Supplementary Information

Understanding 2D-IR Spectra of Hydrogenases: A Descriptive and Predictive Computational Study

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Table S1: Summary of relevant quantities discussed in the manuscript (all in cm^{-1}).‡

model	mode	ω_{H}^{a}	$\omega_{0\to1}^{a}$	$\omega_{1\to2}^{a}$	$\Delta\omega_{\mathrm{H}-1}^{a}$	$\Delta\omega_{1-2}^{a}$	$\Delta\omega_{a/b}$	$\Delta\omega_{1-2}^{a}{}'$	$\Delta\omega_{a/b}{}'$	$\Delta\omega_{1-2}^{a}{}''$	$\Delta\omega_{1-2}^{a}{}'''$	$\Delta\omega_{1-2}^{a}{}''''$	$\Delta\omega_{1-2}^{a}{}'''''$	$\Delta\omega_{a/b}{}'''''$
Ni_a-S	vCO	1911	1891	1868	20	23	-	15	-	15	23	21	23	-
	vCN_{as}	2068	2041	2022	27	19	] 21	17	] 20	-6	18	17	14	] 21
	vCN_{s}	2078	2050	2041	28	9		9		12	9	9	14	
Ni_a-C	vCO	1919	1896	1873	23	23	-	16	-	16	22	19	23	
	vCN_{as}	2074	2048	2028	25	20	] 13	18	] 12	6	19	18	18	] 13
	vCN_{s}	2086	2057	2041	29	16		15		14	16	15	18	
1	vCO	1951	1925	1902	26	23	-	16	-	16	18	18	23	
	vCN_{as}	2108	2082	2063	27	19	] 24	16	] 22	-12	18	16	12	] 24
	vCN_{s}	2116	2089	2084	27	5		5		10	5	6	12	
2	vCO_{as}	2008	1981	1968	28	13	] 24	10	] 18				11	] 24
	vCO_{s}	2046	2017	2007	29	10		8					11	
	vCN	2150	2121	2098	29	24	-	21	-				24	

‡ω_{H}^{a} – harmonic frequency of mode a; $\omega_{0\to1}^{a}$ – fundamental frequency of mode a; $\Delta\omega_{\mathrm{H}-1}^{a}$ – difference between ω_{H}^{a} and $\omega_{0\to1}^{a}$; $\Delta\omega_{1-2}^{a}$ – intramode anharmonicity, all vibrational degrees included in the anharmonic analysis; $\Delta\omega_{1-2}^{a}{}'$ – intramode anharmonicity, only *interacting* vCO and vCN vibrations included in the anharmonic analysis; $\Delta\omega_{1-2}^{a}{}''$ – intramode anharmonicity, only *non-interacting* vCO and vCN vibrations included in the anharmonic analysis; $\Delta\omega_{1-2}^{\mathrm{vCO}}{}'''$ – intramode anharmonicity, only *interacting* vCO, vCN, vFe–CO/CN, and δFe–CO/CN vibrations included in the anharmonic analysis; $\Delta\omega_{1-2}^{\mathrm{vCO}}{}''''$ – intramode anharmonicity, only *interacting* vCO, vCN, and vFe–CO vibrations included in the anharmonic analysis; $\Delta\omega_{1-2}^{a}{}'''''$ – intramode anharmonicity, all vibrational degrees included in the anharmonic analysis, *no* consideration of 2-2 Darling-Dennison resonances; $\Delta\omega_{a/b}$ – intermode anharmonicity (coupling between modes a and b), all vibrational degrees included in the anharmonic analysis. $\Delta\omega_{a/b}{}'$ - intermode anharmonicity, only *interacting* vCO and vCN vibrations included in the anharmonic analysis; $\Delta\omega_{a/b}{}'''''$ – intermode anharmonicity, all vibrational degrees included in the anharmonic analysis, *no* consideration of 2-2 Darling-Dennison resonances. $\Delta\omega_{a/b}$, $\Delta\omega_{a/b}{}'$, and $\Delta\omega_{a/b}{}'''''$ refer to pairs of symmetric and antisymmetric bond stretching modes, as indicated. δ – bending vibration; ν – stretching vibration.

