

Structure and Dynamics of Solvent Shells around Photoexcited Metal Complexes.

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The Supplementary Information presents validation computations and simulations for Mulliken and NBO charges and the vibrational spectroscopy of the Ru(II) complex in solution.

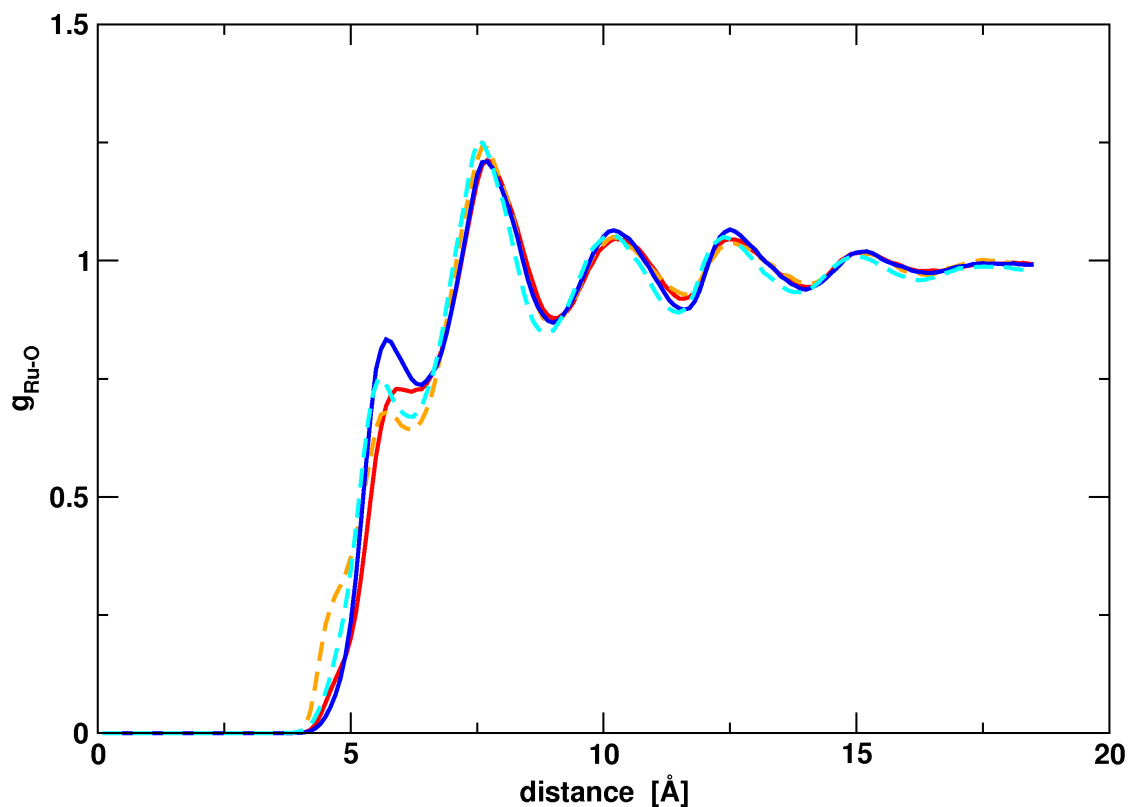


FIG. 1: Radial distribution function (RDF) for Ru-O_{Wat} determined for Ru(II) and Ru(III) with Mulliken and NBO charges. With Mulliken charges (red, solid) the first water shell around the Ru(II)-complex is at 5.9 Å which shifts to 5.7 Å for NBO charges (orange, dashed). The difference of 0.2 Å is related to the decreased charge of Ru(II) (0.59e) from an NBO analysis compared to a Mulliken charge of 0.72e (see Table 1 in the SI). For the Ru(III) complex the first shell is at 5.7 Å (Mulliken charge 1.01e for Ru(III); blue, solid) compared to 5.6 Å for NBO charges (Ru(III) charge of 1.01e; cyan, dashed). For the second, third and subsequent solvation shells, no appreciable effects are observed for the two different charge concepts.

¹ Omberg, K. M.; Schoonover, J. R.; Treadway, J. A.; Leasure, R. M.; Dyer, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 7013–7018.

