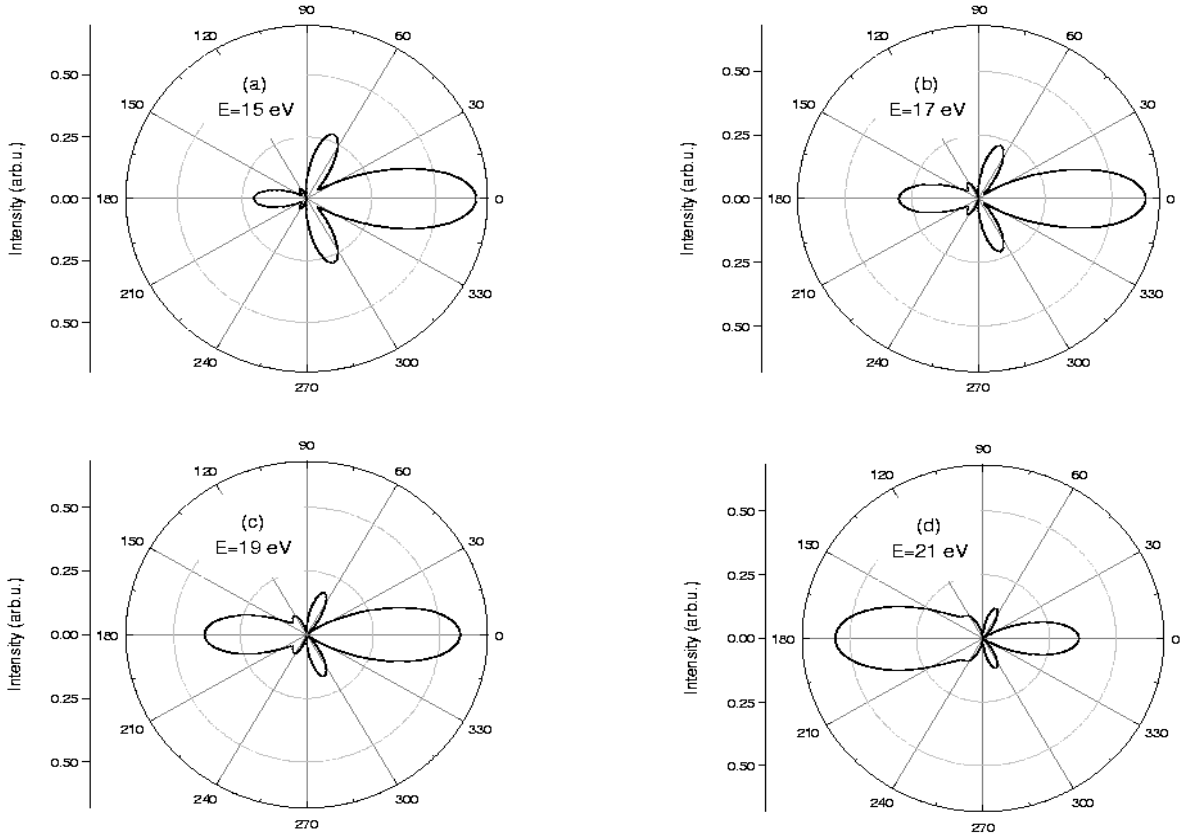

Figure 2. Theoretical calculation of the angular distribution of electrons photoemitted from the K shell of C in CO, using our NSMS method, at different electron kinetic energies E. Other parameters as for figure 1.

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