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Integration of EXAFS, Spectroscopic and DFT Techniques for Elucidation of the Structure of Reactive Diiron Compounds

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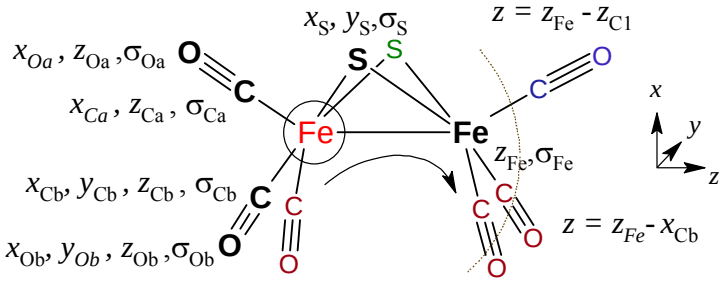
Supplementary material

1. Constraint and restraints of the XAFS models.
2. Fits of the XAFS of **1P**, **1F**, **2**, $\mathbf{2^{2-}}$, **3**, **4S**, **4P** and **4PP**.
3. Cartesian coordinates of DFT optimised vacuum phase structures
4. Observed and calculated (B3LYP/6-311+G(d) and C-PCM continuum solvation) IR spectra in the ν(CO) region.
5. Observed and calculated (B3LYP/LanL2DZdp in vacuum phase) IR spectra in the ν(CO) region.
6. DFT calculated energies of the isomers of **4PP** and **1F**.

1. Constraint and restraints of the XAFS models:

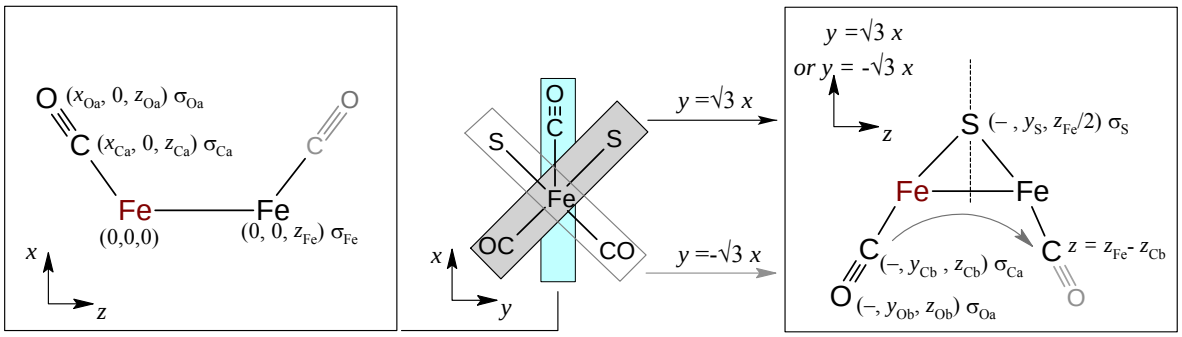
a. **$C_{2v}F_{21}$**



Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}F_{21}$	**Fe**	1	1	0, 0, 2.54	$E_0 > -15 \pm 1$
	S	2	1	0.93, -1.61, 1.25	$E_0 < 0 \pm 1$
	S′	2	1	0.93, 1.61, 1.25	$S_0^2 > 0.5 \pm 0.1$
	C_a	3	1	0.60, 0, -1.70	$S_0^2 < 1 \pm 0.1$
	C_b	3	1	-0.90, -1.54, -0.20	$\sigma^2_{all} < 0.02 \pm 0.01$
	C_b'	3	1	-0.90, 1.54, -0.20	$\sigma^2_{all} > 0.001 \pm 0.001$
	C_b''	4	1	-0.90, -1.54, 2.69	$CO_{angle} = 180 \pm 1°$
	C_b'''	4	1	-0.90, 1.54, 2.69	
	O_a	5	1	0.60, 0, -1.70	
	O_b	5	1	-1.47, -2.52, -0.33	
	O_b'	5	1	-1.47, 2.52, -0.33	

