dd Excitations in CPO-27-Ni Metal–Organic Framework: Comparison between Resonant Inelastic X-ray Scattering and UV–vis Spectroscopy

The *dd*-excitations in CPO-27-Ni MOF - A comparison between UV-Vis and resonant inelastic X-ray scattering spectroscopy

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Inorg. Chem. **2013**, *52*, 5633−5635

dx.doi.org/10.1021/ic400350w

The *dd*-excitations in CPO-27-Ni MOF - A comparison between UV-Vis and resonant inelastic X-ray scattering spectroscopy

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Supporting Information Placeholder

ABSTRACT: We identify the *dd*-excitations in the metal organic framework CPO-27-Ni by coupling resonant inelastic X-ray scattering (RIXS) and UV-Vis spectroscopy and we show that the element-selectivity of RIXS is crucial to reveal the full *dd*-multiplet structure that is not visible in UV-Vis. The combination of calculations using crystal field multiplet theory and density functional theory can reproduce the RIXS spectral features crucially improving the interpretation of the experimental data. We obtain the crystal field splitting and the magnitude of the electron-electron interactions and correct previously reported values. RIXS instruments at synchrotron radiation sources are accessible to all researchers and the technique can be applied to a broad range of systems.

Charge-neutral *dd* excitations are of paramount importance in the study of materials that host 3*d* transition metal (TM) ions.[1] In chemistry, the *dd* excitations are traditionally probed by UV-Vis spectroscopy. The UV-Vis spectrum may be separated into two regions referred to as *dd* and charge-transfer (CT) respectively. The former are intra-atomic excitations that may reflect the crystal-field splitting and electron-electron interactions while the latter arise from metal (ligand) to ligand (metal) (ML or LM) and ligand to ligand (LL) CT transitions. Often, *dd* and CT excitations are well separated in energy and the identification of the regions is easily achieved.

However, materials with inorganic and organic components may present intricate optical spectra. Examples can be found in the family of the metal organic framework (MOF) CPO-27-M (M = Mn, Co, Ni, etc).[2] The LL-CT region of the CPO-27-M organic linker (*i.e.* dhtp = 2,5-dihydroxyterephthalic acid) rises at very low energy and may overshadow part of the *dd* excitations.

Resonant inelastic X-ray scattering (RIXS) can be used to overcome this problem.[3-6] RIXS is an element-selective *photon-in/photon-out* spectroscopic technique in which the energy of the incoming photon can be tuned to induce transitions into bound excited states (*i.e.* resonances). In the case of hard X-ray RIXS experiments on 3*d*-TM systems the K absorption pre-edge can be used as resonance (see the Supporting Information, SI). The excited states may relax with the emission of a photon. The energy transferred to the system (*photon-in* energy minus *photon-out* energy) during the RIXS process may be on the order of a few eV and thus allows to observe *dd* and CT excitations.

We show that the element selectivity of RIXS is crucial to observe the full multiplet structure of the metal ions in the case of CPO-27-Ni[7] and we provide the crystal field splitting (Δ) and the Racah parameters[8] that are of prime significance for the investigation of the electron-electron interactions.

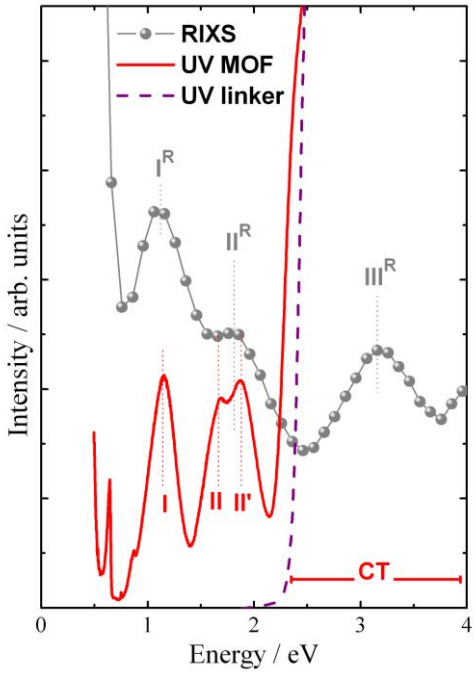

Figure 1. UV-Vis (red line) and RIXS (gray points) spectra of CPO-27-Ni. The UV-Vis spectrum of the organic linker of the MOF is also reported (dashed line).

