Experimental and DFT Investigations Reveal the Influence of the Outer Coordination Sphere on the Vibrational Spectra of Nickel-Substituted Rubredoxin, a Model Hydrogenase Enzyme

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Supporting Information

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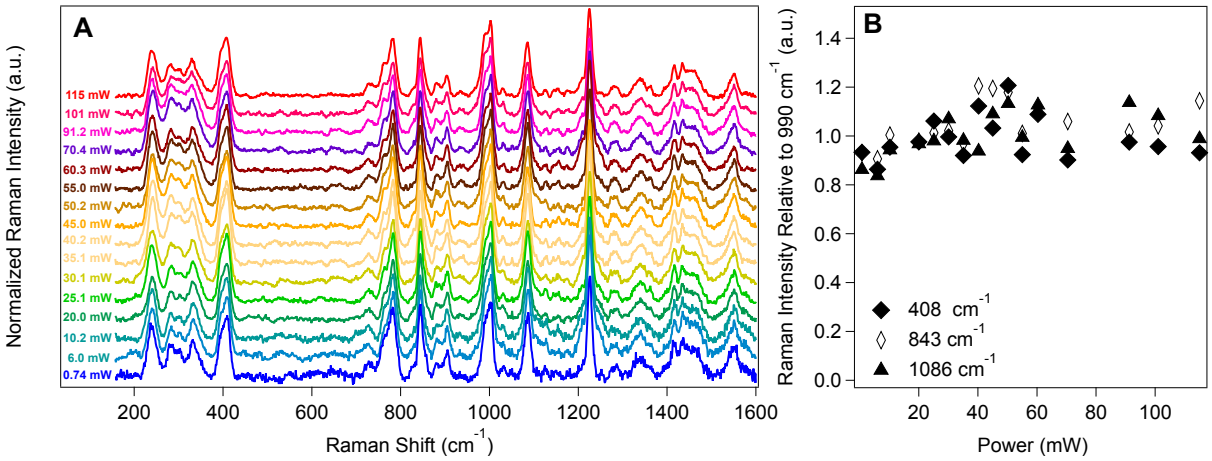


Figure S1. Power dependence of resonance Raman spectra of NiRd (λ_{ex} = 458 nm). (A) Spectra of NiRd at various laser powers normalized to the non-resonant phosphate buffer peak at 990 cm^{-1}. (B) Comparison of NiRd band intensities at 408 cm^{-1}, 843 cm^{-1}, and 1086 cm^{-1} relative to the phosphate peak at 990 cm^{-1} as a function of laser power.

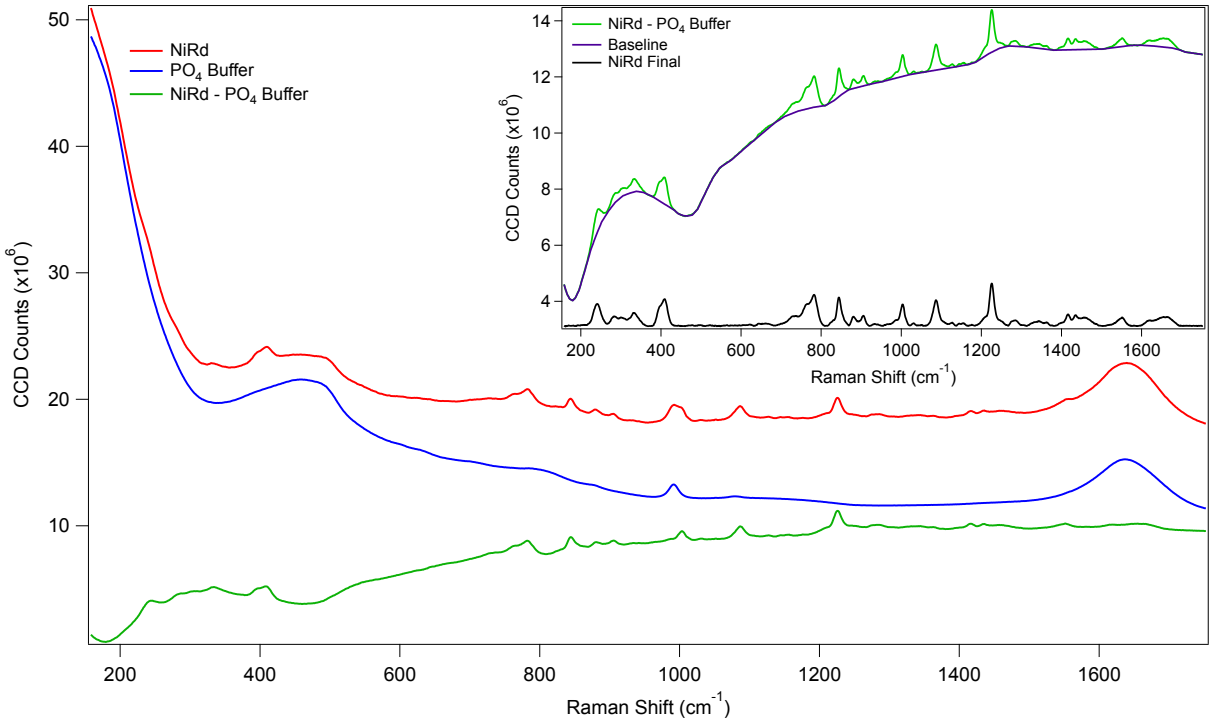


Figure S2. Summed raw resonance Raman spectra of NiRd (red) and phosphate buffer (blue) and the corresponding data workup. λ_{ex} = 458 nm; P_{ex} = 30 mW; $t_{collection}$ = 2 hrs each sample. The buffer-corrected spectrum (green) was generated by subtracting a sufficient ratio of the buffer spectrum from the NiRd spectrum to remove features attributed to non-resonant buffer peaks (e.g., the HPO_4^{2-} peak at 1000 cm^{-1}). (*Inset*) A spline baseline (purple) was subtracted from the buffer-corrected NiRd spectrum to remove any remaining broad features attributed to fluorescence, glass peaks, or non-sample based scattering, giving the final, corrected NiRd spectrum (black).

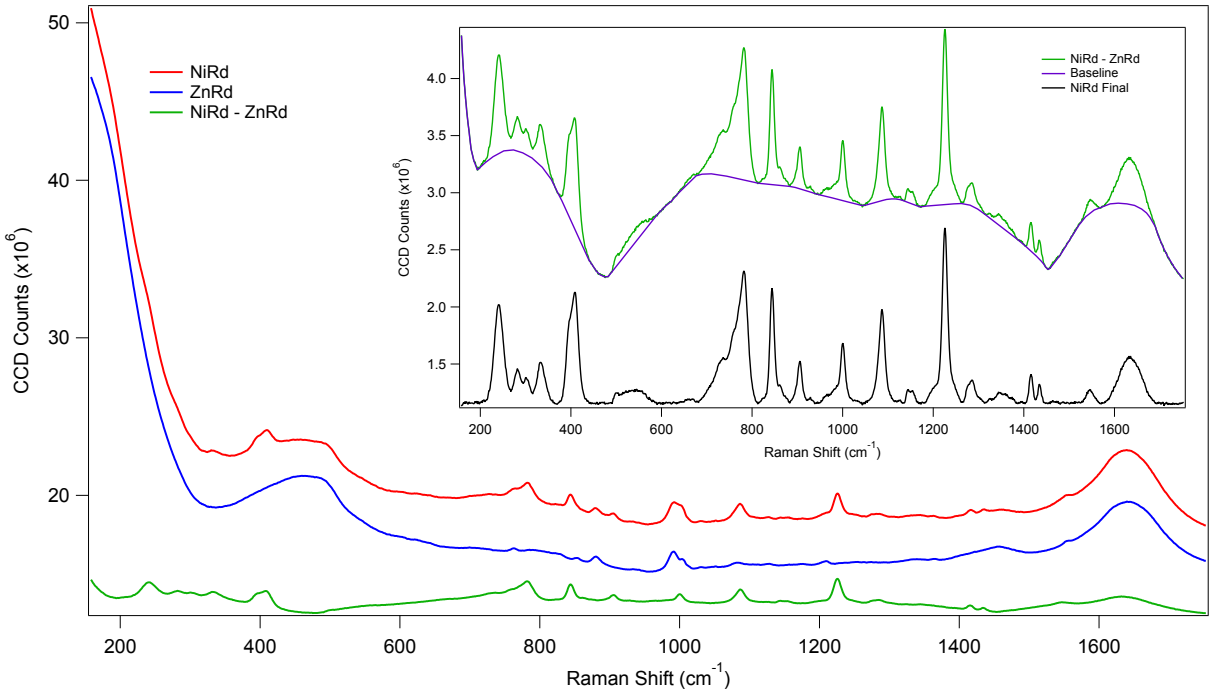
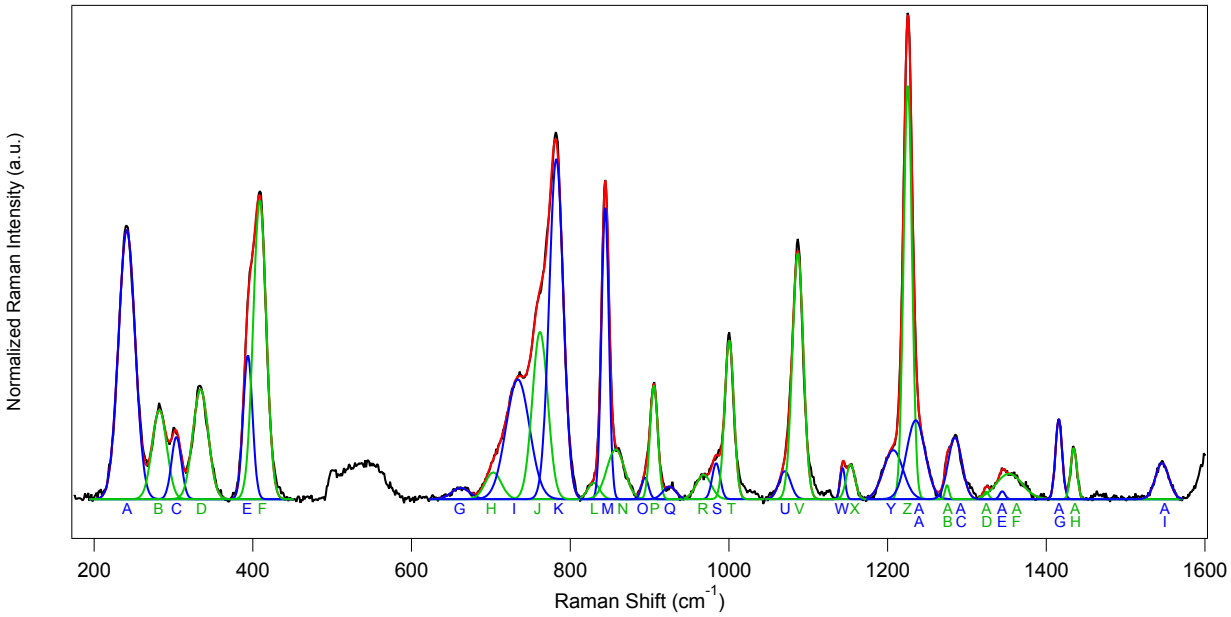


Figure S3. Summed raw resonance Raman spectra of NiRd (red) and ZnRd (blue) and the corresponding data workup. λ_{ex} = 458 nm; P_{ex} = 30 mW; $t_{collection}$ = 2 hrs each sample. The ZnRd-subtracted spectrum (green) was generated by subtracting a sufficient ratio of the ZnRd spectrum from the NiRd spectrum to remove features attributed to non-resonant protein peaks (e.g., the phenylalanine peak at 1004 cm^{-1}). (*Inset*) A spline baseline (purple) was subtracted from the ZnRd-corrected NiRd spectrum to remove any remaining broad features attributed to fluorescence, glass peaks, or non-sample based scattering, giving the final NiRd spectrum with bands that are solely attributed to resonance enhancement of the nickel-thiolate active site (black).



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
Center (cm^{-1})	241.1	282.1	303.6	334	393.6	408.6	661.7	702.9	733.8	761.9	782.3	829.5	844	857.2	894.2	905.4	924.7	968
Width (cm^{-1})	24.4	21.6	14.6	22.7	13.7	19.1	26.6	24.1	34.7	22.7	20.9	17.5	10.8	26.5	10.5	11.4	19.1	22.1
	S	**T**	**U**	**V**	**W**	**X**	**Y**	**Z**	**AA**	**AB**	**AC**	**AD**	**AE**	**AF**	**AG**	**AH**	**AI**	
Center (cm^{-1})	983.7	1000.4	1070.4	1086.8	1143.2	1153.3	1207	1225.4	1235.5	1274.9	1284.9	1324.3	1344.5	1353.2	1415.7	1434.6	1546	
Width (cm^{-1})	11.8	13.5	17.4	16.2	7.25	13	28.9	12.4	27.5	5.84	20.27	7.05	7.9	38.6	9.74	9.12	20	

Figure S4. Gaussian decomposition of resonance Raman spectrum of NiRd (458 nm excitation). Bands were fit to a sum of overlapping Gaussian functions (red) and decomposed into individual peaks (blue or green). Each peak is labeled with a letter, and the corresponding peak positions and widths are given in the table below.

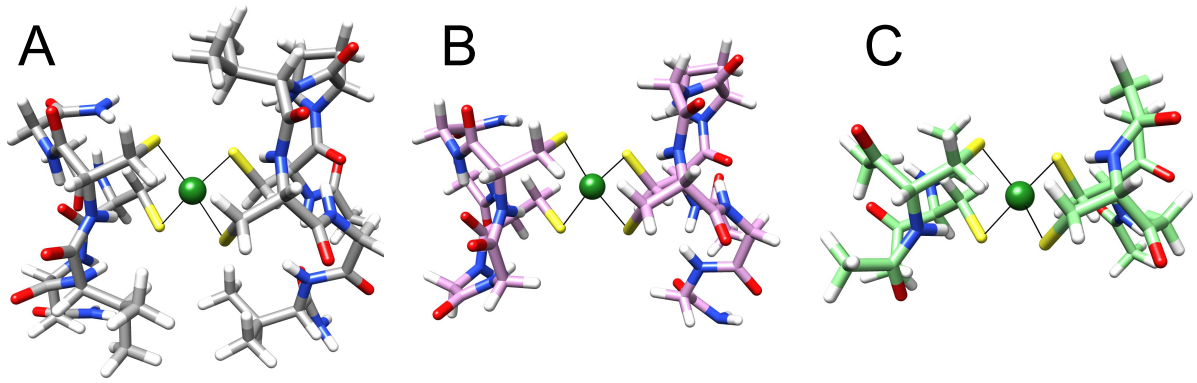


Figure S5. Optimized geometries of the different $Ni^{II}Rd$ models used in the DFT calculations with all atoms shown. (A) Full $Ni^{II}Rd$ model; (B) Backbone $Ni^{II}Rd$ model; and (C) $[Ni^{II}(NACA)_4]^{2-}$ model.

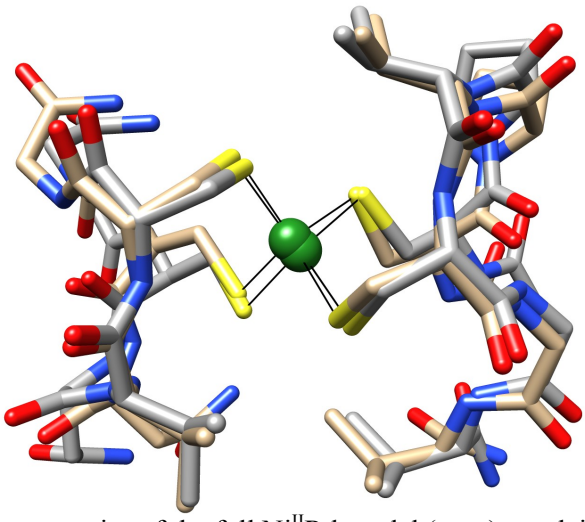


Figure S6. DFT-optimized geometries of the full Ni^{II}Rd model (gray) overlaid with the unconstrained Ni^{II}Rd model (tan). Hydrogen atoms are omitted for clarity.