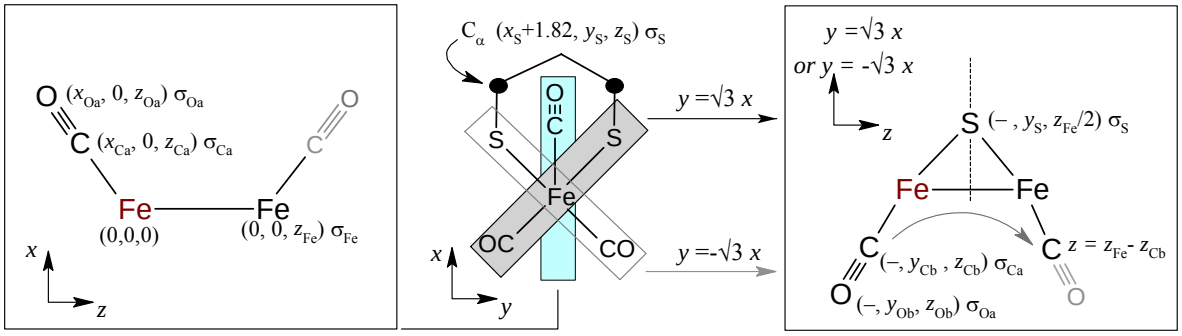
Refined atoms are shown as bold

b. **$C_{2v}P_{16}$**



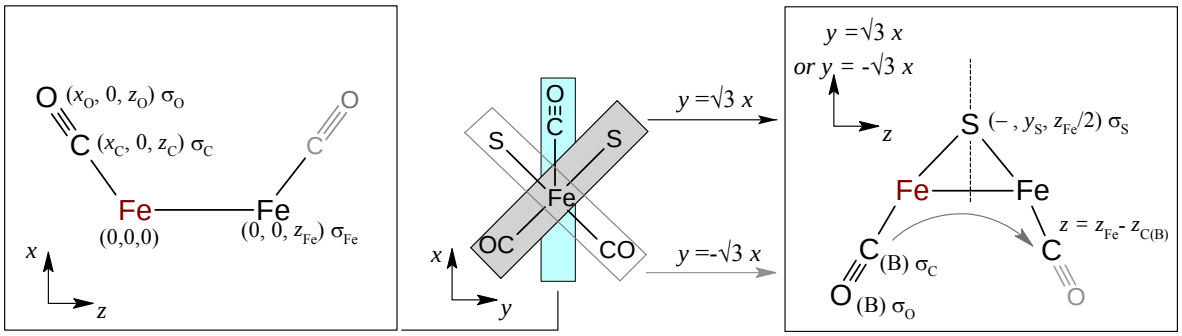
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}$	**Fe**	1	1	0, 0, 2.54	$E_0 > -15 \pm 1$
	S	2	1	0.94, -1.57, 1.27	$E_0 < 0 \pm 1$
	S′	2	1	0.94, 1.57, 1.27	$S_0^2 > 0.5 \pm 0.1$
	C_a	3	1	0.58, 0, -1.68	$S_0^2 < 1 \pm 0.1$
	C_b	3	1	-0.89, -1.54, -0.27	$\sigma^2_{all} < 0.02 \pm 0.01$
	C_b'	3	1	-0.89, 1.54, -0.27	$\sigma^2_{all} > 0.001 \pm 0.001$
	C_b''	4	1	-0.89, -1.54, -2.74	$CO_{angle} = 180 \pm 1°$
	C_b'''	4	1	-0.89, 1.54, -2.74	
	O_a	5	1	0.95, 0, -2.78	
	O_b	5	1	-1.46, -2.53, -0.44	
	O_b'	5	1	-1.46, 2.53, -0.44	

c. $C_{2v}P_{16}C_\alpha$



Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_\alpha$	**Fe**	1	1	0, 0, 2.54	$E_0 > -15 \pm 1$
	S	2	1	0.94, -1.57, 1.27	$E_0 < 0 \pm 1$
	S′	2	1	0.94, 1.57, 1.27	$S_0^2 > 0.5 \pm 0.1$
	C_a	3	1	0.58, 0, -1.68	$S_0^2 < 1 \pm 0.1$
	C_b	3	1	-0.89, -1.54, -0.27	$\sigma^2_{all} < 0.02 \pm 0.01$
	C_b'	3	1	-0.89, 1.54, -0.27	$\sigma^2_{all} > 0.001 \pm 0.001$
	C_b''	4	1	-0.89, -1.54, -2.74	$CO_{angle} = 180 \pm 1°$
	C_b'''	4	1	-0.89, 1.54, -2.74	
	O_a	5	1	0.95, 0, -2.78	
	O_b	5	1	-1.46, -2.53, -0.44	
	O_b'	5	1	-1.46, 2.53, -0.44	
	C_α	6	1	2.76, -1.57, 1.27	
	C_α'	6	1	2.76, 1.57, 1.27	