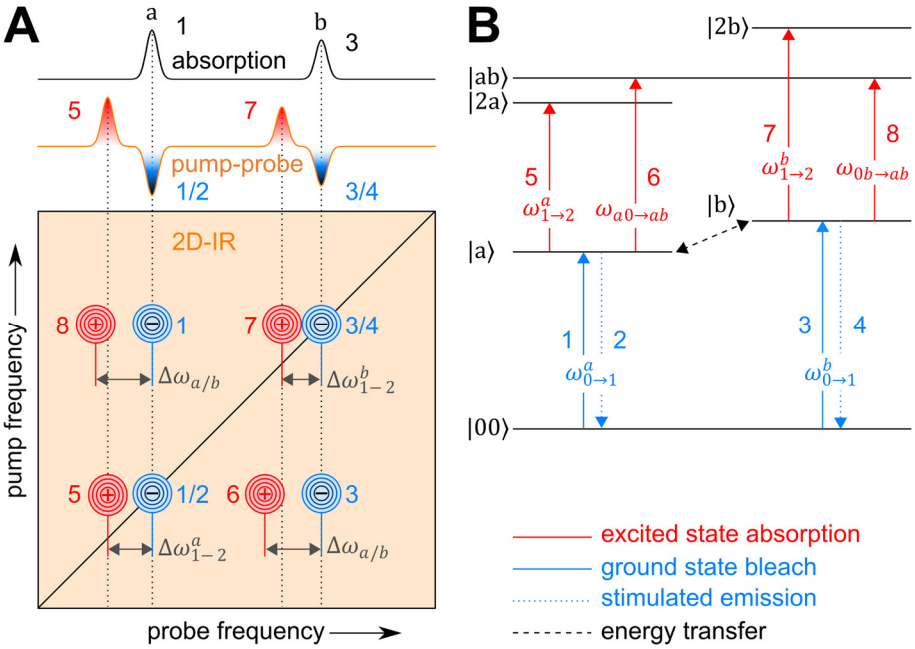

Figure S1: Infrared spectra **(A)** and three-level energy scheme **(B)** for two coupled vibrational modes a and b. Indicated quantities are introduced in the manuscript. ω_{H} and $\Delta\omega_{\mathrm{H}-1}$ are hypothetic quantities (resulting from the harmonic approximation) and thus not included in the scheme.

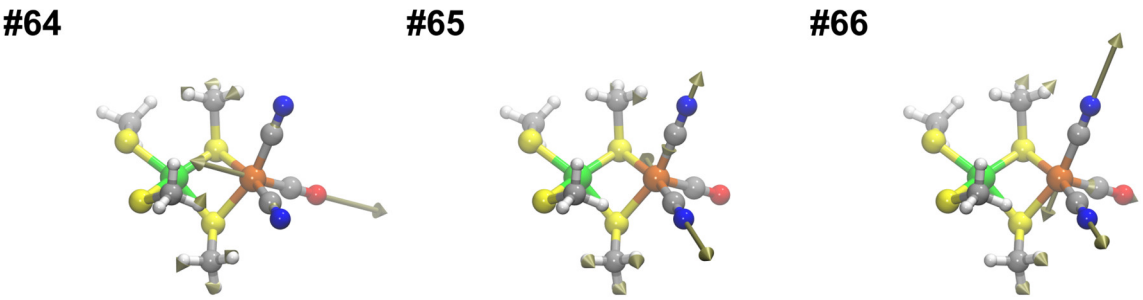

Figure S2: Normal mode eigenvectors (in Cartesian displacement coordinates) of vCO, νCN_{as}, and νCN_{s} ligand stretch vibrations of the Ni_a-S state of [NiFe] hydrogenase (modes #64–#66). Vectors are uniformly scaled for proper cognition.

