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Effect of vibrations on the pre-edge features of x-ray absorption spectra

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The influence of atomic vibrations on x-ray absorption near edge structure (XANES) is calculated by assuming that vibrational energies are small with respect to the instrumental resolution. The resulting expression shows that, at the K -edge, vibrations enable electric dipole transitions to $3s$ and $3d$ final states. The theory is applied to the K -edge of Al in α -Al₂O₃ and of Ti in TiO₂ rutile and compared with experiment. At the Al K -edge, sizeable transitions towards $3s$ final states are obtained, leading to a clear improvement of the agreement with experimental spectra. At the Ti K -edge, electric dipole transitions towards $3d$ final states explain the temperature dependence of the pre-edge features.

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Vibronic coupling describes the interaction between electrons and atomic motions. It plays a prominent role in optical spectroscopy where it is the source of the color of many pigments and gemstones [1]. For instance, the red color of Black Prince's ruby is due to "d-d" transitions of chromium impurities in a spinel crystal. But these transitions are forbidden because chromium occupies an inversion center of the spinel lattice. They become allowed when vibrations break inversion symmetry.

In the x-ray range, vibrations far from the edge are taken into account through a Debye-Waller factor $e^{-2k^2\sigma^2}$ [2]. If the validity of this factor is assumed to extend to the near-edge region, where $k \simeq 0$, then vibrations seem negligible in XANES spectra.

However, three arguments indicate that vibronic coupling can be sizeable in the XANES region: (i) Vibronic coupling was detected by x-ray resonant scattering experiments at the Ge K -edge [3, 4]; (ii) Some XANES peaks seem to be due to forbidden transitions to $3s$ states, a prominent example being the Al K -edge in minerals [5]; (iii) A temperature dependence of the pre-edge structure was observed at the Ti K -edge in SrTiO₃ [6] and TiO₂ [7].

In the optical range, the effect of vibrations is usually taken into account through the Franck-Condon factors. In the x-ray range, Fujikawa and coll. showed in a series of papers of increasing sophistication [8, 9, 10] that the effect of the Franck-Condon factors can be represented by the convolution of the "phonon-less" x-ray absorption spectrum with the phonon spectral function. Such a convolution leads to a broadening of the peaks with increasing temperature but this effect is hardly observable in the pre-edge region.

Moreover, in the x-ray range it was shown that the large core-electron-phonon coupling of the $1s$ core hole of carbon in diamond induces a strong lattice distortion and significant anharmonic contributions [11].

The key observation is that all these effects can be easily taken into account if the vibrational energies are small with respect to the XANES spectral resolution (core hole

lifetime + instrumental resolution). This condition is certainly not satisfied at the C K -edge [11] but it becomes reasonable at the Al and Ti K -edges. In that range the XANES resolution is around one eV whereas the energy of vibrational modes is of the order of a few hundredths of eV although, of course, several phonons can be simultaneously present.

In this paper, we first use this observation to derive a manageable expression for the vibronically-coupled x-ray absorption spectra. Then, we apply the so-called *crude Born-Oppenheimer* approximation to further simplify this expression, so that only the core-hole motion remains. The resulting equation is compared with experiment in two different cases. At the Al K -edge in α -Al₂O₃ (corundum), vibrations induce transitions to $3s$ final states. These ($1s \rightarrow 3s$) monopole transitions explain a pre-edge peak that is completely absent from standard calculations. At the Ti K -edge in TiO₂, $1s \rightarrow 3d$ transitions are induced by vibrations. This explains why only the first two pre-edge peaks grow with temperature.

XANES formula within the Born-Oppenheimer framework. According to the Born-Oppenheimer approximation [12, 13], the wavefunction of the system of electrons and nuclei can be written as the product $\chi_n^j(\bar{\mathbf{Q}})\psi_n(\mathbf{r}; \bar{\mathbf{Q}})$, where \mathbf{r} is the electronic variable and $\bar{\mathbf{Q}} = (\mathbf{Q}_1, \dots, \mathbf{Q}_N)$ collectively denotes the position vectors of the N nuclei of the system. The electronic wavefunction $\psi_n(\mathbf{r}; \bar{\mathbf{Q}})$, with energy $\epsilon_n(\bar{\mathbf{Q}})$, describes the state of the electrons in a potential where the nuclei are fixed at position $\bar{\mathbf{Q}}$. The ground state corresponds to $n = 0$. The origin of the nuclear variables is chosen so that $\bar{\mathbf{Q}} = \mathbf{0}$ is the equilibrium position, i.e. $\epsilon_0(\mathbf{0})$ is the minimum of $\epsilon_0(\bar{\mathbf{Q}})$.