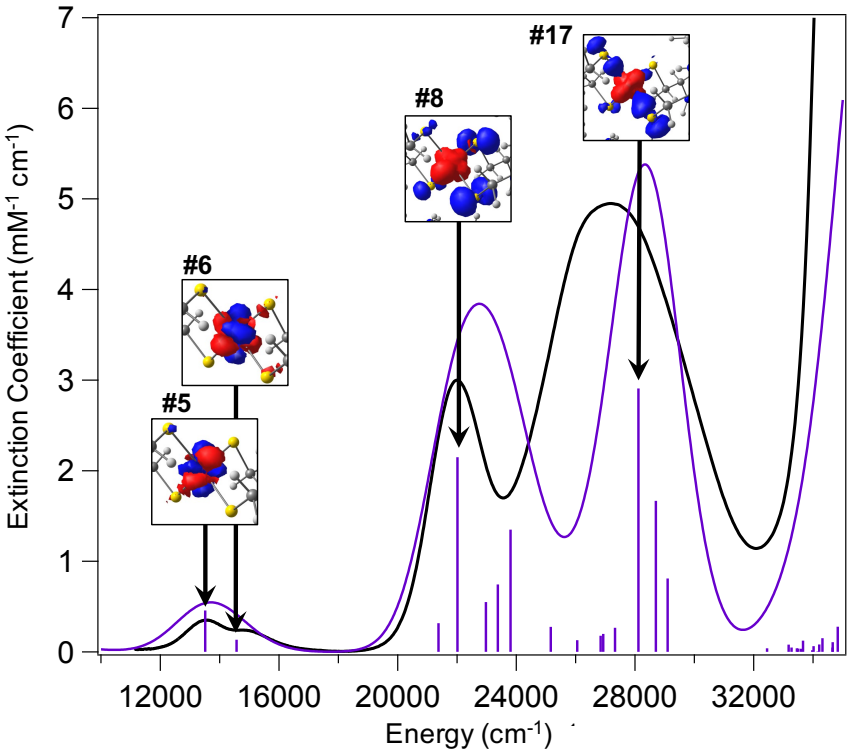


Figure S7. Optical absorption spectrum (black) of $Ni^{II}Rd$ overlaid with TD-DFT-calculated optical transitions for the full unconstrained model of $Ni^{II}Rd$ (purple). Electron difference densities for indicated transitions are shown; blue reflects negative electron density in the excited state while red reflects positive density.

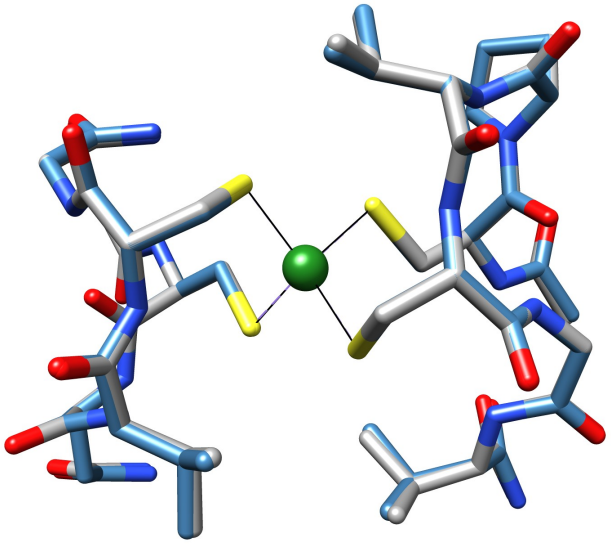


Figure S8. DFT-optimized geometries of the full Ni^{II}Rd model optimized with the SVP basis set (gray) and the TZVP basis set (dark blue) used for the non-coordinating atoms. The def2-TZVPP basis set was used for the nickel and sulfur atoms in both cases. Hydrogen atoms are omitted for clarity.

Table S1. Tabulated bond lengths, bond angles, and hydrogen-bonding distances in the *Cp* $Ni^{II}Rd$ crystal structure (PDB 1R0J) and the following DFT geometry-optimized models: full $Ni^{II}Rd$, backbone $Ni^{II}Rd$, full $Ni^{III}Rd$, backbone $Ni^{III}Rd$, $[Ni^{II}(NACA)_4]^{2-}$, and low-spin (S=0) $Ni^{II}Rd$.

	1R0J	Full Ni(II)Rd				Ni(II)Rd-Backbone			Full Ni(III)Rd		Ni(III)Rd-Backbone		NACA Ni(II)Rd		Ni(II)Rd low spin	
	X-Ray	B3LYP	ΔB3LYP[a]	Def2-TZVP	ΔTZVP[a]	B3LYP	ΔB3LYP[a]	ΔB3LYP[b]	B3LYP	ΔB3LYP[b]	B3LYP	ΔB3LYP[c]	B3LYP	ΔB3LYP[b]	B3LYP	ΔB3LYP[b]
Bond Lengths (Å)																
Ni-S_6	2.254	2.345	0.091	2.341	-0.004	2.335	0.081	-0.010	2.234	-0.111	2.227	-0.108	2.318	-0.027	2.329	-0.016
Ni-S_9	2.381	2.282	-0.099	2.278	-0.004	2.294	-0.087	0.012	2.204	-0.078	2.212	-0.082	2.297	0.025	2.270	-0.012
Ni-S_{32}	2.477	2.332	-0.145	2.331	-0.001	2.359	-0.118	0.027	2.217	-0.115	2.234	-0.125	2.318	-0.014	2.312	-0.020
Ni-S_{35}	2.134	2.287	0.153	2.285	-0.002	2.285	0.151	-0.002	2.198	-0.089	2.209	-0.076	2.290	0.003	2.277	-0.010
Angle (◦)																
S_6-Ni-S_9	121.449	111.148	-10.301	109.9	-1.248	119.790	-1.659	8.642	108.494	-2.654	110.072	-9.718	109.078	-2.07	110.765	-0.383
S_6-Ni-S_{32}	116.046	111.360	-4.686	112.4	1.360	110.606	-5.440	-0.754	116.913	5.553	115.930	5.324	110.383	-0.977	114.282	2.922
S_6-Ni-S_{35}	105.050	98.381	-6.669	98.8	0.481	93.527	-11.523	-4.854	95.218	-3.163	93.454	-0.073	98.573	0.192	97.516	-0.865
S_9-Ni-S_{32}	101.833	94.900	-6.933	94.9	0.000	96.997	-4.836	2.097	95.743	0.843	96.438	-0.559	98.523	3.923	94.418	-0.482
S_9-Ni-S_{35}	104.128	129.468	25.340	129.6	0.168	127.166	23.038	-2.302	137.256	7.788	138.082	10.916	114.432	-15.036	130.000	0.532
S_{32}-Ni-S_{35}	107.107	111.692	4.585	111.5	-0.292	108.676	1.569	-3.016	104.649	-7.043	103.885	-4.791	125.585	13.893	110.730	-0.962
Hydrogen Bonding[d]																
CYS6-VAL8	3.629	3.557	-0.072	3.549	-0.008	3.449	-0.180	-0.108	3.614	0.057	3.585	0.136	-----	-----	3.537	-0.020
CYS6-CYS9	3.672	3.676	0.004	3.649	-0.027	3.609	-0.063	-0.067	3.521	-0.155	3.595	-0.014	3.399	-0.277	3.629	-0.047
CYS9-TYR11	3.543	3.314	-0.229	3.296	-0.018	3.437	-0.106	0.123	3.393	0.079	3.367	-0.070	-----	-----	3.315	0.001
CYS32-VAL34	3.513	3.436	-0.077	3.464	0.028	3.345	-0.168	-0.091	3.471	0.035	3.361	0.016	-----	-----	3.413	-0.023
CYS32-CYS35	3.580	3.493	-0.087	3.506	0.013	3.496	-0.084	0.003	3.364	-0.129	3.352	-0.144	3.522	0.029	3.467	-0.026
CYS35-VAL37	4.077	3.649	-0.428	3.631	-0.018	3.536	-0.541	-0.113	3.510	-0.139	3.441	-0.095	-----	-----	3.598	-0.051

[a]Compared to the X-ray crystal structure
[b]Compared to the full $Ni^{II}Rd$ structure
[c]Compared to the backbone $Ni^{II}Rd$ structure
[d]Distances reflect heavy-atom separation distances, e.g., d(S-N)

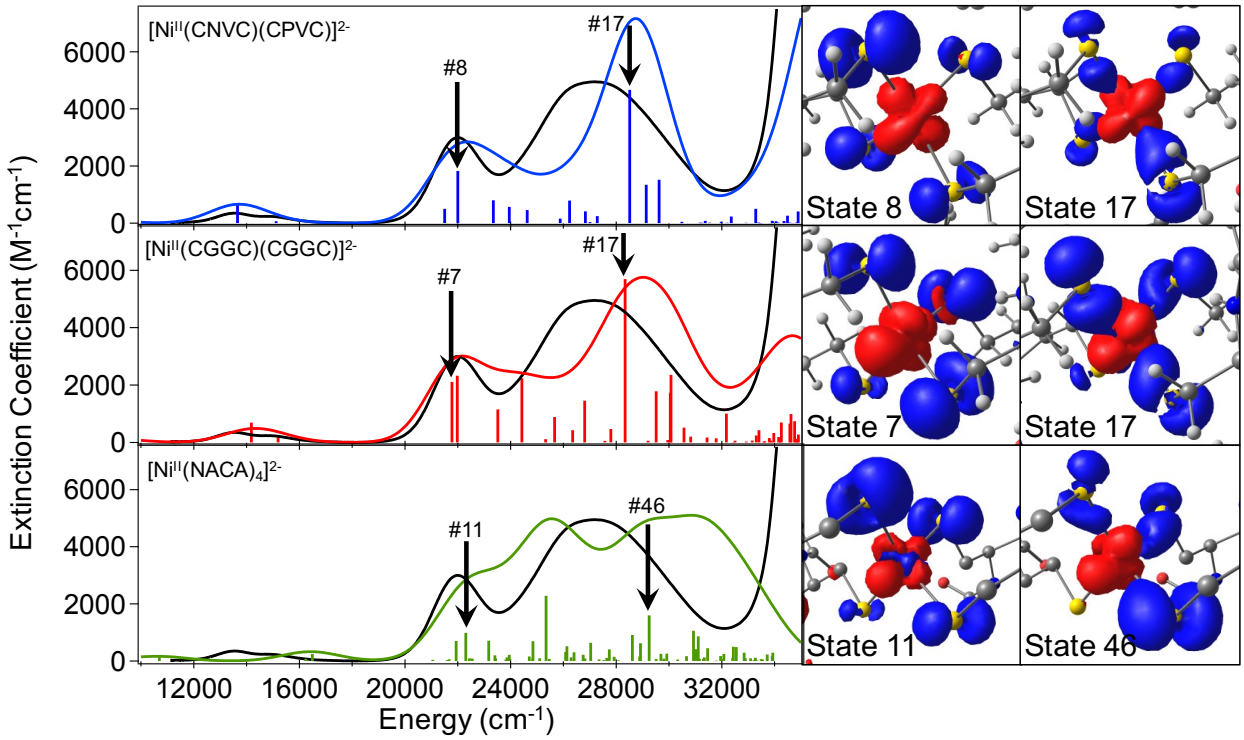
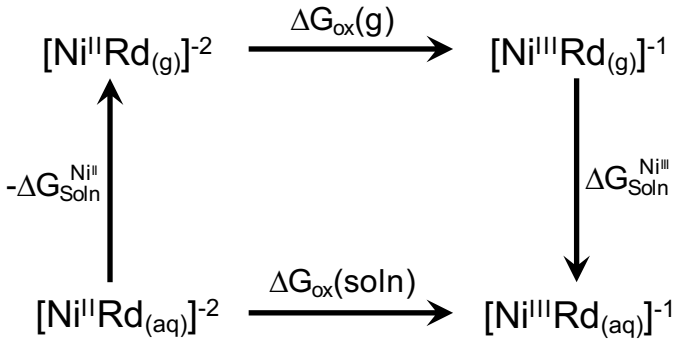


Figure S9. (*Left*) Optical absorption spectrum of $Ni^{II}Rd$ (black) overlaid with TD-DFT-calculated optical spectra for the full ($[Ni^{II}(CNVC)(CPVC)]^{2-}$) $Ni^{II}Rd$ model (blue), the backbone ($[Ni^{II}(CGGC)(CGGC)]^{2-}$) $Ni^{II}Rd$ model (red), and the $[Ni^{II}(NACA)_4]^{2-}$ model (green); a +1,500 cm^{-1} offset was applied only to the $[Ni^{II}(NACA)_4]^{2-}$ model spectrum. (*Right*) Electronic difference density plots for the indicated transitions; blue reflects negative electron density in the excited state while red reflects positive density.

Methodology for calculating reduction potentials

The reduction potential of the $Ni^{III/II}Rd$ one-electron couple was calculated from the optimized gas-phase structure ($[Ni^{II}Rd_{(g)}]^{2-}$) using the thermodynamic cycle given below (Scheme S1).



Scheme S1. Thermodynamic cycle used to calculate reduction potential of $Ni^{III/II}Rd$ couple.

The reduction potential of the $Ni^{III/II}Rd$ couple was calculated by considering the solution-phase free energy changes, $\Delta G_{ox}(soln)$, from the nickel(II) to the nickel(III) state using eq. 1:[1]

$$E^{Ni(III/II)}_{Calc} = \frac{\Delta G_{ox}(soln)}{nF} \quad (1)$$

where F is Faraday's constant (96,487 C/mol) and n is the number of moles of electrons involved in the reaction (n = 1).

$\Delta G_{ox}(g)$ is calculated by considering the difference in the Gibbs free energy between $Ni^{II}Rd$ and $Ni^{III}Rd$ obtained directly from the vibrational frequency calculation. $\Delta G^{Ni(III)}_{soln}$ and $\Delta G^{Ni(II)}_{soln}$ are solvation energies determined by taking the difference in total electronic energies between the gas-phase structure and the solvated, gas-phase geometry. The sum of the three values in eq. 2 are equal to $\Delta G_{ox}(soln)$.

$$\Delta G_{ox}(soln) = -\Delta G^{Ni(II)}_{soln} + \Delta G_{ox}(g) + \Delta G^{Ni(III)}_{soln} \quad (2)$$

The reduction potential, which is the inverse of the oxidation potential, is reported relative to the standard hydrogen electrode (SHE) using eq 3. The calculated SHE absolute potential, $E^{H+/H2}_{SHE}(V)$, of 4.281 V was used.[2]

$$E^{Ni(III/II)}_{Calc,SHE}(V.\,vs\,SHE) = E^{Ni(III/II)}_{Calc}(V.) - E^{H+/H2}_{SHE}(V.) \quad (3)$$

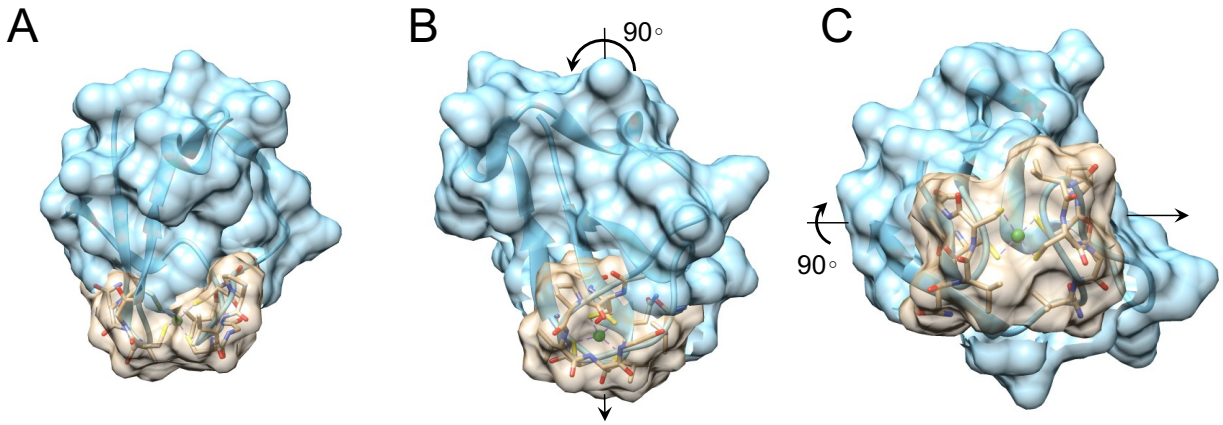


Figure S10. Different snapshots of the van der Waals surface of the crystal structure of *Dd* Rd (blue) and the full active site computational model of NiRd (tan). (A) Top-down view of the protein; (B) Protein rotated 90◦ along one axis; (C) Protein rotated 90◦ along the other axis.

