

From Ligand Fields to Molecular Orbitals: Probing the Local Valence Electronic Structure of Ni²⁺ in Aqueous Solution with Resonant Inelastic X-ray Scattering

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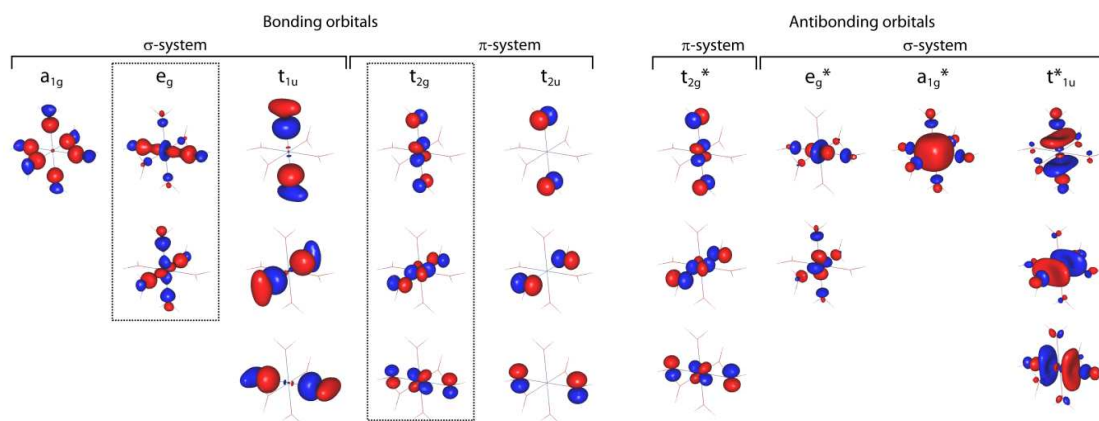


Fig. S1. Orbital plots derived from the RASSCF ground state calculation.

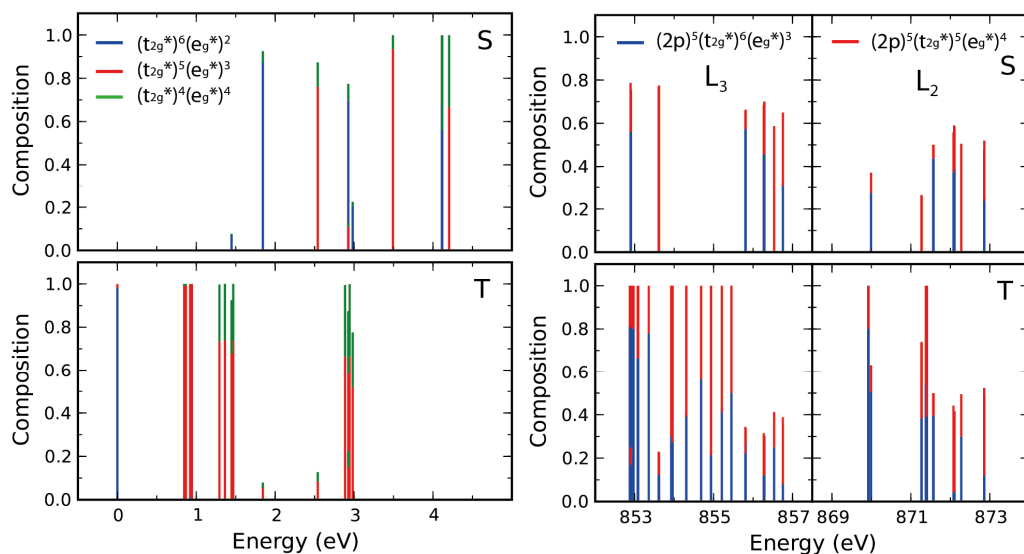


Fig. S2. Orbital and spin composition of the ligand-field (LF) (left) and core-excited states (right) in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ as derived from the RASPT2 calculations. S and T denote singlet and triplet states for the configurations discriminated by color and according to their t_{2g}^* and e_g^* occupations.

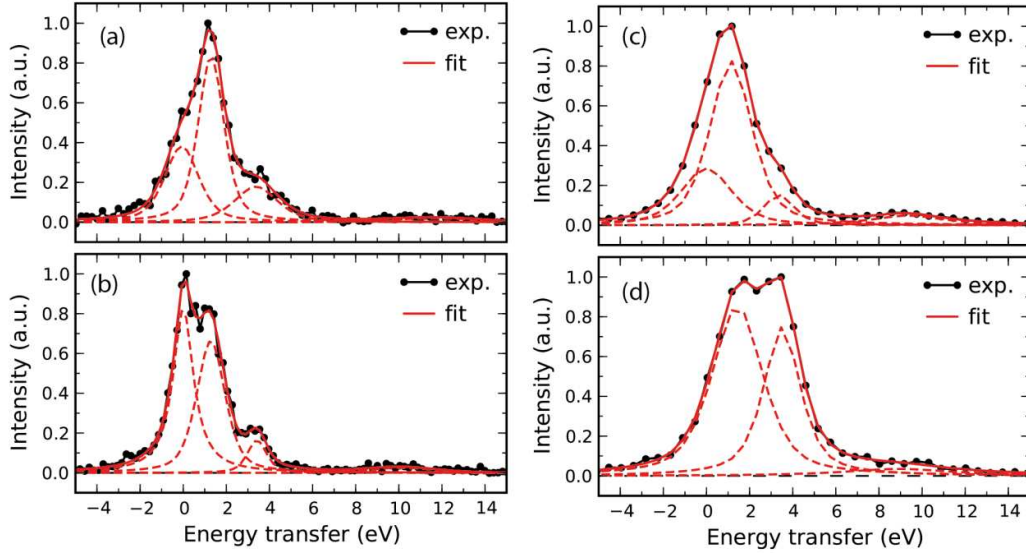


Fig. S3. Experimental RIXS spectra from Fig. 3 of the main text with fitted pseudo-Voigt profiles used to determine the peak positions. (a) RIXS spectrum at resonance A (incident photon energy 853.2 eV) for horizontal polarization. (b) RIXS spectrum at resonance A (incident photon energy 853.2 eV) for vertical polarization. (c) RIXS spectrum at resonance A (incident photon energy 853.2 eV) for horizontal polarization. (d) RIXS spectrum at resonance B (incident photon energy 855.6 eV) for horizontal polarization. The corresponding fitted peak positions are listed in Tab. S1. Measurements in (a) and (b) [in (c) and (d)] were done in separate beamtimes at the UE-52-SGM [U41] beamline, see Methods.

Table S1. Fitted experimental RIXS peak positions.

Spectrum	peak	position (eV)
Fig. S3(a)	elastic (${}^3A_{2g}$)	-0.1
	LF1 (${}^3T_{2g}$)	1.3
	LF2 (${}^3T_{1g}$)	3.4
	CT	11.1
Fig. S3(b)	elastic (${}^3A_{2g}$)	0
	LF1 (${}^3T_{2g}$)	1.3
	LF2 (${}^3T_{1g}$)	3.5
	CT	9.5
Fig. S3(c)	elastic (${}^3A_{2g}$)	0
	LF1 (${}^3T_{2g}$)	1.1
	LF2 (${}^3T_{1g}$)	3.4
	CT	9.4
Fig. S3(d)	LF1	1.4

	LF2 ($^1T_{1g}$)	3.5
	CT	8.9