Figure 1 shows the UV-Vis spectrum of CPO-27-Ni (see SI). It presents four main features respectively at ~0.60 eV (overtone of water), 1.10 eV (I), 1.70 eV (II), 1.80 eV (II') and the CT region starting at about 2.5 eV. The comparison of the UV-Vis spectra of dhtp (i.e. MOF organic linker) and of CPO-27-Ni shows that the low lying CT region of the MOF is mainly due to its organic components (LL-CT).

Eight electrons occupy the 3*d*-levels of a free Ni^{2+} ion. The Russel-Saunders-term for the ground state of a d^8-ion is $^3A_{2g}$ in O_h symmetry. No *dd*-excitations should be observed in the UV-Vis spectrum for systems in O_h symmetry according to the dipole selection rules. However, they gain spectral intensity when there is a large overlap between the vibrational functions of the final and initial states (vibronic coupling) as has been proposed for NiO.[9] The features labelled **I**, **II** and **II'** in Figure 1 were recognized as *dd*-excitations of the Ni^{2+} ion in O_h symmetry and assigned respectively to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions.[10, 11] This assignment is in contradiction to

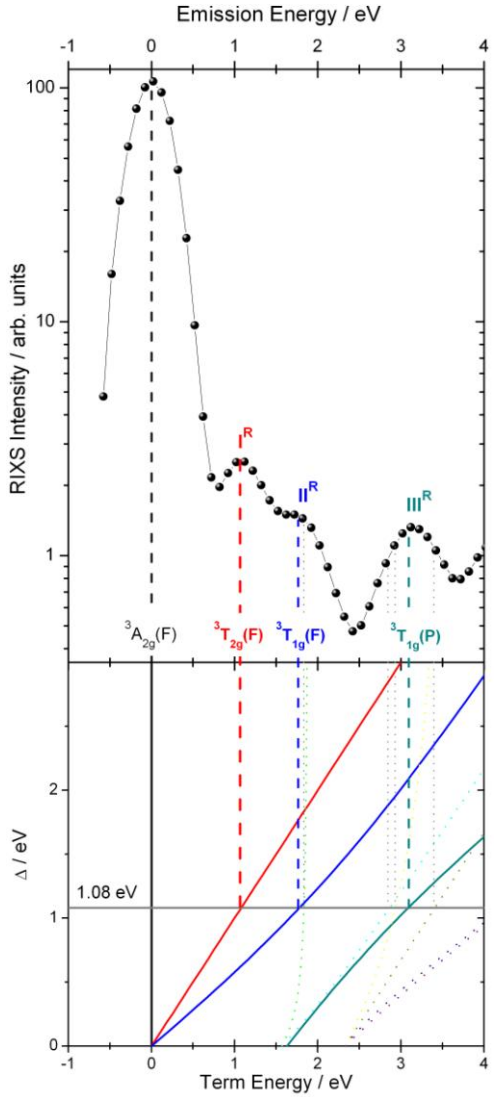

Figure 2. RIXS spectrum (top) and Tanabe-Sugano diagram (bottom). The RIXS intensities are reported in logarithmic scale. The Tanabe-Sugano diagram is presented in absolute scale using B = 1.08 eV and presents spin-allowed (continuous-lines) and forbidden (dotted-lines) transitions.

experiments performed using resonant inelastic soft and hard X-ray scattering which observed *dd*-excitations lying in a wider range.[12-14] For instance, Huotari et *al.*[13] reported for NiO three *dd*-bands at 1.06 eV, 1.73 eV and 2.96 eV. Moreover, using the assignment of Ref.[10] we obtain that the Racah parameter B (estimated using the Underhill-Billing equations)[15] is equal to 0.013 eV, *i.e.* about nine times lower than previously reported data on materials with Ni^{2+} in O_h symmetry.[15, 16] There is thus a discrepancy in the assignment of the features observed for CPO-27-Ni that can be clarified by comparing UV-Vis and RIXS spectroscopy. The spectral resolution in RIXS is considerably lower than in UV-Vis spectroscopy but the technique is element selective.