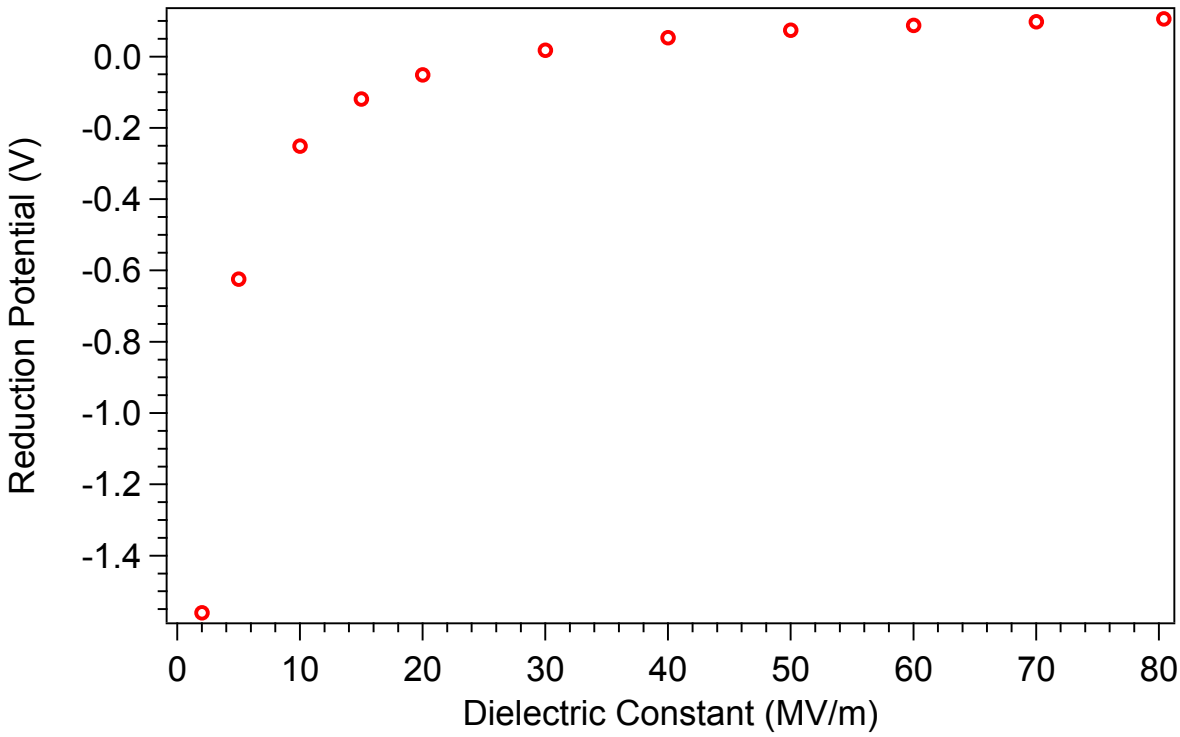


Figure S11. Calculated $Ni^{III/II}$ reduction potential for the full NiRd model as a function of dielectric constant within the COSMO solvation model.

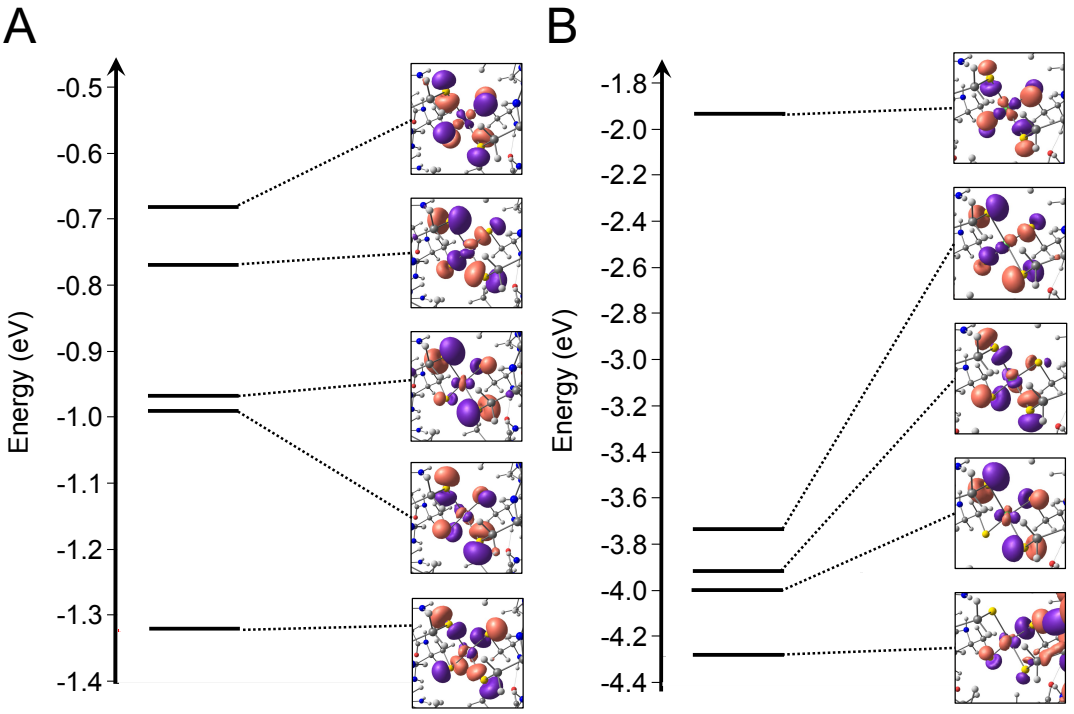


Figure S12. Semi-quantitative d-orbital splitting diagrams for (A) $Ni^{II}Rd$ (S=1) and (B) $Ni^{III}Rd$ (S=1/2). The purple and pink lobes represent phases of the orbitals.

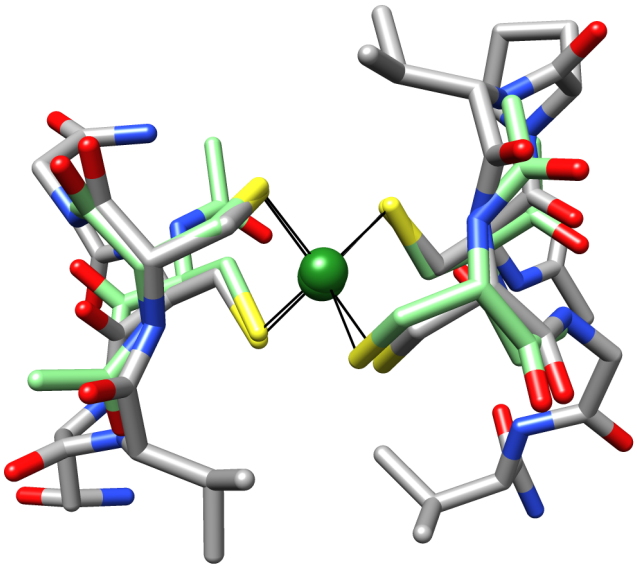


Figure S13. DFT-optimized geometries of the full $Ni^{II}Rd$ model (gray) overlaid with the $[Ni^{II}(NACA)_4]^{2-}$ model (green). Hydrogen atoms are omitted for clarity.

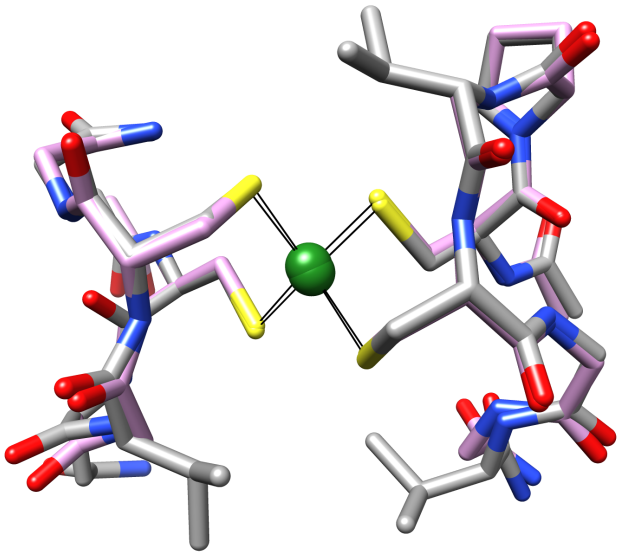


Figure S14. DFT-optimized geometries of the full Ni^{II}Rd model (gray) overlaid with the backbone Ni^{II}Rd model (pink). Hydrogen atoms are omitted for clarity.

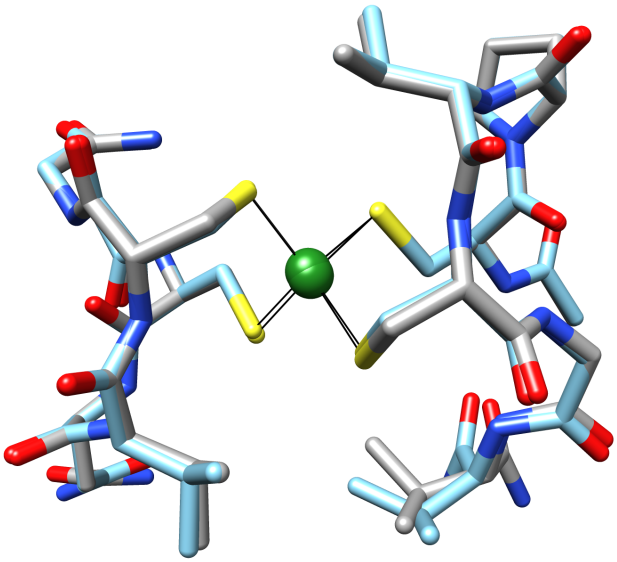


Figure S15. DFT-optimized geometries of the full Ni^{II}Rd model (gray) overlaid with the full Ni^{III}Rd model (blue). Hydrogen atoms are omitted for clarity.

Table S2. Calculated TD-DFT vertical transition energies (cm^{-1}), oscillator strengths, and extinction coefficients of the full and backbone $Ni^{II}Rd$ models for indicated states.

	State 5			State 6			State 7			State 8			State 10			State 17		
	Energy	f_{osc}	ε ($mM^{-1}cm^{-1}$)	Energy	f_{osc}	ε ($mM^{-1}cm^{-1}$)	Energy	f_{osc}	ε ($mM^{-1}cm^{-1}$)	Energy	f_{osc}	ε ($mM^{-1}cm^{-1}$)	Energy	f_{osc}	ε ($mM^{-1}cm^{-1}$)	Energy	f_{osc}	ε ($mM^{-1}cm^{-1}$)
Full	13654	0.0073	0.636	15118	0.0008	0.070	21503	0.0058	0.505	22001	0.0211	1.831	23950	0.0065	0.462	28508	0.0538	4.669
Backbone	14181	0.0048	0.697	15193	0.0012	0.179	21776	0.0146	2.113	21981	0.0160	2.328	24428	0.0154	2.239	28336	0.0393	5.694

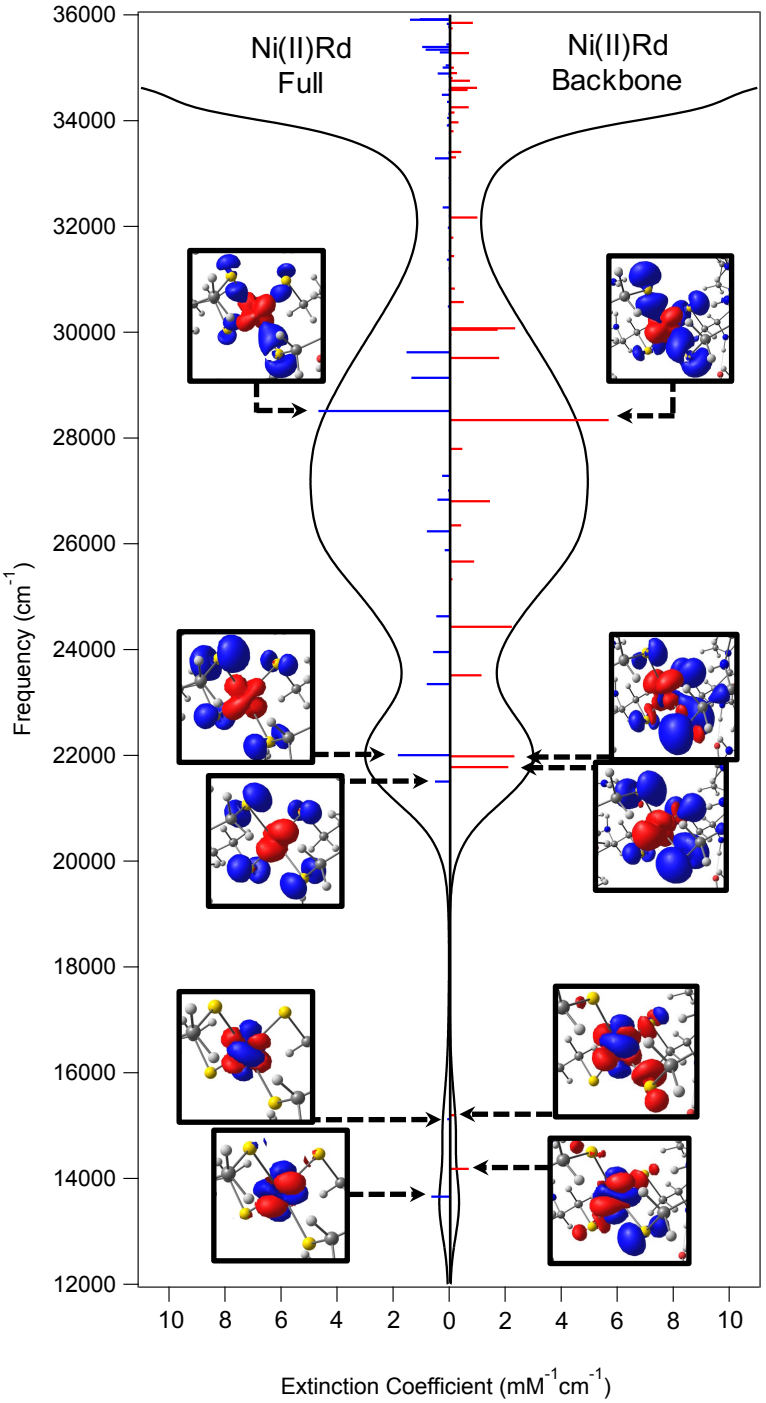


Figure S16. Vertically aligned calculated TD-DFT transitions for the full (*left*) and backbone (*right*) Ni^{II}Rd models. (*Inset*) Electron difference density plots for indicated transitions; blue reflects negative difference density in the excited state while red reflects positive difference density.

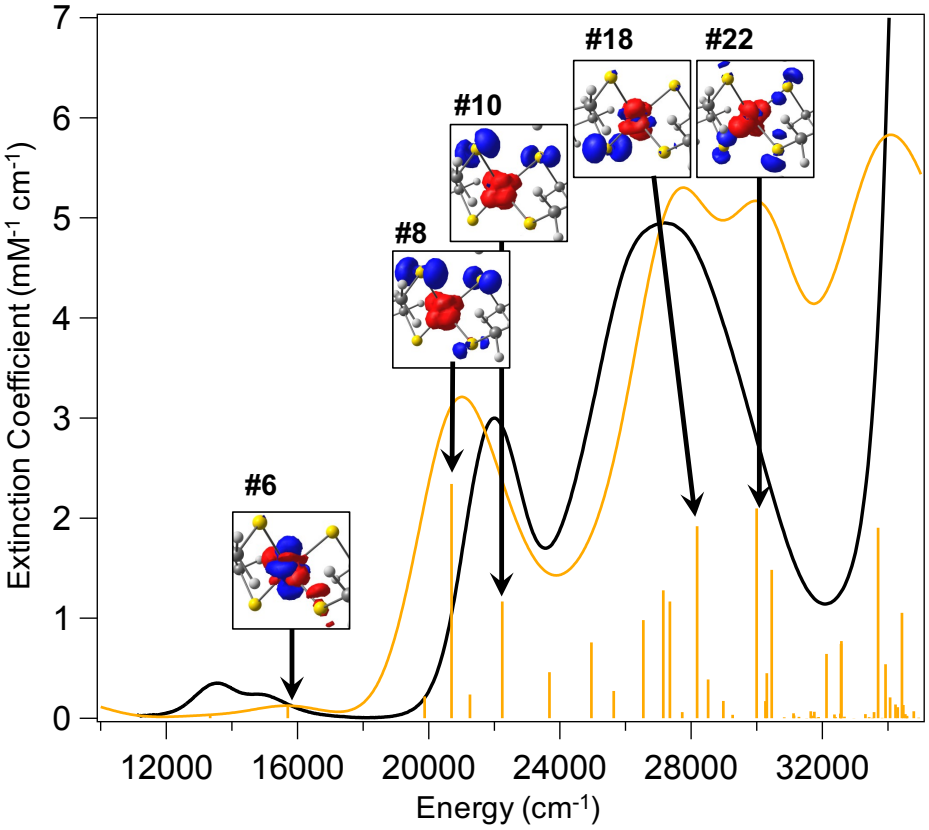


Figure S17. Optical absorption spectrum (black) of Ni^{II}Rd overlaid with TD-DFT-calculated optical transitions for the *Cp* Ni^{II}Rd crystal structure geometry (orange). Electron difference densities shown for indicated transitions; blue reflects negative difference density in the excited state while red reflects positive difference density.