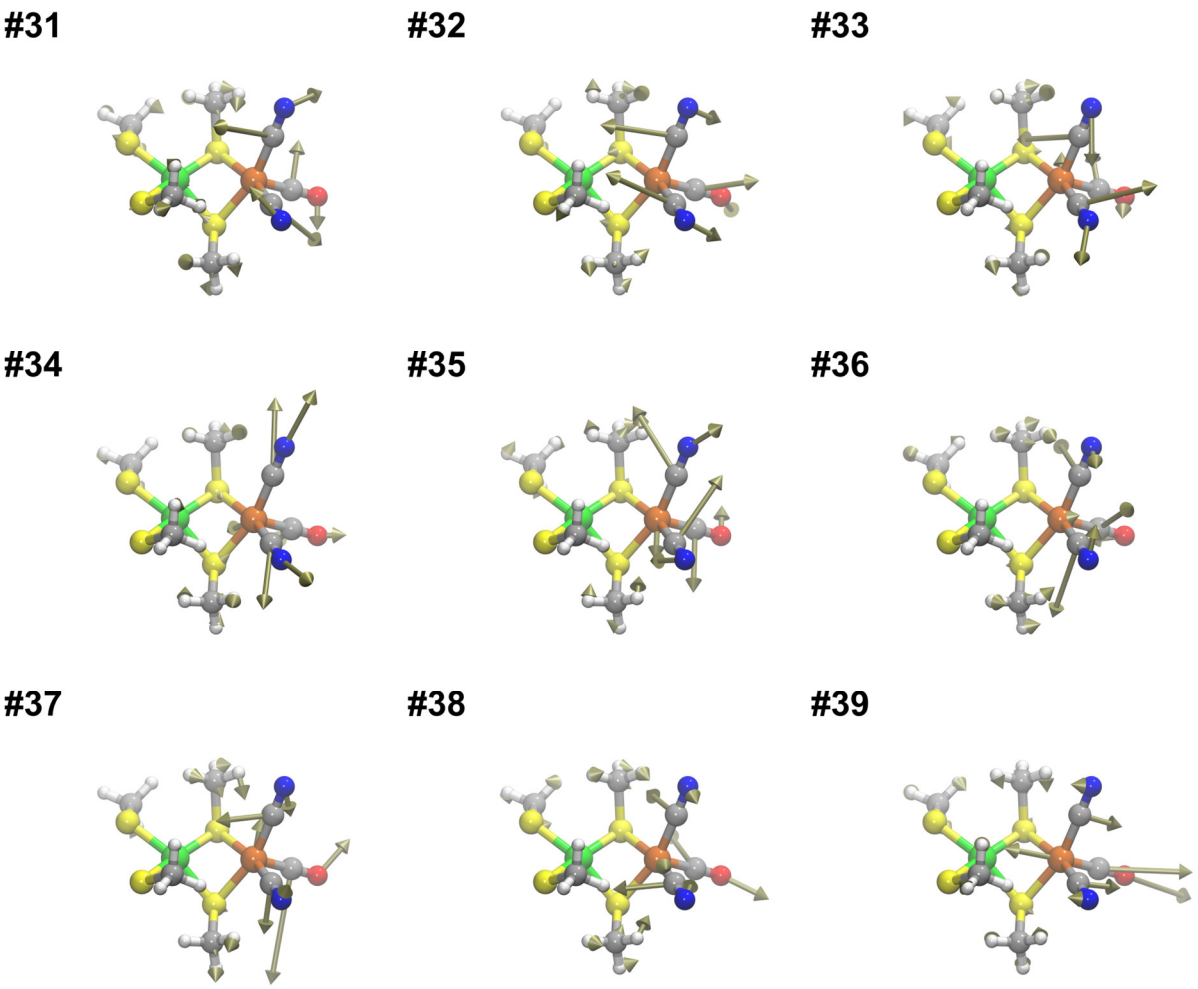

Figure S3: Normal mode eigenvectors (in Cartesian displacement coordinates) of νFe–CO/CN and δFe–CO/CN metal-ligand vibrations of the Ni_a-S state of [NiFe] hydrogenase (modes #31–#39). Vectors are uniformly scaled for proper cognition.