4

Basis on Ru(II)	Basis set	Ruthenium		Nitrogen		1.1'-Carbon		2.2',3-Carbon		Hydrogen	
		Mulliken	NBO	Mulliken	NBO	Mulliken	NBO	Mulliken	NBO	Mulliken	NBO
LanL2DZ	6-31G(d,p)	0.72	0.59	-0.52	-0.43	0.19	0.12	-0.08	-0.21	0.15	0.26
LanL2DZ	6-311(d,p)	1.00	0.61	-0.56	-0.44	0.18	0.14	-0.07	-0.17	0.15	0.23
SDD	cc-PVTZ	0.53	0.53	-0.19	-0.39	0.02	0.11	-0.08	-0.17	0.16	0.23
Basis on Ru(III)	basis set	Mulliken	NBO	Mulliken	NBO	Mulliken	NBO	Mulliken	NBO	Mulliken	NBO
LanL2DZ	6-31G(d,p)	1.01	1.01	-0.56	-0.46	0.20	0.12	-0.07	-0.19	0.18	0.28
LanL2DZ	6-311(d,p)	1.20	1.02	-0.60	-0.47	0.20	0.14	-0.06	-0.15	0.17	0.24
SDD	cc-PVTZ	0.81	0.99	-0.21	-0.43	0.03	0.12	-0.07	-0.15	0.18	0.24

TABLE I: Partial atomic charges for the Ru(II) and Ru(III) complex from Mulliken and NBO analyses for different basis sets. Charges on the nitrogen, 1,1'-carbon (carbons directly bond to N), 2,2',3-carbon (carbons bond to N over 2 to 3 bonds) and hydrogen atoms are averaged.