Table S3. Calculated frequencies for the $Ni^{II}Rd$ full model compared to experimental frequencies (ν), isotope shifts (δ), dimensionless displacements (Δs) for given excited states, and mode descriptions for select vibrational normal modes. Experimental vibrational frequencies were determined by fitting each band to a Gaussian lineshape.

						Dimensionless normal coordinate displacement (Δ)		
$\nu_{calc, (H2O)}$ (cm^{-1})	$\nu_{expt, (H2O)}$ (cm^{-1})	$\nu_{calc, (D2O)}$ (cm^{-1})	$\nu_{expt, (D2O)}$ (cm^{-1})	$\delta H_{,calc}$ (cm^{-1})	$\delta H_{,expt}$ (cm^{-1})	State 8	State 17	Mode Description[a]
244.27	241.08	242.89	241.28	-1.38	0.20	0.657927	0.346208	$\delta(B_1)$ S-Ni-S
277.08	282.08	275.66	281.34	-1.42	-0.74	0.382879	1.187006	$\nu(A_1)$ Ni-S
304.69	303.44	304.60	303.01	-0.09	-0.43	0.406295	0.52849	$\nu(B_2)$ Ni-S_6
307.84		307.19		-0.65		0.220485	0.711182	$\nu(B_2)$ Ni-S_{32}
335.73	333.91	336.23	332.71	0.50	-1.20	0.344768	-0.013597	$\nu(B_2)$ Ni-S
415.59	393.80	412.23	393.22	-3.36	-0.58	0.112537	-0.084804	δ(Ni-S_6-C)
418.34	408.65	414.94	408.01	-3.40	-0.64	-0.121766	0.047518	δ(Ni-S_{32}-C)
502.44	-----	480.69	-----	-21.75	-----	-0.106749	-0.026013	δ(S_9-C-C)
510.18	-----	490.73	-----	-19.45	-----	0.184249	0.087303	δ(S_{35}-C-C)
661.21	669.51	653.93	-----	-7.28	-----	-0.04008	-0.177381	ν(S_{35}-C)
664.06		669.08	-----	5.02	-----	-0.111204	-0.081166	ν(S_9-C)
743.24	733.23	730.53	734.77	-12.71	1.50	0.100964	0.043519	w(C_9-C-C)
778.55	782.59	777.85	781.04	-0.70	-1.55	-0.174294	-0.111595	ν(S_6-C)/w(C_9-C-C)
854.72	844.05	834.21	841.00	-20.51	-3.05	0.095615	0.051679	w(C-C-C)
862.89		856.73		-6.16		0.074731	0.034492	w(C_{32}-C-C)/ w(C_{35}-C-C)
867.97		867.98		0.01		-0.043387	-0.060528	w(C_{32}-C-C)/ w(C_{35}-C-C)
925.96	905.53	912.73	903.92	-13.23	-1.61	0.096089	0.061618	δ(C_9-C-C)/ δ(C_{32}-C-C)
927.61		925.45		-2.16		-0.044238	-0.086644	δ(C_9-C-C)/ δ(C_{32}-C-C)/ δ(C_{35}-C-C)
1010.92	1000.43	998.24	1002.51	-12.68	2.08	0.078009	0.02264	ν(C_{35}-C)
1018.97		1004.98		-13.99		-0.059868	-0.002294	ν(C_9-C)
1115.15	1087.24	1121.15	1088.26	6.00	1.02	0.050302	0.015891	t(H-C_9-H)
1119.03		1123.69		4.66		0.101217	0.050511	t(H-C_{35}-H)
1153.50	1143.01	1144.85	1144.34	-8.65	1.33	0.036976	0.004609	δ(C_9-C-N)/ ν(C_9-N)
1156.77		1160.80		4.03		-0.025669	-0.030537	δ(C_{32}-C-N)/ ν(C_{32}-N)
1168.45	1153.16	1186.44	1157.86	17.99	4.70	-0.044422	0.010294	t(H-C_{32}-H)/ ν(C_{32}-C)
1175.71		1195.58		19.87		-0.037956	0.033807	t(H-C_6-H)/ ν(C_6-C)
1218.57	1207.00	1226.57	-----	8.00	-----	-0.021567	0.02374	t(H-C_9-H)/ t(H-C_{35}-H)

1224.49		1232.05	-----	7.56	-----	-0.044225	0.026554	t(H-C_9-H)/ t(H-C_{35}-H)
1246.17	1225.50	1248.04	1226.22	1.87	0.72	-0.057262	-0.033833	t(H-C_9-H)/ν(C_9-C)
1251.14		1255.01		3.87		0.101394	0.024829	t(H-C_{35}-H)/ ν(C_{35}-C)
1311.37	1274.68	1322.87	1276.02	11.50	1.34	-0.01502	0.010169	w(H-C-H)/ δ(S_{32}-C-C)
1317.99	1284.70	1312.08	1288.91	-5.91	4.21	-0.003162	0.010968	w(H-C_9-H)/ δ(S_9-C-C)
1361.71	1350.95	1360.61	1343.55	-1.10	-7.40	-0.024922	-0.017432	r(H-C_9-H)/ δ(C_9-C-C)
1443.34	1415.74	1441.55	1414.93	-1.79	-0.81	0.051485	-0.00585	δ(H-C_9-H)
1447.29	1434.58	1442.93	1429.66	-4.36	-4.92	0.045848	0.000048	δ(H-C_{35}-H)

[a]Mode description utilizes the following symbols: ν = stretch, δ = bend, w = wag, t = twist, r = rock

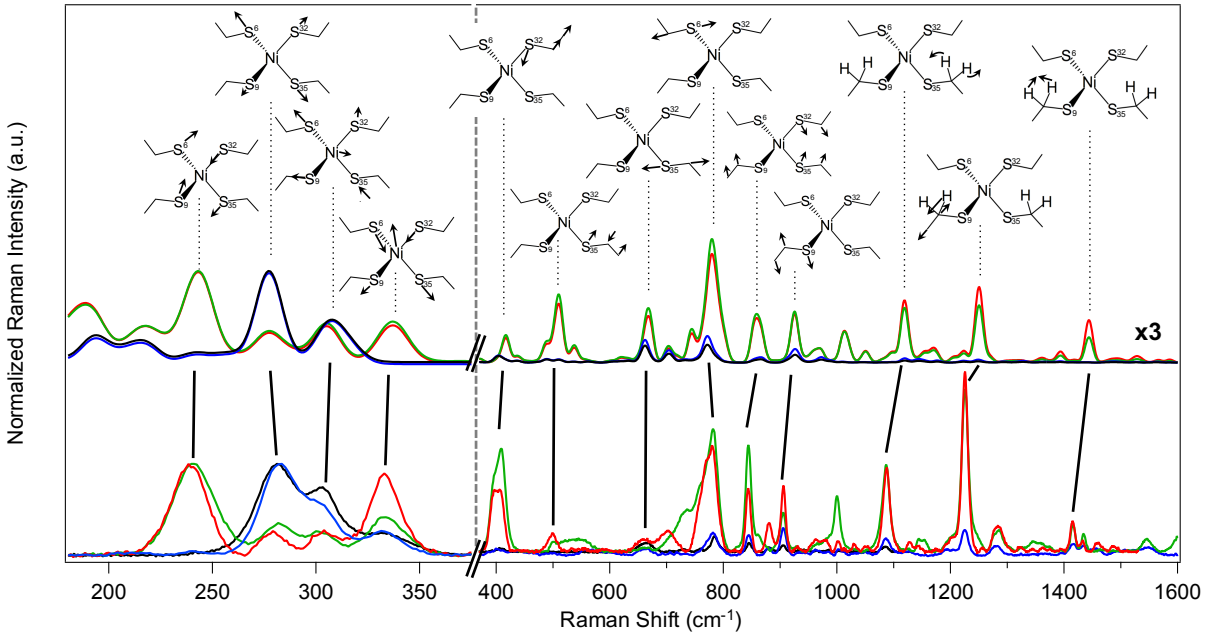


Figure S18. Intensity-normalized resonance Raman spectra of NiRd showing relative peak intensities across the four excitation wavelengths compared to the calculated spectra of the full NiRd model. Experimental (bottom) and calculated (top) spectra at 364 nm (black) and 407 nm (blue) were normalized to the 282 cm^{-1} peak, while the 458 nm (green) and 488 nm (red) spectra were normalized to the 241 cm^{-1} band to facilitate direct relative intensity comparisons. The high frequency region of the spectra are shown on a different abscissa, and the intensities of the calculated spectra were scaled three-fold to better visualize the peaks. Lines between bands are shown to indicate correspondence and resultant mode assignments. (*Inset*) Vector diagrams of the vibrational modes associated with the calculated spectra.

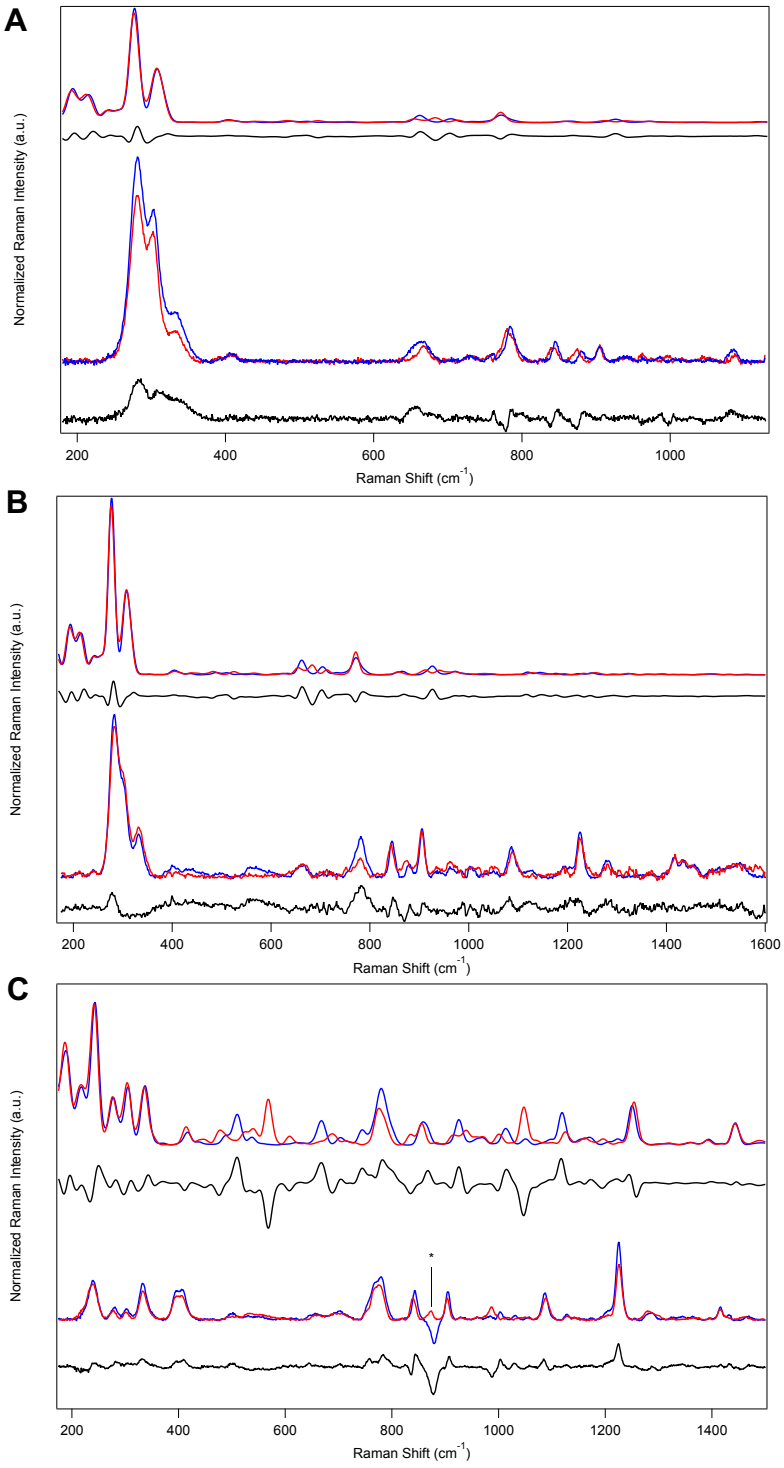


Figure S19. Calculated (*top*) and experimental (*bottom*) resonance Raman spectra of NiRd with (A) 364 nm, (B) 407 nm, and (C) 488 nm excitation in buffered H_2O (blue), D_2O (red), and the corresponding difference spectrum (H – D, black).

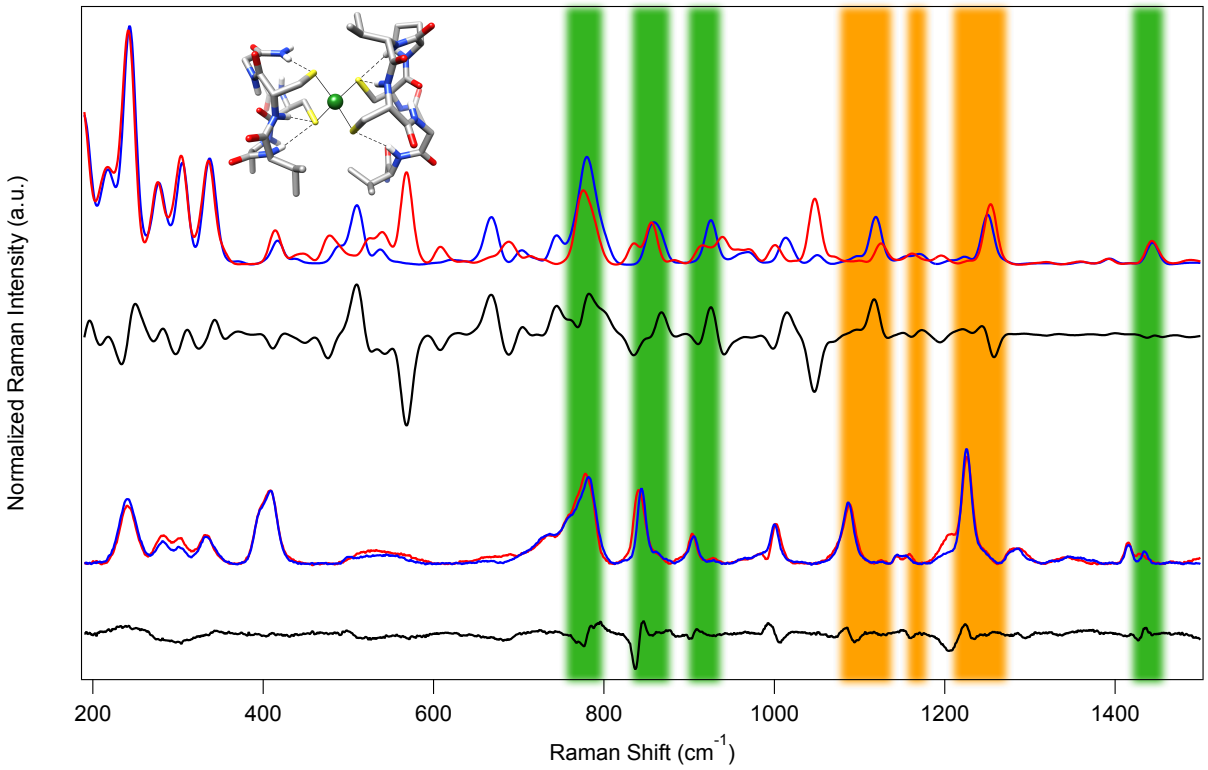


Figure S20. Calculated (*top*) and experimental (*bottom*) resonance Raman spectra of NiRd in buffered H_2O (blue) and D_2O (red). The frequency shifts resulting from exchangeable protons are highlighted; green reflects bands that are downshifted in D_2O, while orange reflects bands that are upshifted in D_2O. (*Inset*) Structure of the active site shown with hydrogen bonding network to cysteine thiolates shown with dotted lines.