d. $C_{2v}P_{12}$

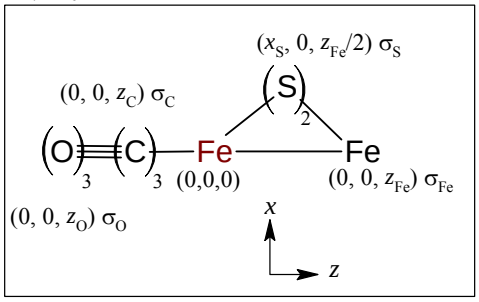


Coordinates of C(B) and O(B)

$$\left(z_{C_a}, \frac{x_{C_a}\sqrt{3}}{2}, \frac{-x_{C_a}}{2}\right), \left(z_{O_a}, \frac{x_{O_a}\sqrt{3}}{2}, \frac{-x_{O_a}}{2}\right)$$

Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{12}$	**Fe**	1	1	0, 0, 2.54	$E_0 > -15 \pm 1$
	S	2	1	0.94, -1.57, 1.27	$E_0 < 0 \pm 1$
	S′	2	1	0.94, 1.57, 1.27	$S_0^2 > 0.5 \pm 0.1$
	C	3	1	0.58, 0, -1.68	$S_0^2 < 1 \pm 0.1$
	C′	4	1	-1.68, -0.50, -0.29	$\sigma^2_{all} < 0.02 \pm 0.01$
	C″	4	1	-1.68, 0.50, -0.29	$\sigma^2_{all} > 0.001 \pm 0.001$
	C‴	4	1	-1.68, -0.50, 2.79	$CO_{angle} = 180 \pm 1°$
	C⁗	4	1	-1.68, 0.50, 2.79	
	O	5	1	0.95, 0, -2.78	
	O′	6	1	-2.78, -0.71, -0.48	
	O″	6	1	-2.78, 0.71, -0.48	

e. $C_{2v}Z_{10}$

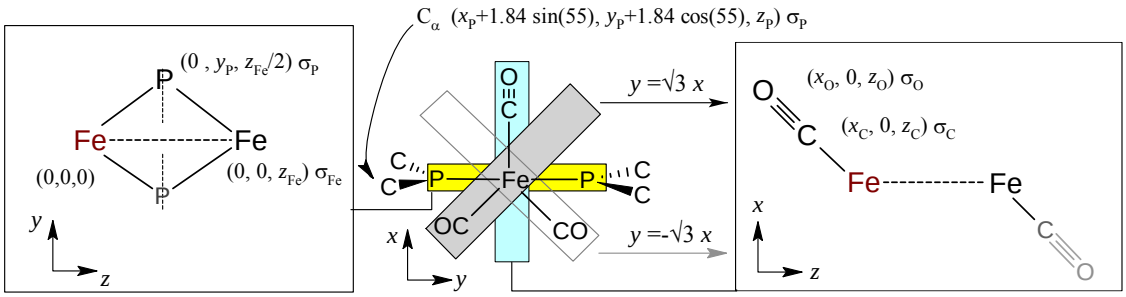


Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}Z_{10}$	**Fe**	1	1	0, 0, 2.54	$E_0 > -15 \pm 1$
	S	2	2	1.80, 0, 1.25	$E_0 < 0 \pm 1$
	C	3	3	0, 0, -1.80	$S_0^2 > 0.5 \pm 0.1$
	O	4	3	0, 0, -2.93	$S_0^2 < 1 \pm 0.1$
					$\sigma^2_{all} < 0.02 \pm 0.01$
					$\sigma^2_{all} > 0.001 \pm 0.001$

f. Model for **2**
Analogous to $C_{2v}P_{16}C_\alpha$ with two C_α atoms.

