

X-ray absorption near the edge

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Abstract

This thesis is devoted to the theoretical study of X-ray absorption phenomena near the ionization edges. It presents results from computational modeling of Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectra of a number of organic compounds including some polymers, amino acids, carbon nitrides and heterocycles.

Character and trends of the investigated NEXAFS spectra have been analyzed and the spectra are assessed in terms of the individual excitation channels and *building blocks*. A few functional groups unique for particular compounds are suggested as good building blocks, because their energy positions and intensities in the spectra are not scrambled by the contributions from other excitation channels. The notion of building blocks essentially simplifies the analysis of theoretical and experimental spectra and can fingerprint the compounds in question.

Another important part of the present study is related to the phenomenon of natural circular dichroism (CD) in X-ray absorption. It has been investigated starting from the simple models of twisted ethylene and propylene oxide to more complicated “real” molecular systems like trans-1,2-dimethylcyclopropane and amino acids. The CD effect for the carbon *K*-shell excitations was found to be quite small but not negligible and gives so a chance to fingerprint compounds.

Due to the nature of X-ray absorption below the ionization threshold, unique information about molecular orbital structure of chemical compounds can be experimentally and theoretically revealed from NEXAFS spectra. The polarization dependence of NEXAFS spectra also gives a clue to structure-to-property relations, especially to the orientation of molecules adsorbed on surfaces. This is illustrated for 10,11-dihydrocinchonidine (DHC) and 2-mercaptobenzoxazole (MBO) adsorbed on Pt(111). It is shown that while the adsorption of DHC occurs with the quinoline moiety more or less parallel to the (111) surface of Pt, the MBO molecules in the multilayer are strongly oriented with a tilt angle of about 48°.

In an attempt to predict high-resolution spectra, we have performed calculations of the vibrational contributions. Applicability of the linear coupling and equivalent core models has been demonstrated with respect to the full potential vibrational analysis and experimental spectra. The importance of the density of multi-mode vibrational states has been demonstrated and utilized in a continuum approach describing extended tails of NEXAFS bands.

The Hartree-Fock approach has been put in test *vs.* Density Functional Theory applied to the modeling and interpretation of NEXAFS spectra, but also to XPS and UPS spectra since these give the relevant edge information. The transition state Kohn-Sham (KS) density functional theory in the form of the unrestricted generalized transition state (UGTS) method has been compared with the separate state Δ KS and *ab initio* Δ SCF descriptions of X-ray photoelectron binding energies and chemical shifts.