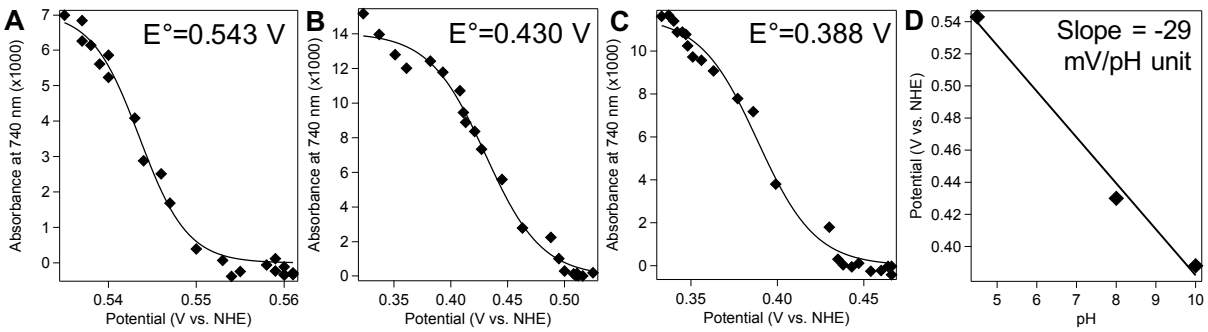


Figure S21. Potentiometric titrations of $Ni^{II}Rd$ with $[Fe^{III}(CN)_6]^{3-}$. Absorbance of NiRd at 740 nm is plotted as a function of measured solution potential in (A) 50 mM acetate, pH 4.5, (B) 50 mM Tris, pH 8.0, and (C) 50 mM CAPS, pH 10.0. (D) Midpoint potential as a function of pH.

Table S4. Calculated electronic and Gibbs free energies in Hartree (E_h) of $[FeCp_2]^+$ and $[FeCp_2]^0$.

	Electronic Energy		***Gibbs Free Energy***
	Gas-phase	**Acetonitrile**	**Gas-phase**
$[FeCp_2]^0$	-1665.00426911206	-1665.01262017523	-1664.86700109000
$[FeCp_2]^+$	-1664.75006883420	-1664.82812574107	-1664.61338495000

Table S5. Calculated electronic and Gibbs free energies in Hartree (E_h) of $Ni^{II}Rd$ and $Ni^{III}Rd$.

	Electronic Energy		***Gibbs Free Energy***
	Gas-phase	**Solution-phase (H_2O)**	**Gas-phase**
$Ni^{II}Rd$ Full	-6666.36123525000	-6666.60363685797	-6665.24801193000
$Ni^{III}Rd$ Full	-6666.30624265000	-6666.44587436237	-6665.18956692000
$Ni^{II}Rd$ Backbone	-6104.75796383368	-6104.99512369138	-6103.93749045000
$Ni^{III}Rd$ Backbone	-6104.70334293496	-6104.82889349978	-6103.88235120000

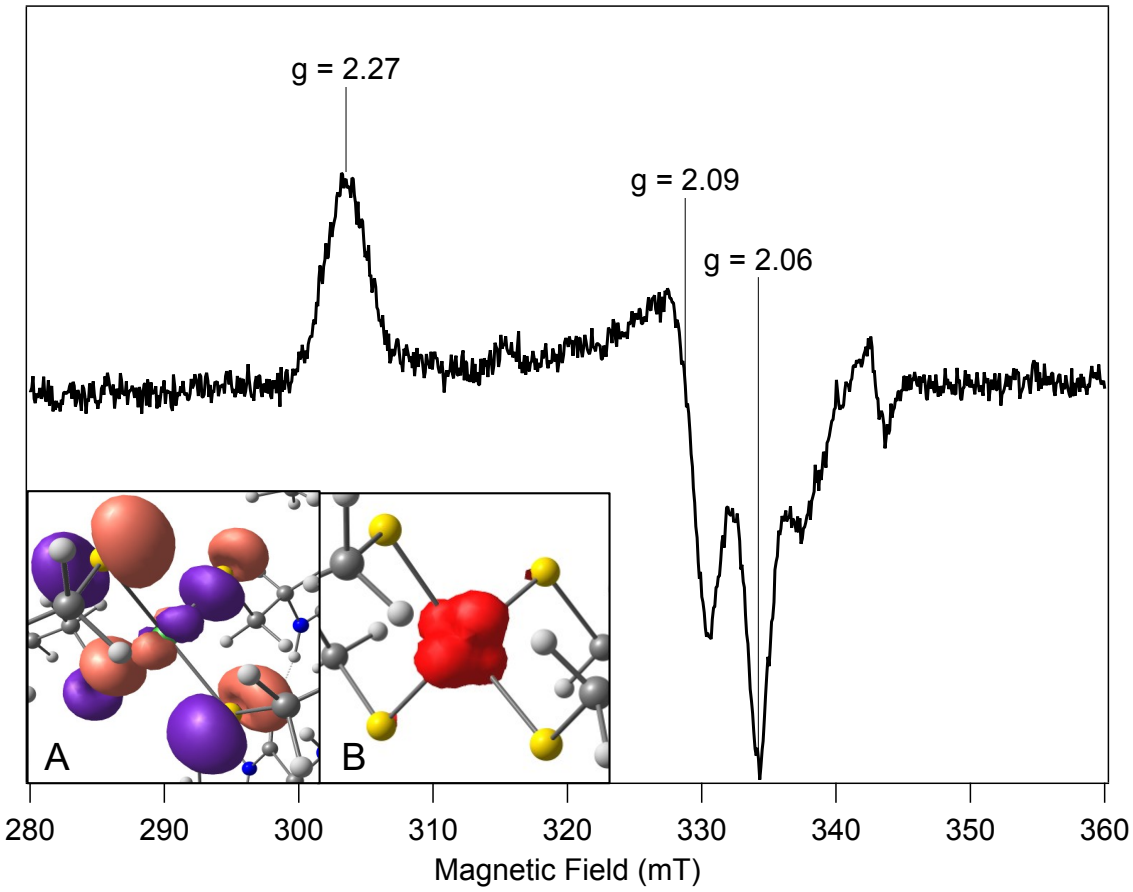


Figure S22. X-Band EPR spectrum of 400 **µ**M NiRd and 800 **µ**M potassium ferricyanide recorded at 10 K. $P_{\mu w}$ = 2.0 mW; Mod. Amp. = 1 mT; ν = 9.6240 GHz. (*Inset*) (A) SOMO and (B) spin density for Ni^{III}Rd. Purple and pink lobes represent phasing in (A) while positive spin density in (B) is shown in red and negative spin density is shown in blue. The contour value is ± 0.011 au. From a Mulliken spin population analysis, 97% of the spin is localized on the nickel center.

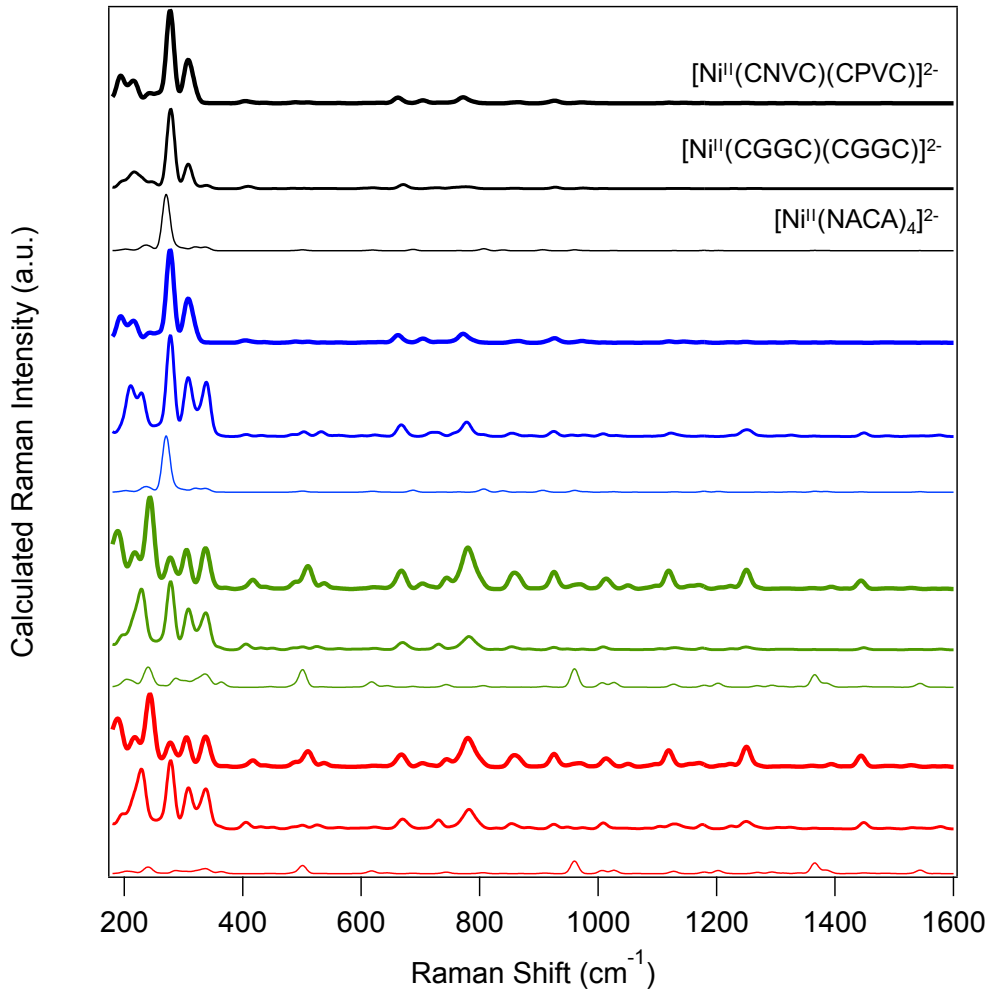


Figure S23. Calculated resonance Raman spectra of the full (thick traces, top lines), backbone (medium-thickness traces, middle lines), and $(NACA)_4$-only (thin traces, bottom lines) Ni^{II}Rd models at 364 nm (black), 407 nm (blue), 458 nm (green) and 488 nm (red).

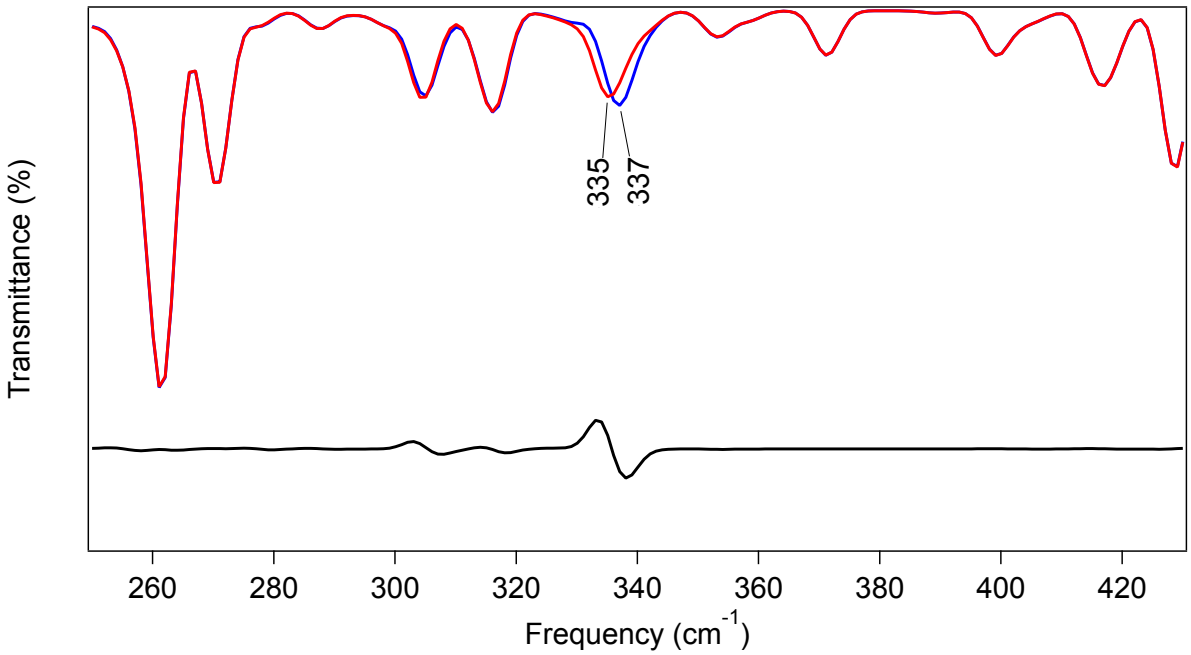


Figure S24. Calculated IR spectra in transmission mode of the full $Ni^{II}Rd$ model with ^{58}Ni (blue) and ^{60}Ni (red). Difference spectrum (^{58}Ni – ^{60}Ni) is shown in black.

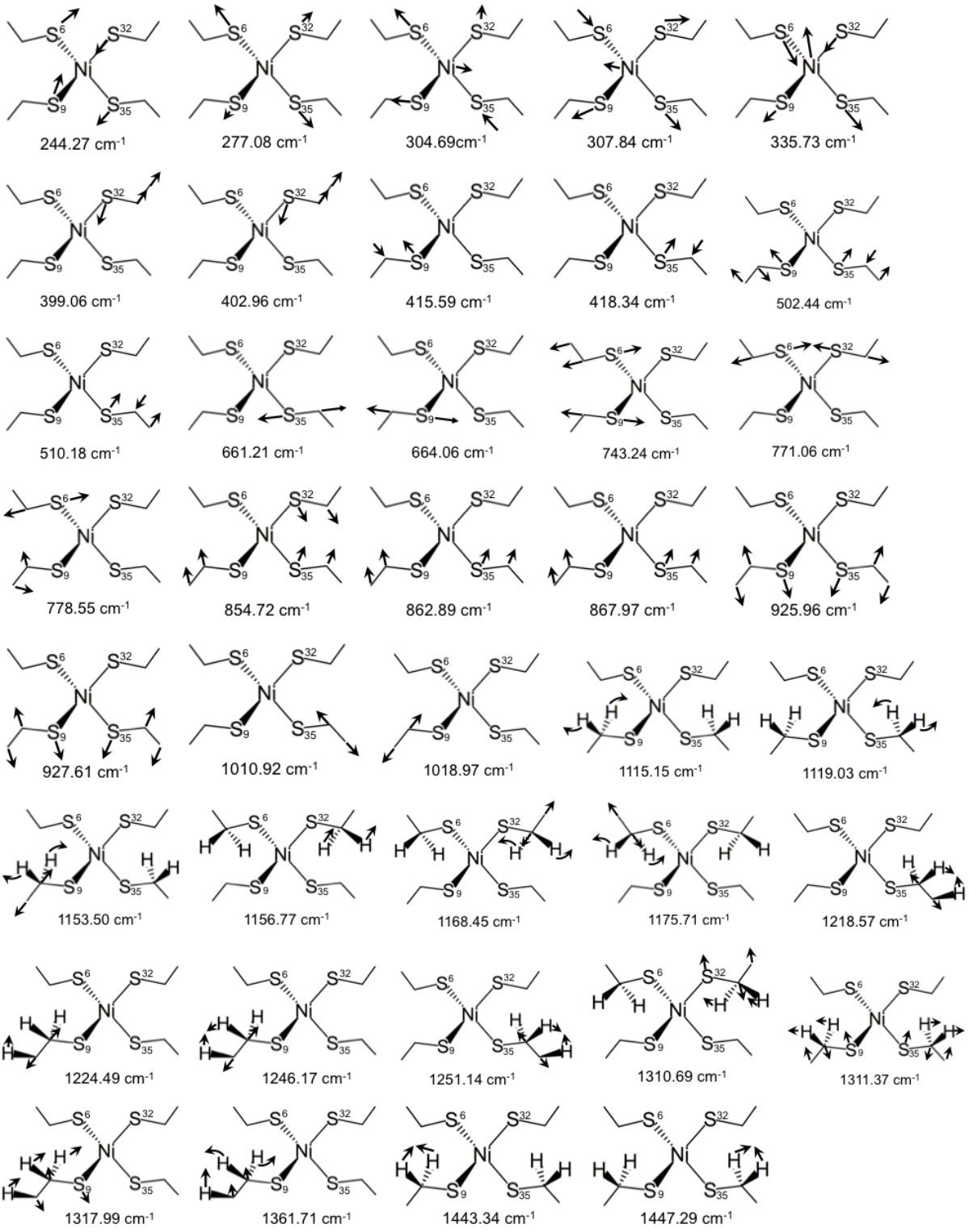


Figure S25. Normal mode vector displacements of the full $Ni^{II}Rd$ model.

