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Theory of x-ray absorption and linear dichroism at the Ca L\textsubscript{2,3}-edge of CaCO\textsubscript{3}

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Abstract. X-ray absorption calculations of Ca L\textsubscript{2,3}-edge spectra of calcium carbonate in its two main crystal phases, calcite and aragonite, are reported. The multichannel multiple scattering theory with a correlated particle-hole wave function and a partially screened core-hole potential is used. Very good agreement with experiment for both CaCO\textsubscript{3} phases is obtained, while the independent particle approximation completely fails. For aragonite, appreciable linear dichroism is predicted in agreement with recent observations.

1. Introduction

Transition element L\textsubscript{2,3}-edge spectra are a major tool for probing the local structure and electronic properties around a metal site in crystals, molecules and nanomaterials. Systems with high point symmetry can be successfully modeled using the crystal field multiplet (CFM) model \cite{1}. In cubic symmetry there is only one crystal field parameter which can be meaningfully fitted to experiment. For lower symmetry, however, the number of free parameters increases quickly and the usefulness of the CFM model becomes questionable. Nanoparticles and composite systems often have very low symmetry. Through X-ray absorption spectroscopy at the L\textsubscript{2,3}-edge small structural and electronic variations at the metal site can be detected \cite{2}. However, without predictive computational methods the structural information cannot be extracted from the data. The development of first principles methods for transition element L\textsubscript{2,3}-edge spectra is thus highly desirable, but has been a long standing theoretical challenge mainly because of the strong atomic-multiplet-like configuration mixing induced by the core-hole in the final state. In the last decade, good progress has been made by a number of new approaches which may be divided into two categories. The first ones are full multiplet approaches where the basis states are Slater determinants of all electrons in d-like orbitals. These methods include small cluster quantum-chemistry schemes \cite{3} such as the complete active space method \cite{4} and the multiplet ligand-field theory using Wannier orbitals \cite{5}. The second class are particle-hole schemes, where configuration mixing is essentially restricted to the core-hole and the excited electron. This effect dominates for the light transition elements, especially for those with a formal (3d\textsuperscript{0}) configuration, where the spectral weight redistribution with respect to the independent particle approximation is largest. Particle-hole schemes include time-dependent density functional theory \cite{6}, the Bethe-Salpeter-Equation (BSE) \cite{7} approach and the multichannel multiple scattering (MCMS) theory developed by the present authors \cite{8, 9}. Note that the general MCMS theory \cite{10} is not limited to particle-hole wave functions, and we have recently devised a scheme for full multiplet coupling in
arbitrary open shell configurations [11]. MCMS inherits the flexibility and physical intuitiveness of standard multiple scattering, the most popular method for X-ray absorption calculations. Previously, we have shown that for light transition elements, MCMS gives excellent results [8, 9] equivalent to those of the BSE [7] but at a much lower computational cost. So far we have focused on bulk systems with rather high symmetry (cubic or tetragonal). Here we apply the MCMS method to systems of very low point symmetry, namely the calcium carbonate phases calcite and aragonite. We investigate the polarization dependence of the absorption spectra, and compare the results with recent experimental data [12, 13].

2. Computational

We use the MCMS method with particle-hole wave function [8, 9]. First, a standard multiple scattering calculation is carried out for the system without absorber which yields the reflectivity of the “environment”. In this real space calculation, the cluster size is increased until convergence of the spectra. For calcite (aragonite) we have used a cluster of 177 (176) atoms and 286 (68) empty spheres which were found largely converged. The atomic and empty sphere potentials have been generated using the local density approximation to density functional theory and the linear-muffin-tin-orbital code [14]. The ground state bulk potential is used for all atoms except the absorber. For the absorber atom, a partially screened core-hole potential is employed. It is a linear mixture $V = (1 - \alpha)V_s + \alpha V_u$ between the statically screened ($V_s$) and the unscreened ($V_u$) core-hole potential. $V_s$ is obtained from a self-consistent supercell calculation with a core-hole on a single Ca atom, i.e. it corresponds to the fully relaxed core-hole. The use of the one-electron Fermi’s golden rule and the potential $V_s$ (i.e. $\alpha = 0$) shall be called “final state rule” (FSR) below. $V_u$ is the sum of the ground state potential and the Hartree potential of the core-hole. $V_u$ is related to a sudden limit, in which the excited electron would feel the bare potential of the core-hole, before relaxation and screening set in [10]. The ratio $\alpha$ is the only empirical parameter of the present theory, and it turns out to be very robust, since we could describe all Ca and Ti compounds with the same value (0.1) [8, 9]. To take account of multiplet effects, i.e. configuration mixing, the $T$-matrix of the absorber atom is calculated using multichannel scattering theory with the variational R-matrix approach. By combining the reflectivity of the environment and the multichannel $T$-matrix, an exact embedding of the configuration-mixed particle-hole wave function into the first-principles electronic structure of the large cluster is achieved. Further theoretical details can be found in our previous articles [8, 9]. The calculated spectra have been shifted to match the experimental energy scale and are broadened with a Lorentzian and a Gaussian, both of 0.2 eV FWHM.