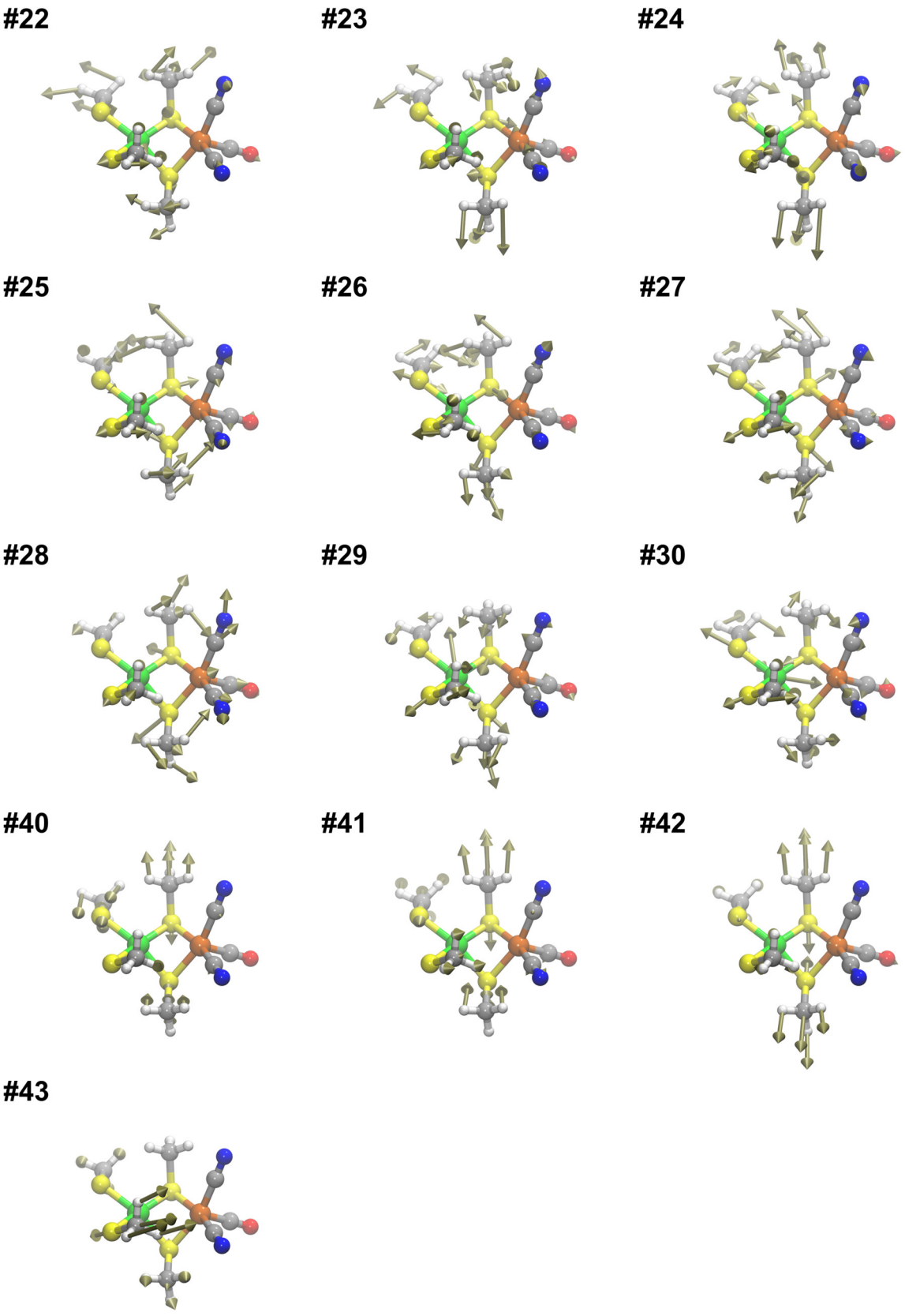

Figure S4: Normal mode eigenvectors (in Cartesian displacement coordinates) of δ/νNi–S vibrations (modes #22–#30) and νSC vibrations (modes #40–#43) of the Ni_a-S state of [NiFe] hydrogenase. Vectors are uniformly scaled for proper cognition.