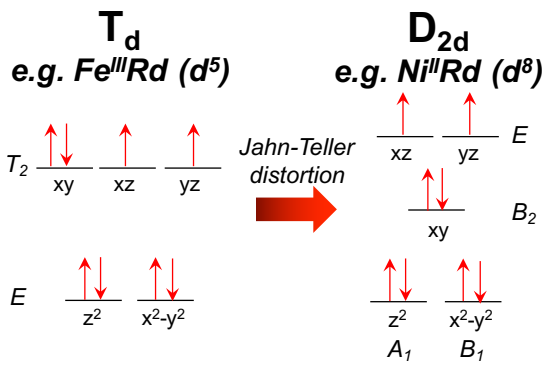


Figure S26. Idealized d-orbital splitting diagram for a T_d d^8 system that undergoes Jahn—Teller distortion to a D_{2d} geometry.

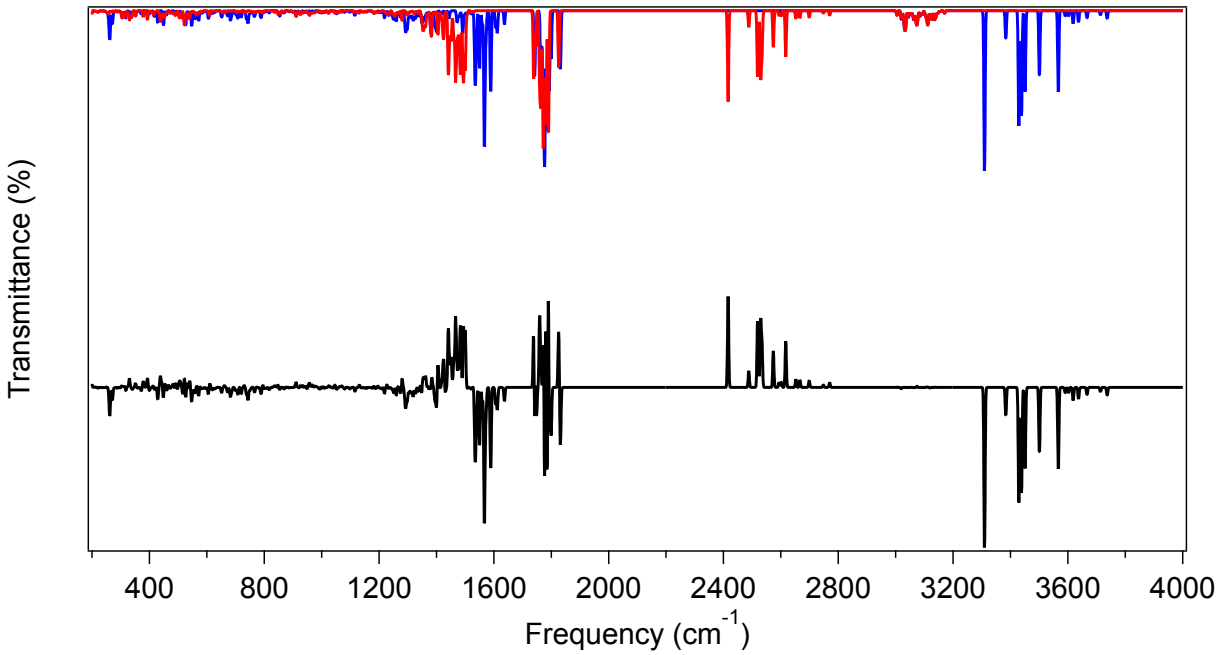


Figure S27. Calculated IR spectra in transmission mode of the full $Ni^{II}Rd$ model in H_2O (blue) and with exchangeable protons replaced with deuterons (red). Difference spectrum (H-D) is shown in black.

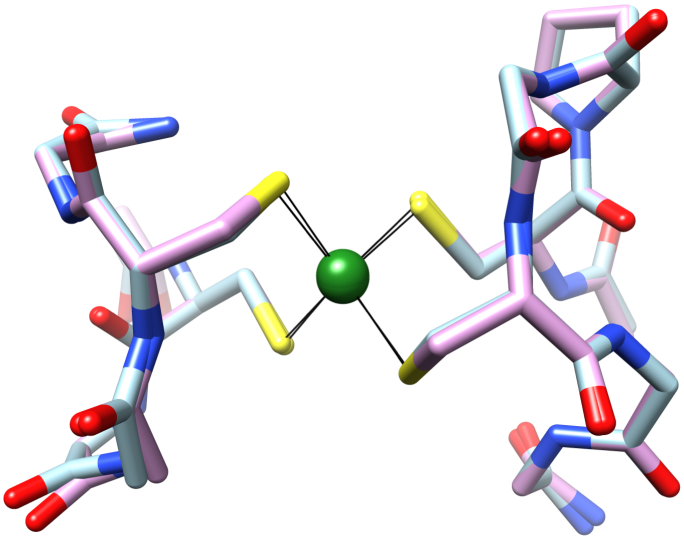


Figure S28. DFT-optimized geometries of backbone Ni^{II}Rd model (pink) and backbone Ni^{III}Rd model (light blue). Hydrogen atoms are omitted for clarity.

Sample input file for geometry optimization and vibrational frequency calculation

```
# calculation parameters
! UKS B3LYP RIJCOSX TightSCF TightOpt Grid4 NoFinalGrid UCO D3  NormalPrint
! def2-SVP def2-SVP/J PrintBasis DecontractAux ZORA  NumFreq

#parallel
%pal
 nprocs 12
end

%scf
 maxiter 500
AutoStart true
end

# VibFreq Parameters
%freq  CentralDiff True
      Increment   0.01
end

#increased basis on Ni and S
%basis
     NewGTO S  "ZORA-def2-TZVPP" end
     NewGTO Ni "ZORA-def2-TZVPP" end
end

%geom Constraints
{ C 0 C } #VAL 5 CA
{ C 7 C } #CYS 6 CA
{ C 17 C } #ASN 7 CA
{ C 42 C } #CYS 9 CA
{ C 52 C } #GLY 10 CA
{ C 68 C } #CYS 32 CA
{ C 78 C } #PRO 33 CA
{ C 100 C } #CYS 34 CA
{ C 110 C } #GLY 35 CA
{ C 117 C } #VAL 36 CA
end
end
* xyz #charge# -2 #spin#  3
(input atom coordinates)
*
```

Sample input file for TD-DFT calculation

```
# calculation parameters
! UKS B3LYP RIJCOSX TightSCF Grid4 NoFinalGrid UCO D3  NormalPrint
! def2-SVP def2-SVP/J PrintBasis DecontractAux ZORA

#parallel
%pal
 nprocs 8
end

%scf
 maxiter 500
AutoStart true
end

%maxcore 1000

%tddft
 NRoots   60
 MaxDim   400
  TDA true
end

#increased basis on Ni and S
%basis
     NewGTO S  "ZORA-def2-TZVPP" end
     NewGTO Ni "ZORA-def2-TZVPP" end
end


* xyz #charge# -2 #spin#  3
(input atom coordinates)
*
```

Sample input file for ORCA ASA

```
# calculation parameters
! UKS B3LYP RIJCOSX TightSCF Grid4 NoFinalGrid UCO D3  NormalPrint
! def2-SVP def2-SVP/J PrintBasis DecontractAux ZORA NMGrad

#parallel
%pal
 nprocs 8
end

%scf
 maxiter 500
AutoStart true
end

%maxcore 1000

%tddft
 NRoots   60
 MaxDim   400
  TDA true
end

#increased basis on Ni and S
%basis
     NewGTO S  "ZORA-def2-TZVPP" end
     NewGTO Ni "ZORA-def2-TZVPP" end
end

# this is ASA specific input
%rr    states 5,6,7,8,9,10,17
      HessName  "/……../NiRD_CXXC_Backbone_B3LYP_VibFreq.hess"
      ASAInput  true
      end

* xyz #charge# -2 #spin#  3
(input atom coordinates)
*
```

Sample input file for single-point energy calculation with solvation

```
! UKS B3LYP RIJCOSX TightSCF Grid4 NoFinalGrid UCO D3  NormalPrint
! def2-SVP def2-SVP/J PrintBasis DecontractAux ZORA COSMO(water)

#parallel
%pal
 nprocs 12
end

%scf
 maxiter 500
AutoStart true
end

#increased basis on Ni and S
%basis
     NewGTO S  "ZORA-def2-TZVPP" end
     NewGTO Ni "ZORA-def2-TZVPP" end
end

* xyz #charge# -2 #spin#  3
 (input atom coordinates)
*
```

Sample input file for EPR g-tensor calculation with solvation

```
! UKS B3LYP RIJCOSX TightSCF Grid4 NoFinalGrid UCO D3  NormalPrint
! def2-SVP def2-SVP/J PrintBasis DecontractAux ZORA COSMO(water)

#parallel
%pal
 nprocs 8
end

%scf
 maxiter 500
AutoStart true
end

%basis
     NewGTO S  "ZORA-def2-TZVPP" end
     NewGTO Ni "ZORA-def2-TZVPP" end
end

%rel     SOCType 3
         SOCFlags 1,3,3,1
end

%eprnmr gTensor   1  # do the g-tensor
       Ori      -3  # choice of origin
       ewin -1000,1000
end

%geom Constraints
{ C 7 C } #CYS 6 CA
{ C 17 C } #ASN 7 CA
{ C 42 C } #CYS 9 CA
{ C 52 C } #GLY 10 CA
{ C 68 C } #CYS 39 CA
{ C 78 C } #PRO 40 CA
{ C 100 C } #CYS 42 CA
{ C 110 C } #GLY 43 CA
{ C 117 C } #VAL 44 CA
end
end

* xyz #charge# -1 #spin#  2
(input atom coordinates)
*
```

Cartesian coordinates of the DFT geometry-optimized full Ni^{II}Rd model in the gas phase

C	9.082758442	14.082091579	11.877862784
C	10.564923618	14.272741536	11.593099467
O	11.420741386	13.462882037	11.927812841
H	8.972954698	13.357106735	12.689112527
H	8.582982076	13.682690848	10.984542552
H	8.601348922	15.032299175	12.143118977
N	10.869941052	15.409712213	10.902838389
C	12.258000007	15.820000000	10.730999998
C	12.813026571	16.201722025	12.116856683
O	12.277557753	17.062981703	12.803302120
C	12.332845230	17.029212335	9.796452294
S	14.018443269	17.707352252	9.615374778
H	10.175372391	16.146064168	10.873000254
H	12.826683542	14.978171120	10.318872225
H	11.942359831	16.745486117	8.811817503
H	11.683190216	17.811390089	10.197005961
N	13.934173893	15.547955190	12.519363124
C	14.534999997	15.772000005	13.826999993
C	14.952657832	17.238244505	14.070523820
O	15.162528533	17.602524152	15.217970856
C	15.823339450	14.937834887	13.967813523
H	14.166244708	14.700153413	12.020888768
H	13.834504018	15.511156104	14.630746005
H	16.202633741	15.094717465	14.981680542
H	16.567192926	15.319344459	13.255235980
N	15.194151413	17.977978986	12.962034180
C	15.696898008	19.338404745	13.032112230
C	14.595968876	20.408572215	13.091205926
O	14.669329807	21.309237002	13.916377766
C	16.696273572	19.582051403	11.872520471
C	16.987840610	21.067031830	11.644393876
C	17.985483932	18.797779070	12.144521438
H	14.897821146	17.641033714	12.044439131
H	16.207098390	19.444777515	13.995450926
H	16.232145883	19.198222803	10.951935742
H	17.770706454	17.753398882	12.405684786
H	18.535710622	19.246110556	12.984709887
H	18.642242136	18.804818641	11.265806432

H	16.096097993	21.594024429	11.291167531
H	17.333195336	21.553828339	12.566827923
H	17.753898446	21.184689433	10.868603776
N	13.601173101	20.322903092	12.164449434
C	12.611788998	21.374888991	12.067283001
C	11.202607789	20.987528158	12.557620766
O	10.321980941	21.836084231	12.629003213
C	12.461841086	21.922101567	10.642517850
S	11.704092204	20.738843208	9.467825074
H	13.641403126	19.615022692	11.427911848
H	12.949730736	22.178717990	12.731540188
H	13.442566621	22.243475955	10.274958215
H	11.806583302	22.797479967	10.693297988
N	10.995992104	19.673214360	12.830721053
C	9.686440000	19.148175000	13.115364002
C	9.039918109	18.353506846	11.975341918
O	8.233800240	17.454925223	12.210528585
H	11.757781638	19.004265367	12.766718515
H	9.704726508	18.476107089	13.981077097
H	9.028946085	19.997679302	13.342844775
N	9.389805952	18.728701689	10.726916594
H	10.086449761	19.453498255	10.511749211
H	8.932803628	18.271086458	9.950550568
C	15.430688612	16.156865096	1.650058160
C	14.204972334	16.836151989	2.243517423
O	13.147341597	16.944359732	1.624797026
H	15.102002921	15.427801123	0.903025380
H	16.050611919	16.915160113	1.152739667
H	16.044136056	15.684177230	2.424331090
N	14.374639430	17.336321684	3.487049954
C	13.294751997	18.058448012	4.133252008
C	12.958458690	19.323519971	3.333165643
O	13.840160874	20.123755783	3.019273228
C	13.716013260	18.433229774	5.557488135
S	12.375267676	19.258445548	6.482022487
H	15.258443311	17.208642700	3.978015185
H	12.416827806	17.405940979	4.180606668
H	14.024121363	17.525214339	6.089021065
H	14.589574969	19.090124506	5.506659280
N	11.658120862	19.564339390	3.041782641

C	11.289606998	20.767459995	2.298923992
C	11.209188253	22.042731734	3.152775250
O	10.935049417	23.106285450	2.609692038
C	9.933092688	20.401032710	1.675938026
C	9.329799672	19.440154523	2.709647629
C	10.538185184	18.625031105	3.191933079
H	12.053226379	20.980903818	1.542455016
H	9.332762941	21.295429621	1.482443655
H	10.097974444	19.878668259	0.723911835
H	8.908298851	20.012484453	3.546538022
H	8.536889596	18.801411382	2.302090212
H	10.723185348	17.744450715	2.560915962
H	10.432740540	18.302146637	4.233713987
N	11.440259855	21.883271694	4.472007591
C	11.455022265	22.998677629	5.396576544
C	12.893085582	23.436318618	5.732828467
O	13.199441221	24.621517425	5.735417989
C	10.645453087	22.672511591	6.672665831
H	11.663749049	20.960332527	4.849609395
H	11.016247822	23.854114734	4.871615583
H	11.180006126	21.890621463	7.225276785
N	13.768537599	22.429868713	6.033830383
C	15.119002023	22.733983966	6.460206976
C	16.235262827	22.220191357	5.547134891
O	17.394488331	22.575747827	5.725586527
C	15.418819054	22.270995504	7.898854300
S	15.604921002	20.461088505	8.135425419
H	13.402957936	21.486500159	6.193127963
H	15.194373374	23.828365561	6.428689942
H	16.369170432	22.726708728	8.195485340
H	14.632007766	22.658428050	8.554505295
N	15.879419947	21.328034887	4.588989619
C	16.839087981	20.821394025	3.646533026
C	17.690049385	19.641764567	4.079666835
O	18.491487749	19.146056283	3.286836031
H	14.904197397	21.140454113	4.377134754
H	16.294454134	20.495224730	2.754819084
H	17.548696715	21.608496634	3.358344324
N	17.541908159	19.153754739	5.333222088
C	18.412744369	18.058793261	5.687154648

C	18.085125894	16.839873078	4.813647351
O	16.944675469	16.486328704	4.550248275
C	18.411619815	17.705127341	7.189878980
C	18.921794582	18.900952727	8.008532020
C	17.066519812	17.179746517	7.698491046
H	16.910339585	19.584216731	6.012332979
H	19.440035268	18.359337216	5.427737830
H	19.149315417	16.890812180	7.281825722
H	16.719920571	16.316112510	7.121269315
H	16.283715036	17.941743399	7.648435602
H	17.145358568	16.879451959	8.750521038
H	19.857290270	19.300938161	7.592568627
H	18.180634710	19.708864945	8.032974578
H	19.110779548	18.593854239	9.044878715
N	19.172176569	16.110591786	4.425438444
H	20.053034650	16.595538099	4.333870458
H	18.989588063	15.376816028	3.753871134
Ni	13.480636071	19.692848577	8.489442023
C	10.555046709	23.884281406	7.601240700
H	10.080827557	23.588879586	8.545645414
H	11.544189289	24.295123254	7.832933925
H	9.960588999	24.690320819	7.145316435
C	9.253251678	22.124988513	6.337948111
H	9.317742842	21.218954278	5.725520006
H	8.720804397	21.863673525	7.261696558
H	8.652646199	22.865303414	5.787932139
C	15.582737666	13.449707036	13.767028628
O	15.134744022	12.725440298	14.634338657
N	15.871848375	12.996996096	12.503323952
H	15.649416733	12.039320169	12.270685457
H	16.278044246	13.590158788	11.795980894