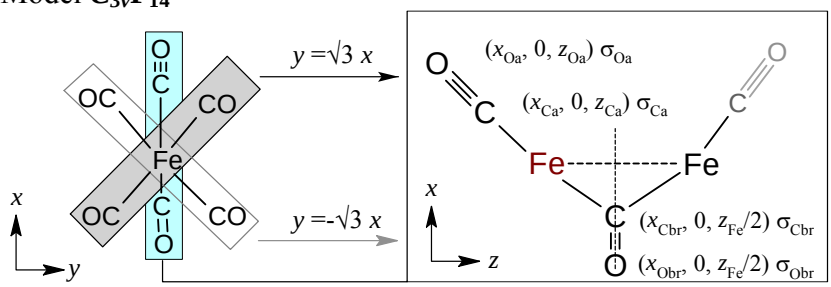
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_\alpha$	**Fe**	1	1	0, 0, 2.62	$E_0 > -15 \pm 1$
	P	2	1	0.89, -1.55, 1.31	$E_0 < 0 \pm 1$
	P′	2	1	0.89, 1.55, 1.31	$S_0^2 > 0.5 \pm 0.1$
	$\mathbf{C_a}$	3	1	0.62, 0, -1.66	$S_0^2 < 1 \pm 0.1$
	$\mathbf{C_b}$	3	1	-0.90, -1.55, -0.12	$\sigma^2_{all} < 0.02 \pm 0.01$
	$\mathbf{C_b'}$	3	1	-0.90, 1.55, -0.12	$\sigma^2_{all} > 0.001 \pm 0.001$
	$\mathbf{C_b''}$	4	1	-0.90, -1.55, 2.74	$CO_{angle} = 180 \pm 1°$
	$\mathbf{C_b'''}$	4	1	-0.90, 1.55, 2.74	
	$\mathbf{O_a}$	5	1	1.06, 0, -2.82	
	$\mathbf{O_b}$	5	1	-1.46, -2.53, -0.19	
	$\mathbf{O_b'}$	5	1	-1.46, 2.53, -0.19	
	$\mathbf{C_\alpha}$	6	2	2.66, -2.09, 1.31	
	$\mathbf{C_\alpha'}$	6	2	2.66, 2.09, 1.31	

g. Model for $\mathbf{2}^{2-}$



Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_{\alpha}$	**Fe**	1	1	0, 0, 3.62	$E_0 > -15 \pm 1$
	P	2	1	0, -1.38, 1.80	$E_0 < 0 \pm 1$
	P′	2	1	0, 1.38, 1.80	$S_0^2 > 0.5 \pm 0.1$
	C	3	1	-0.62, 0, -1.66	$S_0^2 < 1 \pm 0.1$
	C′	3	1	-0.90, -1.55, -0.12	$\sigma^2_{all} < 0.02 \pm 0.01$
	C″	3	1	-0.90, 1.55, -0.12	$\sigma^2_{all} > 0.001 \pm 0.001$
	?C7	4	1	-0.90, -1.55, 3.74	$CO_{angle} = 180 \pm 1°$
	?C8	4	1	-0.90, 1.55, 3.74	
	O	5	1	1.06, 0, -2.82	
	O′	5	1	-1.46, -2.53, -0.19	
	O″	5	1	-1.46, 2.53, -0.19	
	C_{α}	6	2	0, -2.95, 1.80	
	C_{α}'	6	2	0, 2.95, 1.80	

h. Model $\boldsymbol{C_{3v}P_{14}}$



Coordinates for CO groups: x=√3 y plane:

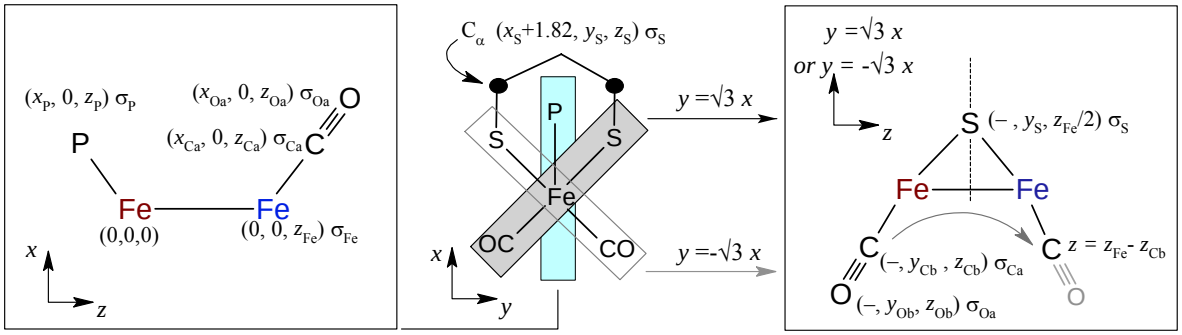
$$C_b\left(\frac{x_{C_a}}{2}, \frac{2x_{C_a}}{\sqrt{3}}, z_{C_a}\right), \quad O_b\left(\frac{x_{O_a}}{2}, \frac{2x_{O_a}}{\sqrt{3}}, z_{O_a}\right)$$