Also at the Ni K-edge transitions from the 1*s* to the 3*d* shell are dipole forbidden but the instrumental sensitivity at a high brilliance synchrotron radiation beam line is sufficient to observe quadrupole transitions and thus *dd*-excitations even in dilute systems.[17] The scattering process induces quadrupole transitions from the ground state $^3A_{2g}(F)$ to the triplet states $^3T_{2g}(F)$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$. Thus the same final states as in UV-Vis spectroscopy

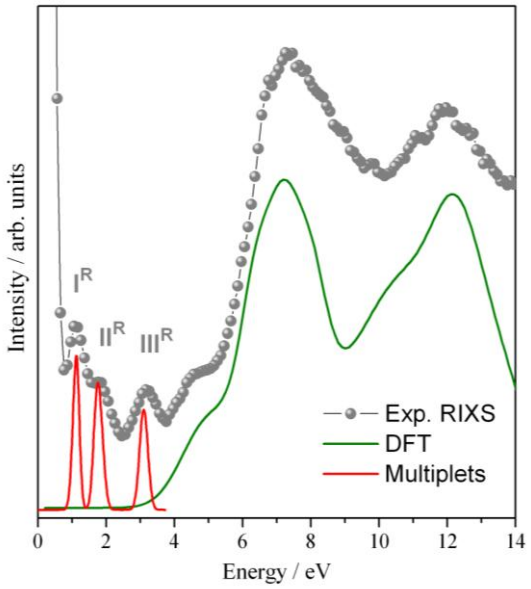

Figure 3. Experimental RIXS spectrum (gray), density functional theory (green) and multiplet theory (red) calculations.

can be observed. The features of the RIXS spectrum have centers of gravity at (1.08±0.04) eV, (1.74±0.04) eV and (3.10±0.04) eV and are labeled respectively, $\mathbf{I^R}$, $\mathbf{II^R}$ and $\mathbf{III^R}$. While $\mathbf{I^R}$ and $\mathbf{II^R}$ are visible in the UV-Vis spectrum (as **I** and **II-II'**, *cf.* Figure 1), $\mathbf{III^R}$ is revealed only in the RIXS spectrum. The features **II** and **II'** are multiplet-features with an energy separation of ~100 meV and they are observed convoluted in the RIXS spectrum (see Figure 1).

The observation of $\mathbf{III^R}$ is crucial to derive the correct value of the Racah parameter B using the Underhill-Billing equations and the nephelauxetic ratio (β). The value of B determined from the RIXS measurement is (0.12±0.05) eV, thus β is 0.90±0.05. The magnitude of β suggests that there is an expansion of the electronic cloud around the Ni^{2+} sites within CPO-27-Ni with respect to the free ions, *i.e.* the chemical bond between Ni and O has some covalent character.

It is possible to observe the energy-level scheme of Ni^{2+} ions in O_h symmetry with allowed and forbidden spin transitions using the Tanabe–Sugano diagram[18, 19] (calculated using B = 0.12 eV) that is shown in comparison with the RIXS spectrum in Figure 2. The energy position of $\mathbf{I^R}$ approximately corresponds to the crystal field splitting.[13] Therefore, the intersection of the line at Δ = 1.08 eV with the curves in the diagram allows the identification of the excited states that mainly contribute to the RIXS spectral features (see Figure2).

The features $\mathbf{I^R}$, $\mathbf{II^R}$ and $\mathbf{III^R}$ and the Racah parameters B (0.12 eV) and C (0.41 eV) can be computed using crystal field multiplet theory calculations, see Figure 3 and SI. The calculations consider only the Ni *d*-orbitals and include the chemical environment via empirical parameters that can be fitted to experiment. The CT excitations are thus not reproduced. It is worth noting that for the present case the ratio C/B is useful only for the evaluation of the relative energy of excited states with spin multiplicity equal to one (*i.e.* spin forbidden transitions).

The RIXS spectrum shows the LMML-CT region in a wider range than it is possible with UV-Vis spectroscopy allowing for a full

analysis. Ground state density functional theory (DFT) calculations performed using ORCA[20] (see SI) are able to reproduce the experimental RIXS LM(ML)-CT features, see Figure 3. Such calculations neglect the core hole potential that has only little effect on the ligand orbitals.