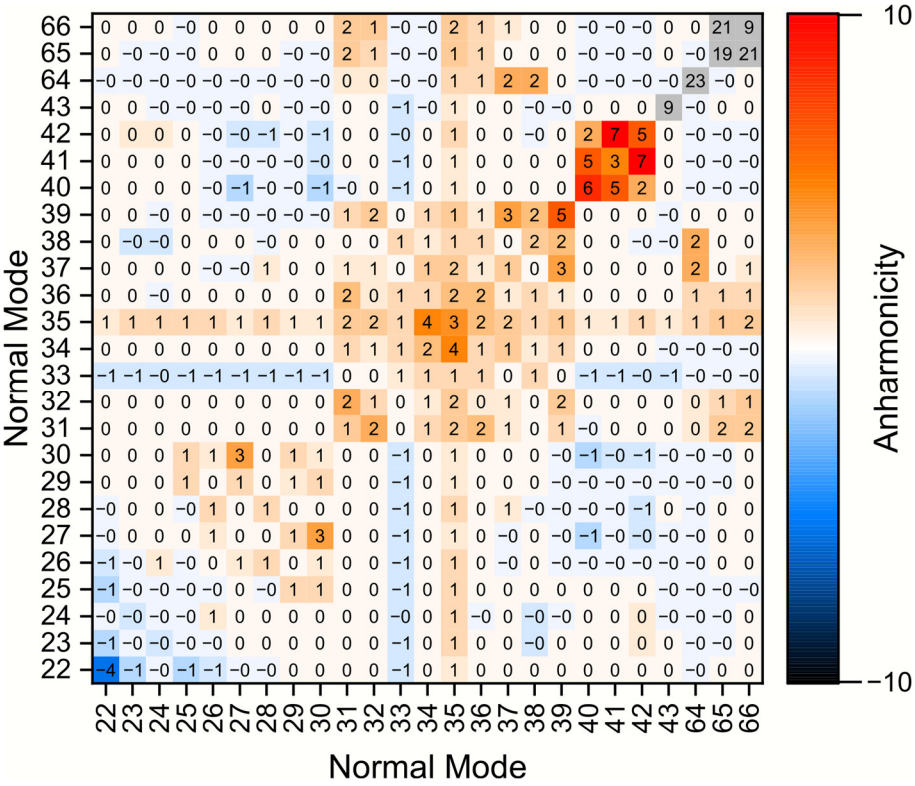

Figure S5: Matrix representation of intramode anharmonicities $\Delta\omega_{1-2}^{a}$ and intermode anharmonicities $\Delta\omega_{a/b}$ of νCO/CN vibrations (modes #64–#66), δ/νFe–CO/CN vibrations (modes #31–#39), δ/νNi–S vibrations (modes #22–#30), and νSC vibrations (modes #40–#43), as calculated for the Ni_a-S state of [NiFe] hydrogenase. Only the indicated vibrational degrees of freedom were included in the anharmonic analysis.

Table S2: Internal-coordinate description of vibrational modes for all computational models.[‡]

Ni_a-S		Ni_a-C		Complex 1/2	
mode #	**type of vibration**	**mode #**	**type of vibration**	**mode #**	**type of vibration**
1–21	delocalized vibration	1–25	delocalized vibration	1–10	delocalized vibration
22–30	δ/νNi–S	26–30	δ/νNi–S		
31–39	δ/νFe–CO/CN	31–39	δ/νFe–CO/CN	11–15 18–20	δ/νFe–CO/CN
		40	δNi–H–Fe		
40–43	νSC	41–44	νSC		
44–63	δCH_3	45–52	δCH_3	16–17 21–37	δCp
		53	νNi–H–Fe		
		54–66	δCH_3/H		
64–66	νCO, νCN	67–69	νCO, νCN	38–40	νCO, νCN
67–78	νCH_3	70–81	νCH_3	41–45	νCp–H

[‡]δ – bending vibration; ν – stretching vibration.