

The Role of CN and CO Ligands in the Vibrational Relaxation Dynamics of Model Compounds of the [FeFe]hydrogenase Enzyme

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Supplementary Information

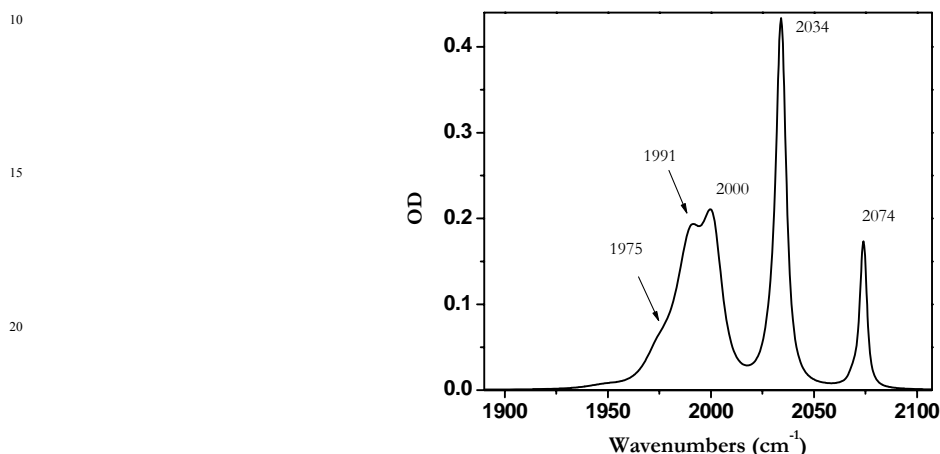


Figure S1: FTIR spectrum of $(\mu\text{-propanedithiolate})\text{Fe}_2(\text{CO})_6$ in DCM solution. The presence of five CO stretching modes is in excellent agreement with previous studies of this system in other solvents.¹

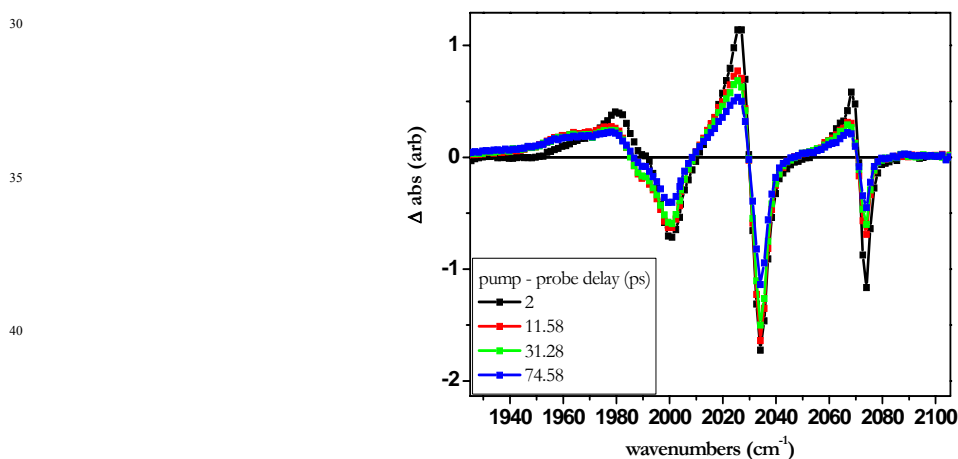


Figure S2: Example pump probe spectra of $(\mu\text{-propanedithiolate})\text{Fe}_2(\text{CO})_6$ in DCM solution recorded with a pump frequency of 2035 cm^{-1} . Spectra were obtained as described for **1** in main text. The spectrum is normalised to the largest signal and the peak sample OD for 2D-IR spectroscopy was ~ 0.4 as for compound **1** in main text. Points represent experimental points, fits are shown as lines.