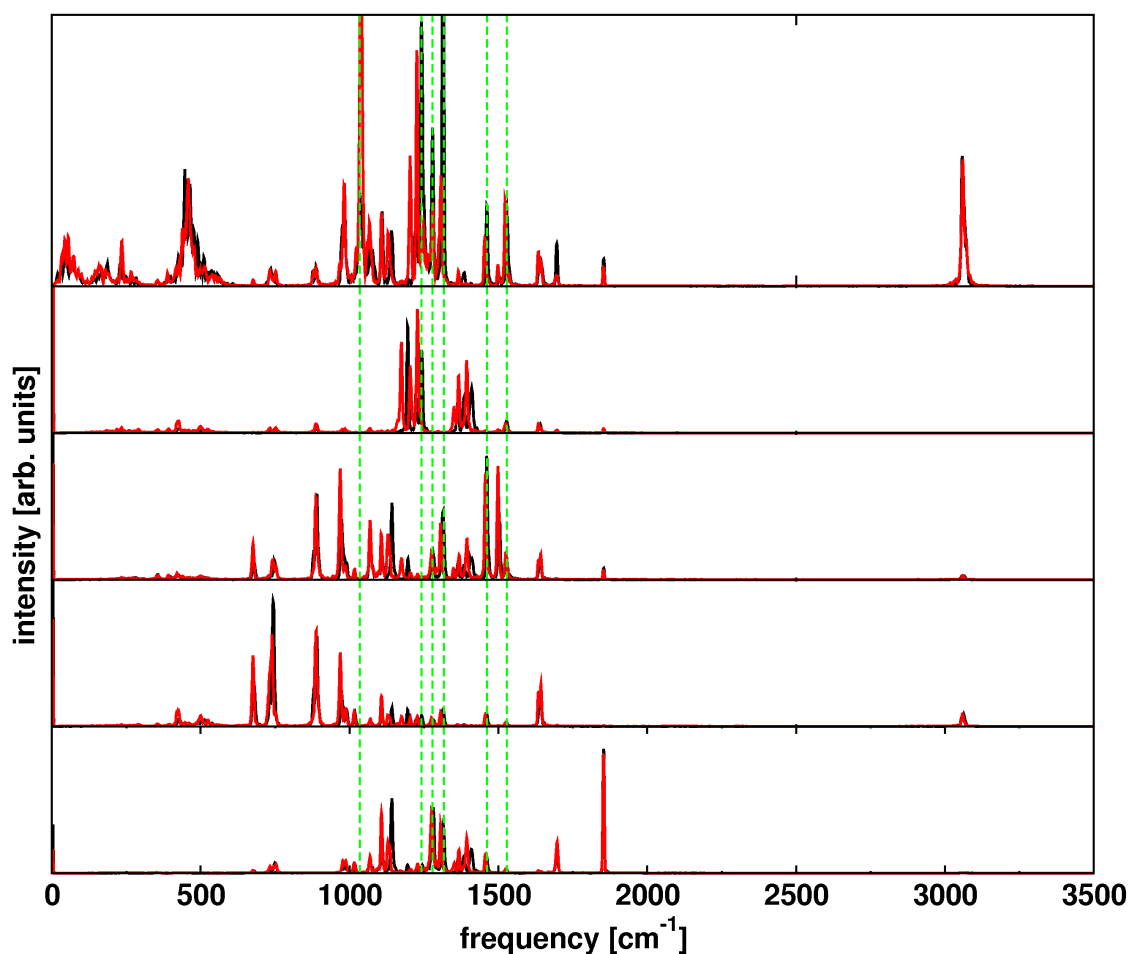


FIG. 2: Top panel: Computed vibrational spectrum of $[\text{Ru}^{\text{II}}(\text{bpy})_3]$. The black curve corresponds to the Ru(II) spectrum with ^{14}N and the red curve is the Ru(II) spectrum for the ^{15}N isotope. Lower panels: Power spectra of the metal-nitrogen, carbon-nitrogen stretch and the CCN and CCH bending vibrations. The color code is identical to that in the upper panel. The power spectra confirm the experimental finding¹ that the modes are highly mixed and assignments to local mode vibrations are difficult. Dashed vertical lines allow to associate signatures in the vibrational spectrum with corresponding peaks in the power spectra.

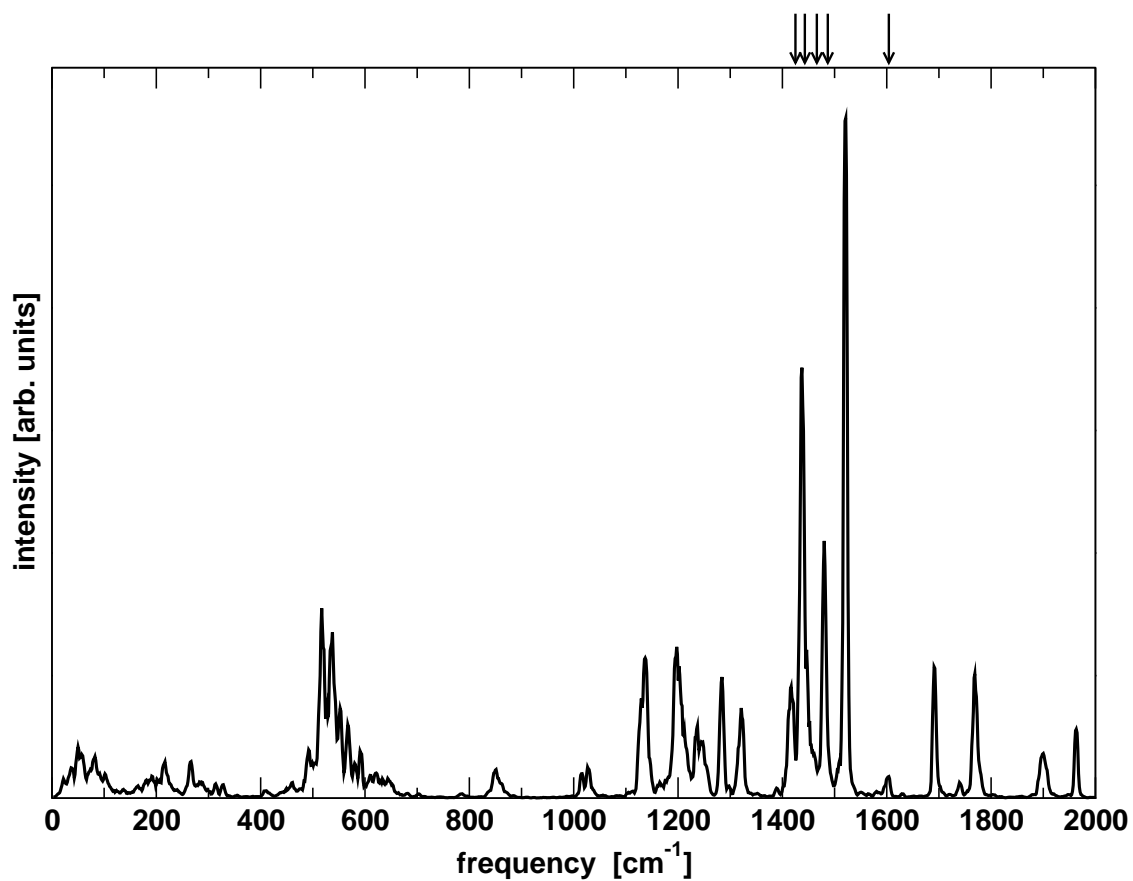


FIG. 3: Infrared spectrum of $[\text{Ru}^{\text{II}}(\text{bpy})_3]$ in water, together with the experimental line positions in the fingerprint region (red bars), measured in acetonitrile.¹ The computed spectrum was shifted by $\approx 190 \text{ cm}^{-1}$ to align the CN-stretching band.¹