For each n , the vibrational wavefunctions $\chi_n^j(\bar{\mathbf{Q}})$ are the orthonormal solutions of the Schrödinger equation

$$(H_{\text{kin}}(\bar{\mathbf{Q}}) + \epsilon_n(\bar{\mathbf{Q}}))\chi_n^j(\bar{\mathbf{Q}}) = E_n^j\chi_n^j(\bar{\mathbf{Q}}).$$

The total energy of the electrons + nuclei system is E_n^j . Within the Born-Oppenheimer approximation, the x-ray

absorption cross-section is

$$\sigma(\omega) = 4\pi^2\alpha_0\hbar\omega \sum_{fj} \left| \int d\bar{\mathbf{Q}} d\mathbf{r} \chi_f^j(\bar{\mathbf{Q}})^* \psi_f(\mathbf{r}, \bar{\mathbf{Q}})^* \varepsilon \cdot \mathbf{r} \right. \\ \left. \times \chi_0(\bar{\mathbf{Q}}) \psi_0(\mathbf{r}, \bar{\mathbf{Q}}) \right|^2 \delta(E_f^j - E_0 - \hbar\omega),$$

where α_0 is the fine structure constant, $\hbar\omega$ the energy of the incident x-rays and ε their polarization vector. The core-hole lifetime and the instrumental resolution can be represented by the convolution of the absorption cross-section with a Lorentzian function $(\Gamma/\pi)/(\omega^2 + \Gamma^2)$. This gives us

$$\sigma_\gamma(\omega) = 4\pi\alpha_0 \sum_{fj} \left| \int d\bar{\mathbf{Q}} d\mathbf{r} \chi_f^j(\bar{\mathbf{Q}})^* \psi_f(\mathbf{r}, \bar{\mathbf{Q}})^* \varepsilon \cdot \mathbf{r} \right. \\ \left. \times \chi_0(\bar{\mathbf{Q}}) \psi_0(\mathbf{r}, \bar{\mathbf{Q}}) \right|^2 \frac{(E_f^j - E_0^0)\gamma}{(E_f^j - E_0 - \hbar\omega)^2 + \gamma^2},$$

where $\gamma = \hbar\Gamma$.

The energy E_f^j can be written as the sum of the electronic energy at equilibrium position ϵ_f and a vibrational energy $E_f^j = \epsilon_f + E_{\text{vib}}^{fj}$. When γ is much larger than the vibrational energy we can neglect the contribution of E_{vib}^{fj} and sum over the vibrational states $\chi_f^j(\bar{\mathbf{Q}})$. The completeness relation gives us

$$\sum_j \chi_f^j(\bar{\mathbf{Q}})^* \chi_f^j(\bar{\mathbf{Q}}') = \delta(\bar{\mathbf{Q}} - \bar{\mathbf{Q}}').$$

Therefore,

$$\sigma_\gamma(\omega) = 4\pi\alpha_0 \int d\bar{\mathbf{Q}} \sum_f \left| \int d\mathbf{r} \psi_f(\mathbf{r}, \bar{\mathbf{Q}})^* \varepsilon \cdot \mathbf{r} \right. \\ \left. \times \chi_0(\bar{\mathbf{Q}}) \psi_0(\mathbf{r}, \bar{\mathbf{Q}}) \right|^2 \frac{(\epsilon_f - \epsilon_0)\gamma}{(\epsilon_f - \epsilon_0 - \hbar\omega)^2 + \gamma^2}. \quad (1)$$

Note that we derived this result without making the harmonic approximation. Therefore, the possible anharmonic behavior due to the core hole [11] is taken into account. Note also that the final and initial energies ϵ_f and ϵ_0 do not depend on $\bar{\mathbf{Q}}$. Therefore, eq. (1) is not the average of standard XANES spectra over various nuclear positions $\bar{\mathbf{Q}}$. In other words, we have here a way to distinguish thermal disorder from static disorder due to impurities and structural defects.

