Numerical quantification of the vibronic broadening of the SrTiO$_3$ Ti L-edge spectrum

KEITH GILMORE, ERIC SHIRLEY, National Institute of Standards and Technology — Calculations of x-ray absorption spectra are typically limited to obtaining the positions and intensities of spectral features, while simply adding broadening artificially to match experimental results. However, spectral widths hold valuable information on the coupling of the notional excited electronic state with the environment. The 2p$^5$3d$^1$ excited state of the Ti$^{4+}$ ion in SrTiO$_3$ experiences Jahn-Teller coupling to e$_g$ distortions of the oxygen cage. Such coupling broadens the electronic transition by involving a variable number of e$_g$ phonons. We quantify this broadening effect by solving a model Hamiltonian, taking parameters for the Hamiltonian from first-principles calculations. Comparison of numerical and experimental results indicates that this vibronic coupling accounts for the majority of the broadening observed for the L$_3$-edge, but only a minority of the L$_2$-edge spectral width.

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