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Electronic Structure of Ni Complexes by X-ray Resonance Raman Spectroscopy (Resonant Inelastic X-ray Scattering)

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Conventional resonance Raman spectroscopy (RRS) is a well-established technique that uses UV−visible radiation to probe the vibrational properties of chromophores.[1] In this communication, we present results with the related technique of X-ray resonance Raman spectroscopy or resonant inelastic X-ray scattering (RIXS). We illustrate the potential of this technique with a study of Ni compounds, using excitation at the K (1s) absorption edge and fluorescence detection of the subsequent 2p to 1s transition. We show that this method combines the merits of both hard X-ray K-edge[2] (1s) and soft X-ray L-edge[3] (2p) absorption spectroscopy.

In the two-step model for 1s2p RIXS,[4] an incident photon with energy Ω promotes a 1s electron into an unoccupied molecular orbital. A 2p electron fills the 1s vacancy and emits a photon with energy ω. Although both incident and emitted photons lie in the hard X-ray range (>5 keV), the final states of the system exhibit the same 2p vacancy encountered in L-edge soft X-ray spectroscopy. This is illustrated for a "1s → 3d" resonance in Figure 1. The intensities and splittings of the spectral features in 1s2p RIXS can be described theoretically by the same Kramers−Heisenberg equation used to describe the UV−visible RRS.[5] The intermediate state with a 1s core hole is reached from the electronic ground state via the dipole or the quadrupole operator. The decay of the 1s hole occurs via the dipole operator into the final state with a 2p vacancy.

Several intermediate and final states can be reached. The splittings and relative intensities of the transitions between the different states contain chemical information which can be displayed in a contour plot, where the two axes are the incident energy Ω and the energy transfer $\Omega - \omega$. The energy transfer or loss $\Omega - \omega$ (final-state energy) scale corresponds with the excitation energy in L-edge spectra (Figure 1), and we obtain L_3 ($2p_{3/2}$)- and L_2 ($2p_{1/2}$)-like spectra by projections along constant incident energy Ω. The natural line width in this case is the same as in L-edge spectroscopy, thus overcoming the short 1s core hole lifetime that considerably broadens the K-edge spectral features.[6] Although the K-edge lifetime still pertains to Ω scans (constant final-state energy $\Omega - \omega$), the reduction in overlapping features yields an effective sharpening in this dimension as well.

Figure 2 illustrates the properties of 1s2p RIXS for Ni in various spin and oxidation states.[7,10] In these contour plots, the intensities

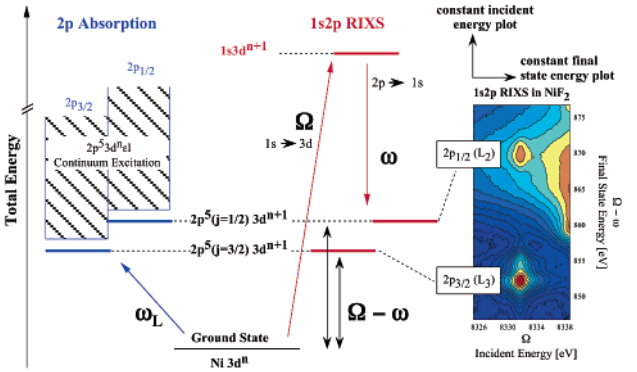

Figure 1. Energy scheme for 1s2p RIXS compared to L-edge absorption spectroscopy. A 1s2p RIXS contour plot for NiF_2 is shown as an example, and the two line plots that we extract from the contour plots are illustrated. The photon energies are denoted ω_L (L-edge), Ω (K-edge), and ω (inelastically scattered).

(on logarithmic scales) are expressed as different colors. Isolated resonant excitations appear as islands along a diagonal in the plots with tails extending parallel to the Ω and $\Omega - \omega$ axes. With increasing excitation energy, the resonances turn into continuum excitations. We focus on the "preedge" excitation region that involves the lowest unoccupied molecular orbitals and on final states with $2p_{3/2}$ vacancies (L_3-edge).

By traversing the contour plots along lines of constant $\Omega - \omega$, one obtains excitation spectra for constant final-state energy (Figure 3).[11] The weak 1s → 3d resonances are now separated from the strong dipole allowed transitions at higher energies. The shifts of the 1s → 3d resonances with oxidation state are clearly visible. The Ni(I) complex has one vacant 3d orbital; accordingly, we only observe one 1s → 3d resonance. For Ni(II), there is either a single vacant 3d orbital (low-spin) or a pair of nearly degenerate 3d orbitals (high-spin); again, we see only a single 1s → 3d resonance. In contrast, two 1s → 3d resonances are observed for the Ni(III) complex. This is consistent with at least some $3d^7$ character in the ground-state configuration. Here, the Ni site has approximately tetragonal symmetry, and the low-spin ($S = {}^1/_2$) configuration yields one unoccupied $3d_{x^2-y^2}$ orbital and a half-filled $3d_{xy}$ orbital.[10] These features are nearly invisible in the transmission spectrum.