Figure 3 shows that combining ground state DFT and crystal field multiplet calculations it is possible to clearly separate the experimental RIXS data into a *dd* and LMML-CT excitation region

Summarizing, it has been shown that element-selective RIXS spectroscopy reveals the full *dd* multiplet structure of CPO-27-Ni that is not accessible in UV-Vis spectroscopy. This allows for correctly determining the Racah parameter B and the nephelauxetic ratio β of the Ni^{2+} sites within the MOF. RIXS experiments can be performed using soft and hard X-rays where the choice mainly depends on the required sample environment. The number of experimental stations that are accessible to all researchers is steadily increasing.

ASSOCIETED CONTENTS

Supporting Information

Description of the experimental and theoretical methods. This material is available free of charges via the internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The European Synchrotron Radiation Facility (ESRF) is gratefully acknowledged for the beamtime allocation. We are grateful to Dr. Sachin Chavan for providing the CPO-27-Ni powder.

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Supporting Information

The *dd*-excitations in CPO-27-Ni MOF - A comparison between UV-Vis and resonant inelastic X-ray scattering spectroscopy

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SI1 Synthesis and structure of CPO-27-Ni

Dietzel et al.[1-6] synthesized $Ni_2(dhtp)(H_2O)_2 \cdot 8H_2O$ (dhtp = 2,5-dihydroxyterephthalic acid) that was named CPO-27-Ni. It belongs to the CPO-27-M (Mg, Co, Ni) family also known as MOF-74 (synthesized by Yaghi and co-workers) and is isostructural to framework materials with Zn^{2+}, Co^{2+} and Mg^{2+} metal component.[7-15]

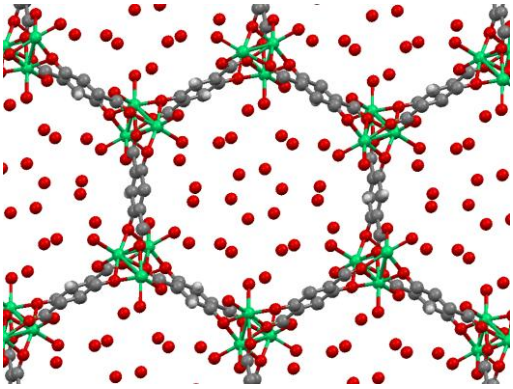

Figure SI1. Representation of hydrated CPO-27-Ni oriented along the [001]direction. Ni, O, C and H are reported in green, red, gray and white respectively. The water molecules within the channels of the MOF are reported without H for clarity.

The framework of as synthesized CPO-27-Ni contains one-dimensional channels, see Figure SI1. They are filled with water that can be removed by a mild thermal treatment. Upon dehydration the crystalline structure is preserved and a material with a high surface area containing unsaturated metal sites organized in helicoidal chains is obtained. The stability of the framework is guarantee by TGA and temperature dependent XRPD measurements.[7, 9, 10] The channels in the honeycomb have a diameter of ~11 Å and they are filled with solvent (isolated red balls in Figure S1). The Ni sites are six-folded coordinated with O. Five O belong to the framework while one belongs to the coordinative water.

SI2 Experimental and Computational Methods

The resonant inelastic X-ray scattering (RIXS) experiment was performed at beamline ID26 of the European Synchrotron Radiation Facility (ESRF). We used the (311) reflection of cryogenically cooled Si crystals to select the energy of the incoming photons. High harmonics were suppressed using Si mirrors operating in total reflections. Three Si (551) analyzer-crystals with bending radius of 2m were mounted on the spectrometer available at ID26 and employed to analyze the scattered photons. An avalanche photo-diode was used as single photon counting detector. The total band-width of the experimental setup as determined by the FWHM of the elastic peak was of 430meV. The spot size on the sample was approximately 0.6 mm horizontally and 0.1 mm vertically.
The full RIXS spectrum reported in Figure 3 was acquired in about twelve hours.
Density functional theory calculations were performed with ORCA[16] at the TPSSh/CP(PPP)/QZVP level of theory imposing the spin multiplicity (2S+1) to three.[17, 18] We used a cluster of about hundred atoms obtained from the structure optimized by Valenzano *et al.* using a periodic approach.[19]
The multiplet calculations were performed using a suite of programs including the codes by Cowan,[20, 21] Butler[22] and Thole - as implemented in the MISSING[23] interface - with starting parameters suggested by Huotari *et al*.[24] for NiO.
The sample of CPO-27-Ni was synthesized according to Diezel *et al*.[6] and measured in its hydrated form (see Figure S1) as self supported powder. The concentration of Ni within the sample was of 23.6% in weight.

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