Now we make a different approximation for the initial and final electronic states. For a K -edge, the $1s$ core level wavefunction is highly localized around the nucleus and it weakly depends on the surrounding atoms. Therefore, we can approximate $\psi_0(\mathbf{r}, \bar{\mathbf{Q}})$ by $\phi_0(\mathbf{r} - \mathbf{Q}_a)$, where \mathbf{Q}_a is the position vector of the absorbing atom and where ϕ_0 is the $1s$ wavefunction of the absorbing atom at equilibrium position. For the final electronic states $\psi_f(\mathbf{r}, \bar{\mathbf{Q}})$ in the presence of a core hole, the variation of the nuclear

coordinates $\bar{\mathbf{Q}}$ in eq. (1) is ruled by the vibrational wavefunction χ_0 of the initial state, which is expected to be rather smooth. Therefore, we make the standard *crude* Born-Oppenheimer approximation, according to which the electronic wavefunction does not significantly vary with $\bar{\mathbf{Q}}$ for small vibrational motions. In other words, $\psi_f(\mathbf{r}, \bar{\mathbf{Q}}) \simeq \phi_f(\mathbf{r})$, where $\phi_f(\mathbf{r}) = \psi_f(\mathbf{r}, \mathbf{0})$. This gives us

$$\sigma_\gamma(\omega) = 4\pi\alpha_0\hbar\omega \int d\bar{\mathbf{Q}} |\chi_0(\bar{\mathbf{Q}})|^2 \sum_f \left| \int d\mathbf{r} \psi_f(\mathbf{r})^* \varepsilon \cdot \mathbf{r} \right. \\ \left. \times \phi_0(\mathbf{r} - \mathbf{Q}_a) \right|^2 \frac{\hbar\gamma}{(\epsilon_f - \epsilon_0 - \hbar\omega)^2 + \gamma^2}.$$

When the crude Born-Oppenheimer approximation is not valid, it is possible to Taylor-expand $\psi_f(\mathbf{r}, \bar{\mathbf{Q}})$ as a function of $\bar{\mathbf{Q}}$ [14]. The integral over electronic variables depends only on the position of the absorbing atom, from now on denoted by \mathbf{R} . Therefore, we can integrate over the other nuclear variables and the expression becomes

$$\sigma_\gamma(\omega) = 4\pi\alpha_0\hbar\omega \int d\mathbf{R} \rho(\mathbf{R}) \sum_f \left| \int d\mathbf{r} \psi_f(\mathbf{r})^* \varepsilon \cdot \mathbf{r} \right. \\ \left. \times \phi_0(\mathbf{r} - \mathbf{R}) \right|^2 \frac{(\epsilon_f - \epsilon_0)\gamma}{(\epsilon_f - \epsilon_0 - \hbar\omega)^2 + \gamma^2}, \quad (2)$$

where $\rho(\mathbf{R}) = \int d\bar{\mathbf{Q}} |\chi_0(\bar{\mathbf{Q}})|^2 \delta(\mathbf{Q}_a - \mathbf{R})$. Within the harmonic approximation, the core displacement distribution has the form [15].

$$\rho(\mathbf{R}) = \exp\left(-\frac{\mathbf{R} \cdot U^{-1} \cdot \mathbf{R}}{2}\right),$$

where U is the thermal parameter matrix [16] that is measured in x-ray or neutron scattering experiments.

Calculation of the matrix element. For a hydrogenoid atom, the $1s$ core-hole radial wavefunction is proportional to e^{-ar} , where $a = Z/a_0$, Z is the atomic number and a_0 the Bohr radius. The $1s$ wavefunction $\phi_0(r)$ of a true atom is close to that of a hydrogenoid one and can be written as a fast converging linear combination of exponentials. Thus, $\phi_0(\mathbf{r} - \mathbf{R})$ becomes a sum of shifted exponentials that can be described by the Barnett-Coulson expansion [17]

$$e^{-a|\mathbf{r}-\mathbf{R}|} = \sum_n (2n+1) P_n(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}) c_n(r, R),$$

with P_n a Legendre polynomial and

$$c_n(r, R) = -\frac{1}{\sqrt{rR}} \left(r < I'_{n+1/2}(ar <) K_{n+1/2}(ar >) \right. \\ \left. + r > I_{n+1/2}(ar <) K'_{n+1/2}(ar >) \right),$$

where $r <$ ($r >$, resp.) is the smaller (larger, resp.) of r and R , $I_\nu(z)$ and $K_\nu(z)$ are the modified Bessel functions and $I'_\nu(z)$ and $K'_\nu(z)$ their derivatives with respect to

z . For notational convenience, we consider that the core wavefunction can be represented by a single exponential $\phi_0(r) = Ce^{-ar}$.

