Conventional resonance Raman spectroscopy (RRS) is a well-established technique that uses UV-visible radiation to probe the vibrational properties of chromophores. 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 (1s) and soft X-ray L-edge (2p) absorption spectroscopy.

In the two-step model for 1s2p RIXS, an incident photon with energy $\Omega$ promotes a 1s electron into an unoccupied molecular orbital. A 2p electron fills the 1s vacancy and emits a photon with energy $\omega$. 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 $\rightarrow$ 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. 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 $\Omega$ and the energy transfer $\Omega - \omega$. The energy transfer or loss $\Omega - \omega$ (final-state energy) scale corresponds with the excitation energy (inelastically scattered). The photon energies are denoted $\omega_L$ (L-edge), $\Omega$ (K-edge), and $\omega$ (inelastically scattered).

Figure 2 illustrates the properties of 1s2p RIXS for Ni in various spin and oxidation states. In these contour plots, the intensities (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 $\Omega$ 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). The weak 1s $\rightarrow$ 3d resonances are now separated from the strong dipole allowed transitions at higher energies. The Ni(I) complex has one vacant 3d orbital; accordingly, we only observe one 1s $\rightarrow$ 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 $\rightarrow$ 3d resonance. In contrast, two 1s $\rightarrow$ 3d resonances are observed for the Ni(III) complex. This is consistent with at least some 3d$^5$ 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. These features are nearly invisible in the transmission spectrum.

Traversing the contour plots parallel to $\Omega$ and $\omega$ at a fixed excitation energy $\Omega$ yields “energy-loss” spectra that involve the same final states as in 2p $\rightarrow$ 3d (L$_2$) absorption spectroscopy (Figure 3). In the following, we discuss the 2p$_{3/2}$ (L$_3$) structure...
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^33d^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. 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. 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, while a low-energy peak ascribed to Ni(III) has been used to characterize Ni oxides. 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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References

7. The RIXS spectra were recorded at the Bio-CAT beamline at the Advanced Photon Source (APS). The incident beam monochromator used a pair of Ni(001) crystals, and the energy bandwidth at 830 eV was 1.0 eV. Radiation damage studies were performed on each sample. The fluorescence spectrometer for the current experiments used three 8.9-cm diameter Ni(200) analyzer crystals. The fluorescence spectrometer bandwidth was approximately 0.8 eV at 7478 eV.
11. Conventional K-edge absorption spectra were recorded at SSRL, beamline 5-7 using a water-cooled Ni(200) double crystal monochromator with an energy bandwidth of ~1.0 eV.
12. L-edge absorption spectra were recorded at the ALS undulator beamline 4.0.2. The calculated energy bandwidth is 0.3 eV at 830 eV.