Cartesian coordinates of the DFT geometry-optimized backbone Ni^{II}Rd model in the gas phase

C	9.234716709	13.647291782	11.529853765
C	10.688372206	13.989731608	11.217359969
O	11.569666293	13.138470761	11.200769713
H	9.214292222	12.882039336	12.312805963
H	8.661009740	14.526005974	11.844786679
H	8.767110902	13.218396556	10.633288416
N	10.904564086	15.301277092	10.922196687
C	12.258000000	15.820000029	10.730999981
C	12.799026718	16.190634073	12.125948138
O	12.265579387	17.054394454	12.814168410
C	12.258334119	17.039715088	9.817244842
S	13.931734447	17.730855647	9.581938537
H	10.183486378	15.970075652	11.194861180
H	12.857171691	15.014664158	10.294498289
H	11.616754565	17.809041084	10.254087300
H	11.832587711	16.759016312	8.846495015
N	13.879191461	15.486741620	12.561001098
C	14.535000021	15.771999993	13.827000015
C	15.290564609	17.113895401	13.885735085
O	15.824755123	17.437656085	14.937268425
H	14.260724774	14.784246312	11.945439076
H	13.791233099	15.816443654	14.632260905
H	15.243394491	14.971535870	14.065090070
N	15.302214378	17.841268736	12.744722930
C	15.790729479	19.200991302	12.694598902
C	14.729244933	20.288508238	12.940426239
O	14.945981827	21.180066799	13.747571972
H	14.848307862	17.501088219	11.896758711
H	16.232497424	19.382048469	11.704289809
H	16.549313018	19.340505951	13.468508421
N	13.593126702	20.212284425	12.180648096
C	12.663999904	21.328999922	12.150000024
C	11.226274522	21.020820102	12.615347262
O	10.391602226	21.916982711	12.649068153
C	12.582131966	22.016114479	10.773771997
S	11.736187688	21.076677083	9.436197115
H	13.572165358	19.540195752	11.408706967
H	13.057140367	22.057745633	12.870157370

H	12.012578575	22.940221723	10.912663520
H	13.597762657	22.280275015	10.458835520
N	10.936309452	19.730734440	12.938532678
C	9.565000080	19.275999066	13.082999980
C	9.204843310	18.344281253	11.912278634
O	8.769417858	17.205506286	12.093283850
H	11.657970470	19.015253110	12.874522122
H	9.417397083	18.700114121	14.003707958
H	8.925759401	20.166540158	13.088344401
N	9.423802347	18.861499679	10.683700089
H	10.001863629	19.691545438	10.510554797
H	9.305615358	18.241206432	9.893945669
C	15.426632813	15.925662316	1.938538429
C	14.194332316	16.699612294	2.386125557
O	13.174021656	16.777768826	1.707649084
H	15.123501439	15.182945455	1.194825601
H	15.926928265	15.446788773	2.788814358
H	16.137551164	16.621264229	1.471385077
N	14.319698660	17.323390078	3.581514961
C	13.205774143	18.065052545	4.149065828
C	12.911000030	19.325000967	3.304000008
O	13.808779331	20.119083513	3.022958001
C	13.564976453	18.455610542	5.586900385
S	12.206650337	19.271656404	6.492600705
H	15.127579398	17.136992969	4.165786292
H	12.326679547	17.412169997	4.157764281
H	14.428438307	19.125452801	5.558372817
H	13.873946041	17.554594783	6.131576968
N	11.629067436	19.556463351	2.950945895
C	11.299111519	20.787812609	2.245198183
C	11.301999962	22.035999048	3.145999992
O	11.161560962	23.138421183	2.631393818
C	9.905063170	20.500374849	1.660453502
C	9.295119355	19.526403286	2.678918627
C	10.483051323	18.651819717	3.103757633
H	12.045567015	20.993707098	1.470619462
H	9.335067866	21.424680396	1.522960485
H	10.010513835	20.011422685	0.682220274
H	8.466807584	18.932249173	2.274150563
H	8.922676468	20.085243092	3.547511174

H	10.389658141	18.306427254	4.139051177
H	10.620267668	17.779459324	2.449184160
N	11.401245675	21.815963977	4.477095065
C	11.511737258	22.899237900	5.429877036
C	12.950073010	23.343647596	5.736797474
O	13.247187965	24.529105822	5.756956643
H	11.566099405	20.877673928	4.849758248
H	10.994843834	23.779268642	5.039229456
H	11.050886695	22.583561601	6.376633509
N	13.826991151	22.330419008	6.004761086
C	15.164822884	22.625495169	6.474781260
C	16.297001005	22.136998984	5.576000024
O	17.452901347	22.478937573	5.791599861
C	15.434345236	22.098411373	7.895331657
S	15.504000240	20.271562033	8.031255125
H	13.438660090	21.402107120	6.193737062
H	15.242437346	23.720261557	6.482970931
H	16.404826422	22.493115057	8.213646710
H	14.661160892	22.490889431	8.564075843
N	15.971667058	21.261066005	4.580835886
C	16.975622757	20.727211958	3.695405852
C	17.761000001	19.506999984	4.199999982
O	18.770007509	19.125635282	3.603162605
H	15.001772042	21.085498133	4.330780760
H	17.727817129	21.486548099	3.449963549
H	16.475356620	20.410342616	2.772309631
N	17.239716713	18.883223722	5.281157876
C	17.895110442	17.743143958	5.895278275
C	17.825999997	16.510000013	4.976000002
O	16.858008686	15.760096638	4.982135137
H	16.542986299	19.377316236	5.849659676
H	18.941321459	17.979037699	6.139302079
H	17.355995991	17.504337929	6.816140477
N	18.897767470	16.368172383	4.144739184
H	19.326496341	17.257862451	3.878043847
H	18.775720390	15.686856702	3.405500740
Ni	13.338978312	19.720260263	8.512712724

Cartesian coordinates of the DFT geometry-optimized NACA Ni^{II}Rd model in the gas phase

N	10.67242585	15.34118893	9.91207449
C	12.01274000	15.79711000	10.25243000
C	12.13496916	15.85329926	11.77367905
O	11.12816346	15.99474948	12.45714062
C	12.21723465	17.19796556	9.60706713
S	13.90079440	17.89034292	9.61563336
N	13.53687055	20.10459396	12.16861025
C	12.60623000	21.22081000	12.20405000
C	11.22425128	20.87763647	12.77925330
O	10.53784629	21.78785356	13.22343535
C	12.45207787	21.89139744	10.82184438
S	11.66128754	20.90748720	9.49774852
N	14.60438669	17.04606551	3.82417643
C	13.50244000	17.87264000	4.28356000
C	13.33375970	19.06154010	3.32813878
O	14.31726118	19.60491610	2.84906755
C	13.72747580	18.31916968	5.74582673
S	12.38920941	19.36144834	6.44668687
N	13.82277488	22.56403233	6.14551679
C	15.09253000	22.95186000	6.73021000
C	16.31827984	22.40082992	5.98024321
O	17.43091359	22.79909018	6.29322354
C	15.17909103	22.64446551	8.23317609
S	15.43780170	20.89534114	8.71601939
Ni	13.41795883	19.84522182	8.46690498
C	16.09746745	21.43089813	4.85428065
C	13.50741030	15.78193215	12.37395155
C	11.92725117	19.47371270	2.99250453
C	10.33935191	14.89142124	8.68126877
C	14.48867928	15.72690253	3.55077563
C	13.22784371	23.28348729	5.17217859
C	14.24255014	19.63175235	13.21918692
O	13.74881786	24.29904414	4.67904870
C	11.85761454	22.81096078	4.73405928
C	15.74725246	15.04117678	3.05757634
O	13.43180488	15.10105307	3.71282283
O	11.18783538	14.57078159	7.83754761
C	8.85603903	14.83361038	8.37780725

C	10.75167836	19.45139946	12.74160794
C	13.99430822	20.25272417	14.58254820
O	15.06268762	18.70911132	13.09124384
H	9.93602655	15.65059904	10.54153194
H	11.53808511	17.90638346	10.09783230
H	11.88998789	17.10950530	8.56513921
H	13.66984372	19.59336317	11.28129738
H	13.45290996	22.19537535	10.49689052
H	11.85588790	22.79906411	10.97967132
H	14.68432869	18.85357224	5.80956776
H	13.82688962	17.41245516	6.35552521
H	13.39588327	21.67289903	6.42651925
H	14.26906280	23.03544559	8.70487998
H	16.02585724	23.21658812	8.63013247
H	15.64395991	21.96354371	4.00457273
H	15.38470138	20.65236180	5.14083813
H	17.04608052	20.98372808	4.53423199
H	14.12608429	15.03179890	11.86513441
H	13.44189487	15.56101042	13.44647434
H	14.00534648	16.75728911	12.23605460
H	11.33124768	19.55560253	3.91076661
H	11.46963315	18.68342007	2.37595593
H	11.91378883	20.41924105	2.43880534
H	11.63025400	21.80127541	5.09589251
H	11.79340284	22.83700609	3.63877671
H	11.10526093	23.50921715	5.12916632
H	16.52541896	15.74521894	2.73780646
H	15.48959292	14.38010064	2.22077817
H	16.15151883	14.41428250	3.86586481
H	8.22891357	14.96614175	9.26822052
H	8.61091780	13.88120945	7.89037614
H	8.61895326	15.63986298	7.66842695
H	11.45175905	18.78407080	13.26045098
H	10.73356597	19.12364897	11.69142677
H	9.75391326	19.36434320	13.18641180
H	12.94287720	20.14629969	14.88686196
H	14.23647272	21.32481123	14.59331435
H	14.62389246	19.74135166	15.31735758
H	15.47225316	17.52259288	3.59584227
H	12.60133121	17.25197169	4.24100436

H	12.74617585	15.09603371	9.84063129
H	15.16053885	24.04293264	6.61306891
H	13.01472100	21.99682492	12.86491637

Cartesian coordinates of the DFT geometry-optimized full Ni^{II}Rd model without constraints in the gas phase

C	8.114066814	15.59405005	12.53924502
C	9.51588413	15.26449929	12.0430949
O	10.04666753	14.1778159	12.23015994
H	7.619362843	14.66213499	12.82687654
H	7.524676729	16.11532574	11.77538569
H	8.154783728	16.26278147	13.40772867
N	10.13538133	16.27606096	11.37487394
C	11.51609217	16.17201122	10.95270477
C	12.46846524	16.14772315	12.15775717
O	12.28187552	16.8177104	13.16734056
C	11.83668868	17.38063889	10.05723547
S	13.59003998	17.66233749	9.61473137
H	9.693207922	17.18956851	11.32070372
H	11.64507462	15.23431448	10.39406042
H	11.25420969	17.30257982	9.132170444
H	11.49452619	18.28066818	10.57291801
N	13.57166694	15.39986547	11.93603087
C	14.76471658	15.35408583	12.75667971
C	15.13414182	16.69998347	13.42208264
O	15.55876725	16.72270206	14.56624529
C	16.00001155	14.95989703	11.89523857
C	15.77346464	13.88221106	10.84154308
O	16.06303446	12.71073385	11.01319165
N	15.20004024	14.3461348	9.686787467
H	13.60369677	14.90649957	11.05414219
H	14.64332691	14.63695323	13.57830277
H	16.3652675	15.85925328	11.38814861
H	16.78234955	14.60188706	12.5698931
H	15.02497239	15.33249019	9.50091384
H	15.07537004	13.69296026	8.92552797
N	15.11507934	17.75855507	12.57678231
C	15.68732353	19.04386883	12.91927189
C	14.65648754	20.16509641	13.08624919
O	14.80744129	20.99986236	13.96867546
C	16.81449385	19.40077875	11.91062798
C	17.16855253	20.88920952	11.88953773
C	18.04617402	18.54293016	12.22432149
H	14.69084232	17.65604519	11.64659265

H	16.11906487	18.93680752	13.9194966
H	16.4402929	19.14596841	10.90802042
H	17.78827415	17.48050813	12.30641583
H	18.81350096	18.6473645	11.4467031
H	18.49048747	18.85180369	13.18112568
H	16.33651363	21.48485039	11.49996703
H	17.41439663	21.25768467	12.89408744
H	18.02631224	21.05916921	11.22646456
N	13.61286767	20.19357497	12.20983042
C	12.62888321	21.25358645	12.28851022
C	11.32637665	20.84735985	12.9903744
O	10.47622555	21.68332459	13.26858172
C	12.3136359	21.90130798	10.93033984
S	11.46055087	20.83009582	9.704949668
H	13.58648717	19.54591804	11.42223926
H	13.06700523	22.02255917	12.93726913
H	11.65300053	22.75118569	11.13037176
H	13.24721868	22.28378954	10.50238351
N	11.15366846	19.52340914	13.23726896
C	9.926372076	19.03598864	13.80385773
C	8.710360276	19.06454047	12.86991468
O	7.590024376	18.83466658	13.30045138
H	11.89273894	18.84532295	13.07611923
H	10.08743175	17.99245517	14.09812967
H	9.633517489	19.60942813	14.6922297
N	8.970313707	19.24818466	11.54139913
H	9.82551812	19.70342879	11.20722555
H	8.153720831	19.39977768	10.96298016
C	15.75337024	15.3098115	2.651598493
C	14.52667502	16.13992055	2.994986336
O	13.57538956	16.24627176	2.225832246
H	15.4533244	14.49701633	1.983437301
H	16.24185497	14.91972144	3.551328509
H	16.46480154	15.95259348	2.114789366
N	14.57679935	16.78093266	4.186277298
C	13.47682967	17.63974772	4.593196965
C	13.35243633	18.82513398	3.626119184
O	14.32522136	19.54446681	3.39448588
C	13.72146904	18.18649378	6.000162552
S	12.31413301	19.18264974	6.605561776

H	15.34186935	16.60321835	4.831344482
H	12.55363732	17.05129592	4.59028782
H	14.6267138	18.80257819	5.986954076
H	13.88759619	17.35521443	6.694741176
N	12.13420519	19.10099405	3.108777477
C	11.95879804	20.24824219	2.222689314
C	11.72045029	21.58925646	2.947039856
O	11.51709915	22.59363225	2.2761184
C	10.74128276	19.85373554	1.375824087
C	9.896056211	19.04356854	2.369144234
C	10.94109589	18.24205175	3.16142684
H	12.86473875	20.3961975	1.625190796
H	10.23979801	20.7380544	0.97049438
H	11.0659444	19.21760939	0.541490149
H	9.360840785	19.72640209	3.042871096
H	9.154195142	18.39466459	1.888640731
H	11.17569973	17.28033796	2.685330873
H	10.63129675	18.06361602	4.197578876
N	11.73979982	21.54851719	4.296989436
C	11.64676064	22.74163805	5.119647141
C	13.04309622	23.2378939	5.534672756
O	13.35059533	24.41844085	5.44548799
C	10.75573747	22.5065127	6.365035076
C	10.58910716	23.79230418	7.178668341
C	9.395293429	21.9145248	5.984673048
H	11.92592087	20.66829622	4.785048304
H	11.23065757	23.53796463	4.492708204
H	11.26250639	21.7804401	7.012995385
H	10.05104933	23.57117361	8.108450047
H	11.55489352	24.23449565	7.447113511
H	10.02508975	24.54756912	6.611756435
H	8.799616119	21.7326685	6.888109467
H	9.50685047	20.95930521	5.460359152
H	8.833150328	22.59921581	5.332400346
N	13.88144097	22.27494421	6.022336804
C	15.17606824	22.63377647	6.56147032
C	16.37278418	22.0962721	5.77211199
O	17.51539128	22.43955411	6.050325908
C	15.3211028	22.2652849	8.044350832
S	15.38537495	20.46860123	8.390065128