To calculate the matrix element, we expand the final state wavefunction over spherical harmonics $\psi_f(\mathbf{r}) = \sum_{\ell m} f_{\ell m}(r)Y_{\ell}^m(\hat{\mathbf{r}})$. The matrix element over the electronic variable is

$$\int d\mathbf{r} \psi_f(\mathbf{r})^* \varepsilon \cdot \mathbf{r} \phi_0(\mathbf{r}, \mathbf{R}) = \sum_{\ell m} X_{\ell}^m(\mathbf{R}),$$

with

$$X_{\ell}^m(\mathbf{R}) = C \sum_{n=0}^{\infty} \int d\mathbf{r} f_{\ell m}^*(r) Y_{\ell}^m(\hat{\mathbf{r}})^* \varepsilon \cdot \mathbf{r} \\ (2n+1)c_n(r, R)P_n(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}).$$

Standard angular momentum recoupling leads to

$$X_{\ell}^m(\mathbf{R}) = \frac{(4\pi)^2 C}{3} \sum_{n=|\ell \pm 1|} \int r^3 dr f_{\ell m}^*(r) c_n(r, R) \\ \sum_{\lambda} (-1)^m Y_1^{-\lambda}(\varepsilon) Y_n^{\lambda-m}(\hat{\mathbf{R}}) C_{1\lambda n m -\lambda}^{\ell m}, \quad (3)$$

where $C_{1\lambda n p}^{k\kappa}$ are Gaunt coefficients. Equation (3) shows that all values of the final state angular momentum ℓ are now allowed. The core-hole wavefunction is still spherical, but with respect to a shifted centrum. Thus, with respect to the original spectrum, it is a sum over all angular momenta given by the Barnett-Coulson expansion. Thus, all final states angular momenta are available in spite of the fact that only electric dipole transitions are allowed. In particular, vibrations allow for dipole transitions to the $3s$ and $3d$ final states at the K -edge.

General features of vibrational transitions. The foregoing approach enables us to draw some general conclusions concerning the effect of vibrations on XAS pre-edge structure. This effect is measurable if the density of non- p states of the system in the final state (i.e. in the presence of a core hole) is large and well localized near the Fermi energy (vibrational transitions towards p -states would be masked by the allowed vibrationless transitions). For example, just above the Fermi level, many aluminum or silicon compounds have a strong density of $3s$ states and many transition metal compounds have a large density of $3d$ states. In the first case, vibrational transitions appear as monopole $1s \rightarrow 3s$ transitions, which are completely excluded with electromagnetic transitions. In the second case, vibrational transitions superimpose upon electric quadrupole $1s \rightarrow 3d$ transitions. Thus, vibrations induce transitions at specific energies in the pre-edge but hardly modify the rest of the XANES spectrum.

A temperature dependence of vibrational transitions is expected if U varies with temperature. This occurs between 0 K and room temperature if the sample has soft modes (i.e. low energy phonons). Otherwise, vibrational

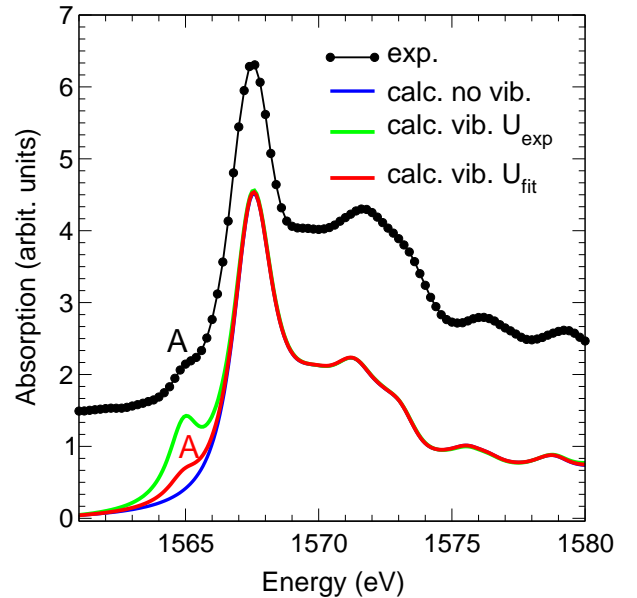


FIG. 1: Experimental [23] and calculated Al K -edge isotropic spectrum of corundum at 300 K. U_{exp} and U_{fit} are the experimental and fitted thermal parameters (see text).

transitions are only due to the zero-point motion of the nuclei. In other words, vibrational transitions are then a consequence of the fact that, even at 0 K, nuclei are not localized at a single point.

We test these conclusions with two examples: the Al K -edge in corundum (where vibrational transitions to $3s$ states are expected) and the Ti K -edge in rutile (where vibrational transitions to $3d$ states and a temperature dependence are expected).