3. Results and discussion

Figure 1 (a,b) shows the local atomic structure around the Ca atom in calcite and aragonite. A central Ca atom and its CO$_3$ ligand units are shown. The point symmetry on the Ca sites is obviously very low. If only the first nearest oxygen atoms are considered, calcite has a weakly distorted octahedral coordination. Rez et al. [12] have modeled the calcite spectra using the CFM model assuming an octahedral crystal field and obtained good results for the unpolarized spectra. Recently, the linear dichroism was measured by the same group and found negligible for calcite [13]. In aragonite, Ca has a 9-fold O coordination, which was approximated by a tetragonal ligand field in the CFM calculations of Refs. [12, 13]. Good agreement with experiment was obtained for the unpolarized spectra, but the linear dichroism, clearly evident in the experimental data, couldn’t be explained with those CFM model calculations [13].

Figure 1 (c) shows the Ca L$_{23}$-edge spectra computed in the independent particle approximation using either the ground state (GS) potential or the statically screened potential $V_s$, corresponding to the FSR, along with the experimental data [12]. With the GS potential, the spectral features are very broad, which reflects the large Ca 3$d$ conduction band width. In
contrast, the experimental peaks are very sharp, which shows that these spectra are highly excitonic, i.e. the core-hole potential pulls the 3d resonance into the band gap, creating a fairly localized final state. This effect can partially be described by adding a fully relaxed core-hole according to the FSR as can be seen in Fig. 1 (c). The peaks in the FSR spectra are narrower than those of the GS spectra and thus the spectral shapes agree better with experiment. While this effect is weak for aragonite, it leads to a strong improvement in the case of calcite, where the FSR peaks are sharp and the relative peak positions agree quite well with experiment. The relative intensities of the four main peaks are, however, totally wrong. This is the case for all spectra obtained in the independent particle approximation, where the L3:L2 branching ratio is necessarily close to statistical (2:1), and thus more than twice larger than the experimental one. In conclusion, the highly excitonic character of the Ca-L$_{23}$-edge spectra can partially be accounted for by using FSR potentials, but all spectra obtained in the independent particle approximation have completely wrong peak intensities.

Figure 2 shows the multichannel calculations with a partially screened core-hole potential, using $\alpha = 0.1$ as in our previous calculations [8, 9]. The L3-L2 splitting (a–b) and in calcite also the T2g-Eg splittings (a1–a2 and b1–b2) are slightly overestimated as compared to experiment. Moreover, the theoretical spectra contain a few weak features not present in the data, namely a peak at 354.5 eV in calcite and shoulders around 350 and 354 eV in aragonite. Apart from these small differences, the agreement with the experimental data is very good in both phases.

Figure 3 shows the calculated spectra for linearly polarized X-rays along Cartesian axes x, y, z. Calcite (space group No. 167) has trigonal symmetry and so x and y polarizations are equivalent. In orthorhombic aragonite (space group No. 62), all three polarizations are different. In calcite the dichroism is negligible in agreement with experiment [13]. This reflects the fact that Ca has an almost perfect octahedral coordination, where all Ca-O bond lengths are identical within 0.1% and the bond angles differ from 90$^\circ$ by less than 3$^\circ$. In aragonite, however, marked linear dichroism is found. First, the main peak intensities are larger for x- than for y or z polarized light in agreement with the crystal field multiplet analysis in Ref. [13]. Second, peak “d” is clearly maximum for z-polarized light. This finding nicely agrees with experiment [13],
Figure 2. Ca L\textsubscript{233}-edge spectra of CaCO\textsubscript{3} computed in multichannel theory (MC) with $\alpha = 0.1$ vs experimental data (Exp) [12]. Peaks are labeled as in [13].

where an increase of the “d” peak was observed when the polarization was turned from the xy-plane to the z-axis.

4. Conclusions
In summary, we have theoretically studied Ca L\textsubscript{233}-edge spectra of CaCO\textsubscript{3} in its main crystal phases calcite and aragonite. Using the multichannel multiple scattering method with a partially screened core-hole potential, we have obtained good agreement with experiment in all cases while the independent particle approximation completely fails. Appreciable linear dichroism is predicted for aragonite which qualitatively agrees with the available experimental data.

References