		Probe frequency (cm^{-1})				
		1975 v=0-1	2026 v=1-2	2034 v=0-1	2068 v=1-2	2074 v=0-1
Pump frequency (cm^{-1})	1975	τ_D 1.3 ± 0.7	τ_R 2.8 ± 0.7	τ_R 1.4 ± 0.7	τ_R 1.4 ± 0.7	τ_R 3.2 ± 1.2
	v=0-1	τ_D 196 ± 13	τ_D 220 ± 20	τ_D 219 ± 14	τ_D 193 ± 18	τ_D 187 ± 20
	2034		τ_D 1.7 ± 0.7	τ_D 2.0 ± 0.8		
	v=0-1	τ_D 179 ± 17	τ_D 183 ± 18	τ_D 158 ± 12	τ_D 205 ± 50	τ_D 230 ± 30
	2074		τ_R 2.8 ± 0.8		τ_D 4.0 ± 2	τ_D 2.7 ± 0.8
	v=0-1	τ_D 160 ± 26	τ_D 188 ± 21	τ_D 184 ± 14	τ_D 170 ± 60	τ_D 173 ± 20

Table S1: Summary of vibrational relaxation dynamics for selected transitions of $(\mu\text{-propanedithiolate})\text{Fe}_2(\text{CO})_6$ in DCM solution. Data were obtained by fitting Gaussian lineshape profiles to pump probe data as in Fig S2 followed by fitting peak amplitudes as a function of time to biexponential functions. τ_D indicates a decay timescale while τ_R indicates a rise time. The data clearly shows that diagonal features are well-represented by a biexponential decay function with a 1-4 ps component and a longer relaxation time on the order of 180-220 ps. The majority of off-diagonal modes display a fast rising timescale of 1-3 ps and a 180-220 ps decay timescale. These dynamics are in good agreement with those observed previously for all-carbonyl hydrogenase model systems^{1, 2} and indicate rapid vibrational population transfer and equilibration between the pumped mode and the off-diagonal CO stretching modes followed by longer vibrational relaxation (T_1).

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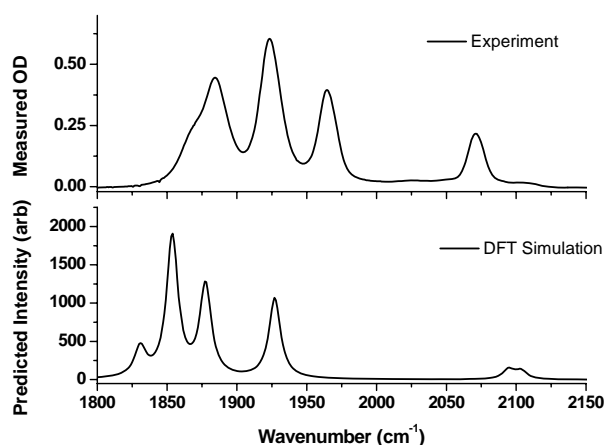


Figure S3: Direct comparison of experimental FTIR spectrum of **1** and simulated infrared spectrum of the axial-equatorial isomeric form of **1** using the methods described in the main text.

Further to the discussion in the main text arising from the effects on the time resolved spectra of coupling between the highest frequency CO stretching mode and the lowest frequency CN mode, which led to the suggestion that the CN peak may consist of two unresolved lineshapes: Fig S3 shows the FTIR spectrum of **1** in DCM alongside the predicted spectrum for the axial-equatorial isomeric form. While the experimental CN peak at 2071 cm^{-1} was well-represented by a Gaussian lineshape function with a width of 13.5 cm^{-1} , the absorption does display a small amount of asymmetry near the peak, though this is not sufficient to justify fitting to two Gaussian functions of the same width, as would be expected if there were two transitions present. Changes in solvent have not been observed to resolve these lines more effectively as compound **1** is only soluble in polar solvents which lead to line broadening. Thus, evidence for a second CN peak is restricted to the peak shift phenomenon observed in the time-resolved 2D-IR data and demonstrates one of the major advantages of 2D-IR spectroscopy.

Notes and references

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2. G. M. Bonner, A. R. Ridley, S. K. Ibrahim, C. J. Pickett and N. T. Hunt, *Faraday Discussions*, 2010, **145**, 429.