H	13.5054927	21.34618199	6.233040323
H	15.24007211	23.72585853	6.462741819
H	14.50115588	22.73430469	8.599623632
H	16.26562362	22.69099432	8.399024809
N	16.09547236	21.22357484	4.770074746
C	17.13180605	20.73365298	3.906662223
C	17.99840893	19.6073251	4.451864108
O	18.99523292	19.24920473	3.813923552
H	15.14374221	20.95898514	4.536963971
H	16.66071132	20.34014992	2.999427287
H	17.82661021	21.53575697	3.628263978
N	17.6009073	19.00398133	5.592974206
C	18.38601147	17.90620105	6.15080598
C	18.02501732	16.62849706	5.359482425
O	17.15666199	15.82535644	5.691278346
C	18.28676003	17.80679438	7.683344889
C	18.7781966	19.12529165	8.304170202
C	16.90721903	17.397908	8.218093602
H	16.82163689	19.393997	6.122224662
H	19.43202704	18.13441697	5.905808945
H	18.99861244	17.01335294	7.96304933
H	19.77944835	19.39252873	7.93872503
H	18.09554692	19.95055876	8.076222116
H	18.82049601	19.0368237	9.394419767
H	16.66467301	16.36995819	7.940708143
H	16.89384042	17.49382278	9.310142022
H	16.11308491	18.04809266	7.842251173
N	18.7469031	16.50323076	4.215010211
H	19.16862213	17.36302639	3.851801011
H	18.42919569	15.80441651	3.556765497
Ni	13.23191947	19.78966177	8.658135905

Cartesian coordinates of the DFT geometry-optimized full Ni^{III}Rd model in the gas phase

C	9.098480915	14.141721060	11.979928239
C	10.578042998	14.350236295	11.714288406
O	11.457377033	13.637771975	12.174921554
H	8.984818312	13.393919603	12.768589875
H	8.601288945	13.777316459	11.070870357
H	8.615446789	15.082654828	12.275218522
N	10.874120315	15.403846223	10.887398844
C	12.257999984	15.819999997	10.730999980
C	12.825886701	16.187778918	12.122863314
O	12.256758549	17.010259915	12.833726178
C	12.290283520	17.061217863	9.825505282
S	13.929894622	17.871651407	9.680098122
H	10.175680467	16.130237087	10.787276299
H	12.841526373	14.997326797	10.299949034
H	11.937763672	16.790012776	8.824233983
H	11.597768787	17.793726236	10.241341663
N	13.987991465	15.595085029	12.486692561
C	14.535000016	15.771999995	13.827000017
C	14.940674835	17.230401345	14.139760508
O	15.098256674	17.572018193	15.299725323
C	15.812408721	14.920356311	13.986430866
H	14.319655085	14.788208982	11.962426527
H	13.787888518	15.497805386	14.583942904
H	16.150377397	15.012856132	15.023809844
H	16.590120167	15.343312809	13.337635593
N	15.213624740	18.000816334	13.055809325
C	15.700729119	19.365405111	13.146281444
C	14.599374291	20.437850325	13.139816559
O	14.673772952	21.394263346	13.894242623
C	16.752885380	19.613372029	12.028914566
C	16.973074755	21.097345475	11.716999900
C	18.069059961	18.922766894	12.405134098
H	14.990772291	17.634905529	12.135323693
H	16.166420985	19.479273936	14.130991396
H	16.361753879	19.144950437	11.112890703
H	17.909046751	17.872180829	12.679829087
H	18.534243228	19.425829971	13.264345568
H	18.781077472	18.954326598	11.571140606

H	16.069884362	21.554882515	11.299605886
H	17.250940174	21.659869527	12.617034861
H	17.769037419	21.211697297	10.970596050
N	13.607155744	20.296364827	12.212186182
C	12.612249538	21.330726525	12.040285775
C	11.193276555	20.957442116	12.514501177
O	10.318161688	21.812046985	12.536941728
C	12.469114887	21.787198123	10.579312258
S	11.609137208	20.615597151	9.445317128
H	13.636770204	19.524471680	11.547366578
H	12.931335465	22.182525930	12.650966994
H	13.453804160	22.046850744	10.179656886
H	11.845535761	22.687346570	10.564156070
N	10.968108577	19.645993762	12.787221092
C	9.655468625	19.162696370	13.131760611
C	8.978692270	18.269417417	12.091436921
O	8.172498298	17.410409089	12.422076336
H	11.728362198	18.971273535	12.801746699
H	9.672960605	18.583905187	14.062579460
H	9.010523335	20.039019935	13.279501372
N	9.309061377	18.518484994	10.796179119
H	9.932646433	19.280658661	10.530711743
H	8.743449989	18.087669636	10.077645204
C	15.441171174	16.282638821	1.656986713
C	14.210598510	16.929187735	2.268595999
O	13.153265121	17.062171951	1.657273449
H	15.124345424	15.478474788	0.985677560
H	15.974407650	17.033657956	1.059292465
H	16.129100678	15.902002725	2.419670448
N	14.369058316	17.382643743	3.534585135
C	13.282464956	18.088976581	4.175381365
C	12.925099648	19.341910175	3.359940075
O	13.799303648	20.151551896	3.051923036
C	13.739062746	18.500910377	5.582483826
S	12.423970577	19.354964445	6.530405003
H	15.247041102	17.255234391	4.036941700
H	12.410926766	17.428048165	4.245513800
H	14.068110610	17.615705029	6.135598467
H	14.595344576	19.170119414	5.484733279
N	11.623902189	19.570047518	3.068348556

C	11.265458084	20.750190696	2.279571343
C	11.182065776	22.050479808	3.094392784
O	10.937134179	23.106644256	2.533092576
C	9.922064094	20.364554211	1.639272939
C	9.307915520	19.406628174	2.668408730
C	10.515645064	18.609050262	3.178686179
H	12.042156265	20.938800258	1.530028746
H	9.314889439	21.249337950	1.425391825
H	10.108222426	19.836633425	0.695165722
H	8.860710364	19.979595176	3.491702240
H	8.531998942	18.755834803	2.249537354
H	10.735057915	17.737801213	2.546652542
H	10.381809157	18.271529008	4.212754130
N	11.389361450	21.911986597	4.423837612
C	11.415746727	23.024955247	5.346831144
C	12.854780391	23.434945344	5.714188005
O	13.166981945	24.608803467	5.828403722
C	10.581457570	22.689864989	6.608406316
H	11.563397277	20.985038715	4.797075291
H	10.993734897	23.891153348	4.825225842
H	11.076995613	21.852762499	7.116339786
N	13.725565579	22.398574708	5.933856148
C	15.058674837	22.631113887	6.441940135
C	16.212325314	22.111796567	5.575418670
O	17.365389682	22.414841000	5.853522191
C	15.265558972	22.085319239	7.865653325
S	15.442424983	20.264525293	8.037261847
H	13.347027270	21.454768774	5.992928033
H	15.174732265	23.721758491	6.479312793
H	16.213353005	22.484048473	8.243889568
H	14.461811099	22.452141507	8.509900278
N	15.888252184	21.248210858	4.583712722
C	16.884248088	20.716814332	3.687394303
C	17.826360179	19.649579226	4.231033732
O	18.732777287	19.233383772	3.521717141
H	14.923358265	21.122673559	4.287797544
H	16.353367891	20.260156528	2.845505887
H	17.534430180	21.510030933	3.295242996
N	17.602044031	19.185183526	5.488883641
C	18.413472151	18.102117691	5.970378601

C	17.755932994	16.758989011	5.609963204
O	16.692461094	16.664300671	5.013524130
C	18.857942640	18.229331082	7.457561766
C	19.272455580	19.675064066	7.765969376
C	17.835314766	17.697677892	8.467950689
H	16.822303320	19.533197101	6.040010554
H	19.319789568	18.140310785	5.348459760
H	19.765773234	17.609814953	7.553676135
H	17.676349456	16.618640449	8.359664347
H	16.866441011	18.190769724	8.360438155
H	18.183285154	17.885127056	9.491234829
H	20.004446995	20.045318533	7.037671470
H	18.413806141	20.353901669	7.732461003
H	19.718993248	19.735131209	8.767008780
N	18.468377593	15.657046382	5.957694976
H	19.313327101	15.721005477	6.503339912
H	18.071288017	14.748040098	5.767336555
Ni	13.373954683	19.688662432	8.505579137
C	10.544509587	23.854541232	7.598829054
H	10.022538756	23.546394543	8.513571917
H	11.549732329	24.189968276	7.876623618
H	10.016292663	24.718910415	7.172472149
C	9.165580733	22.235180544	6.231654301
H	9.185109588	21.380841199	5.545985422
H	8.610849048	21.932355465	7.129073990
H	8.607878726	23.044923896	5.739170517
C	15.635154477	13.473934691	13.545188547
O	15.500244592	13.182852514	12.364297608
N	15.646100892	12.536030793	14.528732663
H	15.642957294	12.789483808	15.504472185
H	15.431303009	11.582220585	14.271539790

Cartesian coordinates of the DFT geometry-optimized backbone $Ni^{III}Rd$ model in the gas phase

C	9.152704474	14.040688936	11.978653979
C	10.621788027	14.272812464	11.674513418
O	11.518823752	13.528956919	12.045111471
H	9.070531472	13.321144273	12.797253869
H	8.647360562	14.978822370	12.242827085
H	8.653064358	13.622704754	11.094303582
N	10.882427539	15.384822346	10.917065277
C	12.258000017	15.820000051	10.730999981
C	12.837258023	16.212313787	12.108414563
O	12.320854770	17.102165905	12.774030745
C	12.264015947	17.058721882	9.821907113
S	13.905129539	17.861419825	9.659523329
H	10.170274143	16.104022652	10.880779000
H	12.840094733	15.001306014	10.291541705
H	11.575626060	17.788941093	10.250567727
H	11.896905172	16.784361487	8.826878282
N	13.953425791	15.552744176	12.509709628
C	14.535000020	15.771999975	13.827000019
C	15.074614152	17.192975869	14.067476798
O	15.319880346	17.546723679	15.207265648
H	14.172155378	14.695164030	12.023184295
H	13.800998690	15.591507050	14.622768602
H	15.365385163	15.071766291	13.968728035
N	15.297435322	17.955153544	12.961701430
C	15.792086894	19.308734819	13.065308722
C	14.763696540	20.453117815	13.050251473
O	15.019288531	21.497983459	13.624816690
H	15.041440348	17.597680368	12.047995610
H	16.497564887	19.505880462	12.245720431
H	16.329920121	19.411508687	14.011532124
N	13.619508470	20.252271246	12.328421724
C	12.663999888	21.328999923	12.149999999
C	11.221073337	21.011211932	12.588700863
O	10.389706955	21.908069734	12.611958881
C	12.574029232	21.815010377	10.687035368
S	11.672639631	20.728774863	9.489867483
H	13.555301910	19.431472307	11.730489006
H	13.017632494	22.161752759	12.766998015

H	12.000284247	22.747824699	10.677443766
H	13.581708879	22.027949464	10.318314521
N	10.919692674	19.705522401	12.820750716
C	9.565000085	19.275999067	13.082999986
C	8.968601987	18.362862090	12.009060605
O	8.195133769	17.458269282	12.295901888
H	11.646396126	18.994347438	12.841671121
H	9.488598951	18.726873062	14.029061286
H	8.944805773	20.179113721	13.151941257
N	9.337164978	18.647260829	10.733819797
H	9.970232273	19.412276751	10.499253638
H	8.858915228	18.168316954	9.983531509
C	15.238756229	15.940415498	1.809120153
C	14.066079161	16.739646765	2.347614598
O	13.038673390	16.932927291	1.704603181
H	14.857531804	15.172588126	1.129091263
H	15.833577945	15.492337432	2.612550968
H	15.887562892	16.615346339	1.234424879
N	14.242769524	17.266542461	3.586072863
C	13.188605022	18.072179192	4.175728050
C	12.911000017	19.325001002	3.304000029
O	13.816580634	20.118865470	3.051817938
C	13.649389599	18.498495350	5.574372014
S	12.362236829	19.360979144	6.549929972
H	15.064279557	17.019809741	4.133092093
H	12.279848493	17.465070764	4.253324198
H	14.507946024	19.159295932	5.456829424
H	13.981417714	17.615040707	6.130822002
N	11.631496815	19.565152194	2.951179577
C	11.319857830	20.798594987	2.236753897
C	11.301999967	22.035999023	3.145999977
O	11.199252578	23.143387520	2.643029396
C	9.948070678	20.514410385	1.600343605
C	9.310193523	19.511976789	2.571658164
C	10.491015313	18.639123563	3.015842401
H	12.091118744	21.008993681	1.488558820
H	9.373533267	21.435373102	1.462581426
H	10.093698389	20.050124804	0.616217980
H	8.506050661	18.919435141	2.120768025
H	8.894785311	20.045183727	3.437160926

H	10.350678932	18.246615840	4.028757457
H	10.677063269	17.795798630	2.337600721
N	11.360003961	21.815765105	4.484817824
C	11.463939811	22.903764451	5.430061918
C	12.888394037	23.329298461	5.819839978
O	13.140707216	24.494256611	6.069357092
H	11.480350857	20.873118070	4.838807024
H	10.986143784	23.791360481	5.007313936
H	10.944947321	22.625125095	6.357956879
N	13.807783643	22.316626791	5.909956447
C	15.123645933	22.567049592	6.455578674
C	16.297001027	22.136998934	5.576000019
O	17.438354270	22.458471809	5.872570729
C	15.335516897	21.963028619	7.856970930
S	15.465124056	20.130594789	7.970773955
H	13.443158265	21.366345167	5.935032710
H	15.199363051	23.657136288	6.556933188
H	16.290234539	22.336512639	8.243885790
H	14.540836120	22.318906771	8.519692138
N	16.008695986	21.298271841	4.541049259
C	17.049956885	20.767380458	3.695461544
C	17.760999980	19.507000043	4.199999992
O	18.744085163	19.063513452	3.614441861
H	15.050194898	21.136580440	4.239824371
H	17.837700964	21.512835379	3.534939571
H	16.610962082	20.509791128	2.724968172
N	17.219821407	18.891927016	5.282862543
C	17.885379944	17.753492827	5.883829336
C	17.825999999	16.509999994	4.975999999
O	16.778180322	15.895510262	4.812384975
H	16.536371118	19.389590640	5.851314246
H	18.928700207	17.996465530	6.131310992
H	17.356030037	17.504483358	6.809003795
N	19.003830379	16.183229531	4.380162658
H	19.616413329	16.969583288	4.187476798
H	18.949625952	15.474895814	3.658557729
Ni	13.368565599	19.695426151	8.515651320

Cartesian coordinates of the DFT geometry-optimized $[FeCp_2]^0$ in the gas phase

Fe	-1.168895595	0.000004047	1.468074051
C	-1.946710401	-1.741632593	0.678908256
C	0.239860207	-0.365867609	2.934936129
C	-0.926593082	-1.229585023	-0.170272067
C	-2.966710056	-0.755968400	0.784619898
C	-1.021259623	-0.073239873	3.525164991
C	0.628919079	0.755975165	2.151535320
C	-1.316532035	0.073229292	-0.589023130
C	-2.577651441	0.365864378	0.001203653
C	-1.411198320	1.229580345	3.106428477
C	-0.391079263	1.741640508	2.257256541
H	-1.935328602	-2.697022068	1.178110168
H	0.789852884	-1.286936004	3.041521015
H	-0.007697577	-1.729824608	-0.430437484
H	-3.863823923	-0.835692975	1.376939458
H	-1.595377123	-0.734291049	4.154158226
H	1.526037972	0.835707477	1.559224324
H	-0.742413125	0.734273207	-1.218022471
H	-3.127642405	1.286932426	-0.105390403
H	-2.330092928	1.729816525	3.366602776
H	-0.402459828	2.697036831	1.758068123

Cartesian coordinates of the DFT geometry-optimized $[FeCp_2]^+$ in the gas phase

Fe	-1.168862143	0.000029337	1.468071461
C	-1.956459825	-1.751276008	0.662881702
C	0.250280765	-0.358719659	2.951574224
C	-0.935117957	-1.238497656	-0.187083939
C	-2.977717806	-0.764614153	0.768448435
C	-1.012351738	-0.065825397	3.542298762
C	0.639951065	0.764632986	2.167743494
C	-1.325452730	0.065813139	-0.606169217
C	-2.588071136	0.358716630	-0.015419860
C	-1.402673841	1.238497594	3.123235575
C	-0.381306075	1.751298893	2.273309758
H	-1.943678765	-2.705478534	1.164854380
H	0.798415917	-1.281612282	3.054229271
H	-0.014100781	-1.737086059	-0.443788735
H	-3.873410380	-0.842558717	1.363587350
H	-1.587709158	-0.728000282	4.169313027
H	1.535648550	0.842572632	1.572613920
H	-0.750132247	0.727960300	-1.233243973
H	-3.136235585	1.281588330	-0.118103306
H	-2.323717544	1.737054765	3.379908502
H	-0.394093768	2.705504140	1.771345018

Supporting References

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