Traversing the contour plots parallel to $\Omega - \omega$ at a fixed excitation energy Ω yields "energy-loss" spectra that involve the same final states as in 2p → 3d ($L_{2,3}$) absorption spectroscopy (Figure 3).[12] In the following, we discuss the $2p_{3/2}$ (L_3) structure

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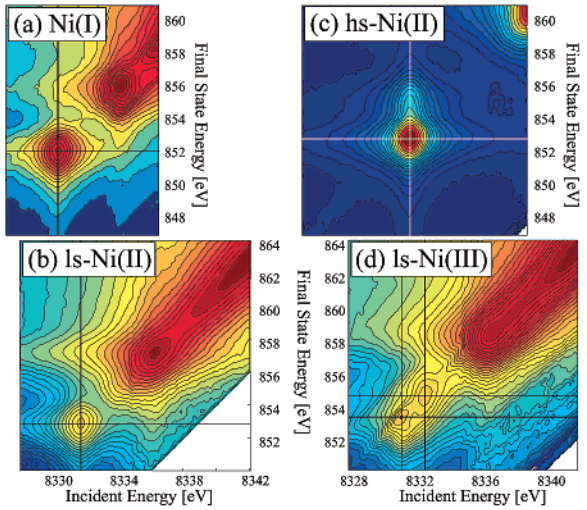

Figure 2. Contour plots for Ni coordination complexes: (a) Ni(I) in [PhTt^{tBu}]NiCO, (b) Ni(II) low-spin (ls) in $(Ph_4As)_2Ni(S_2C_2(CF_3)_2)_2$, (c) Ni-(II) high-spin (hs) in NiF_2, and (d) Ni(III) low-spin in [Ni(η^4-DEMAMPA-DCB)]$^-$. The vertical (constant incident energy) and horizontal (constant final-state energy) lines correspond to the line plots shown in Figure 3.

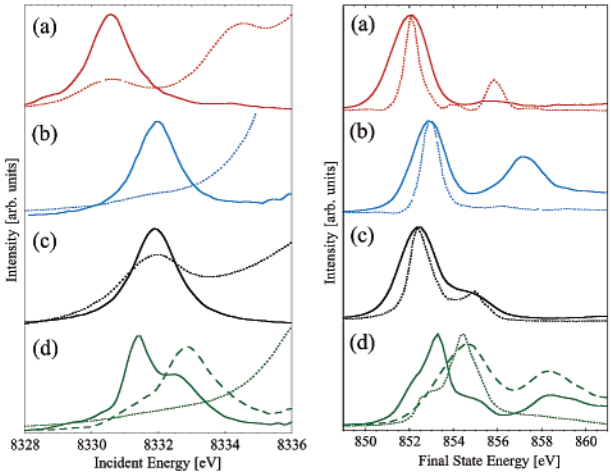

Figure 3. Conventional absorption spectra (dotted lines) compared to RIXS line plots (solid/dashed lines) as indicated in Figure 2 for the four Ni coordination complexes. (Left panel) K-preedge absorption spectra and RIXS constant final-state energy plots. (Right panel) L_3-edge absorption spectra and RIXS constant incident energy or energy-loss plots.

below 855.5 eV final-state energy. In this case, exciting the 1s → 3d intermediate resonance of the Ni(I) complex yields final states with a $2p^53d^{10}$ configuration. The energy loss spectrum does not show any splitting because of the filled 3d shell. Within the experimental resolution, a symmetrical peak is also observed for low-spin Ni(II). In contrast, the high-spin Ni(II) and low-spin Ni-(III) L_3 energy-loss spectra exhibit asymmetries due to multiplet structure.[13] These features arise from (2p,3d) and (3d,3d) Coulomb and exchange interactions. Additional structures arise from orbital energy splittings in the case of Ni(III). Multiplet splitting yields information on the valence and spin state of the metal center, and various L-edge studies have used these features to characterize metal centers.[3] Specifically, in L-edge spectroscopy, the high-energy shoulder in the L_3 line has been used as a diagnostic of high-spin Ni(II) in metalloproteins,[14] while a low-energy peak ascribed to Ni(III) has been used to characterize Ni oxides.[15] The energy-loss spectra show features above the $2p_{3/2}$ structure. Comparison with Figure 2 shows that the intensity of these features arises from resonances at higher incident energies.

In summary, we have demonstrated the potential of 1s2p RIXS spectroscopy for characterization of Ni complexes. By extension, this approach should be applicable to a wide range of transition metals, as well as final states with 3p or valence electron excitations. The 1s2p RIXS enables to separate out the lowest K-edge resonances (preedge features). It potentially offers the resolution of L-edge soft X-ray spectroscopy in the energy loss spectra combined with the bulk sensitivity of hard X-rays. The line widths in the RIXS energy-loss spectra reported here are broadened by instrumental resolution. Improvements in X-ray optics will remove this limitation. The sensitivity of RIXS is high enough to examine transition metals in metalloproteins. This technique promises to be a valuable probe of electronic structure.

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