The Al K -edge in corundum. The X-ray absorption cross section within the crude Born-Oppenheimer approximation has been implemented in the XSpectra package [18] of the Quantum-espreso suite of codes [19]. To calculate the integral over \mathbf{R} in eq. (2), it is found sufficient to compute the integral over a cube of size 2Λ , where Λ is the largest eigenvalue of the matrix U . This cube is cut into 27 smaller cubes where the integral is carried out using eq. (25.4.68) of Ref. 20. The technical details of the self-consistent calculation are the same as in Refs. [21, 22].

Figure 1 shows the result for experimental mean displacements $\sigma_1 = \sigma_2 = 0.048 \text{ \AA}$, $\sigma_3 = 0.049 \text{ \AA}$ [24]. The mean displacements σ_i are the square root of the eigenvalues of U and they have a more direct physical meaning than U . The vibrational transitions are observed exactly at the position of the pre-edge peak which is absent from the calculation without vibrations. However, the vibrational transitions are overestimated and a better agreement is obtained when setting the mean displacements to 0.026 \AA . Therefore, computed vibrational transitions show up at the right position but with a too large inten-

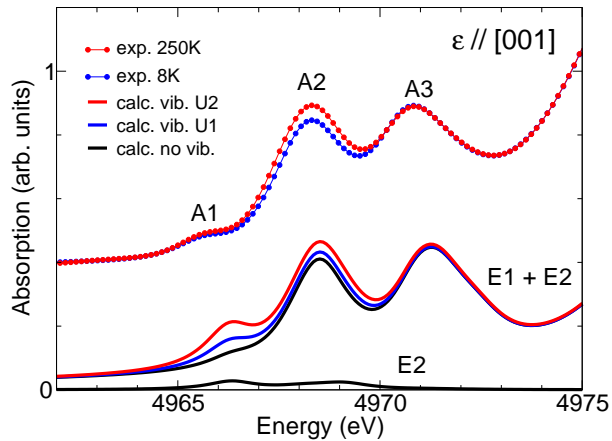


FIG. 2: Experimental [7] and calculated Ti K pre-edge spectrum of rutile. $E1$ and $E2$ are electric dipole and quadrupole transitions.

sity. A part of this discrepancy might be due to the fact that the experimental thermal parameters include some amount of static disorder, but most of it probably comes from the crude Born-Oppenheimer approximation. The main vibrational transitions come from the *relative* displacement of the aluminum atom with respect to the six oxygen first neighbors. The vibrational modes involving an overall motion of the aluminum atom with its oxygen octahedron contribute to the thermal parameter U although they do not contribute to the vibrational transitions. Because of the crude Born-Oppenheimer approximation, the vibrations are summarized in the thermal parameter, which overestimates the real effect of vibrations. A similar phenomenon occurs with the EXAFS Debye-Waller factor which is different from the one determined by x-ray diffraction because only relative displacements must be taken into account. This point will now be confirmed with the Ti K -edge absorption in rutile.

The Ti K -edge of rutile. With the Ti K -edge of rutile, we test the limit of the crude Born-Oppenheimer approximation. Indeed, this approximation assumes that the final state wavefunction does not change when the crystal vibrates. This might be reasonable for the Al $3s$ states because they are poorly localized and overlap the oxygen $2p$ orbitals, but this is not true for the $3d$ states of Ti in rutile, which are localized near the Ti nucleus.

Figure 2 shows the experimental and theoretical Ti K -edge spectrum of rutile with the polarization parallel to the c axis and at two temperatures. A similar result is obtained when ε is perpendicular to the c axis. The mean displacements $\sigma_1, \sigma_2, \sigma_3$ used in the calculations are, in Å, 0.0028, 0.0027, 0.0023 for $U1$ (8 K) and 0.0043, 0.0042, 0.0035 for $U2$ (250 K). They have been chosen to approximate the intensity of peak A2 at low

and room temperatures, respectively. These values are more than ten times smaller than the experimental values [25]. Moreover, when the thermal factor is adjusted to be consistent with the temperature variation of the second peak, then the temperature variation of the first peak is overestimated. This can probably be attributed to the crude Born-Oppenheimer approximation. Despite these drawbacks, several aspects of the experimental vibrational transitions are correctly reproduced: (i) only the first and the second peaks exhibit a temperature dependence, the rest of the spectrum is not modified; (ii) the peaks do not shift and do not broaden; (iii) the peaks increase with temperature.

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