etc.

For $\boldsymbol{C_{3v}P_{12}}$ additionally $x(O_{br}) = x(C_{br})$-1.18 and $\sigma(O_{br}) = \sigma(C_{br})$

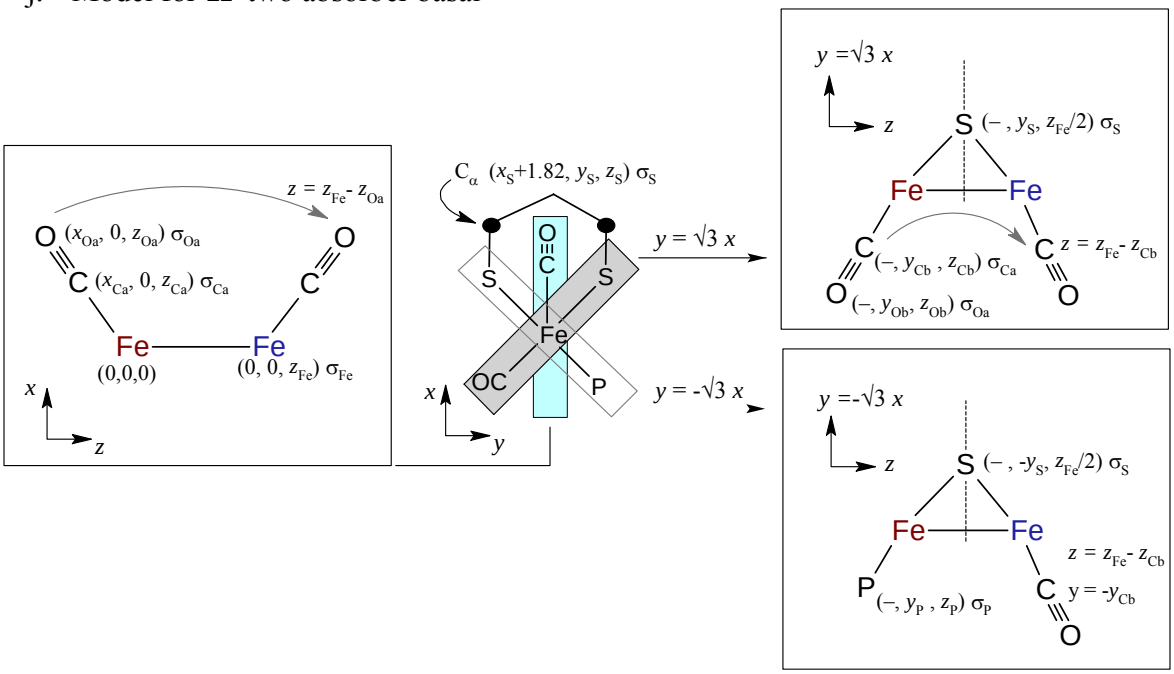
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{3v}P_{14}$	**Fe**	1	1	0, 0, 2.52	$E_0 > -15 \pm 1$
	C_{br}	2	3	1.57, 0, 1.26	$E_0 < 0 \pm 1$
	O_{br}	3	3	2.73, 0, 1.26	$S_0^2 > 0.5 \pm 0.1$
	C_a	4	3	-1.58, 0, -0.94	$S_0^2 < 1 \pm 0.1$
	C_a'	4	3	-1.58, 0, 3.47	$\sigma^2_{all} < 0.02 \pm 0.01$
	O_a	5	3	-2.51, 0, -1.57	$\sigma^2_{all} > 0.001 \pm 0.001$
					$CO_{termangle} = 180° \pm 1°$

i. Model for **1P** two absorber apical



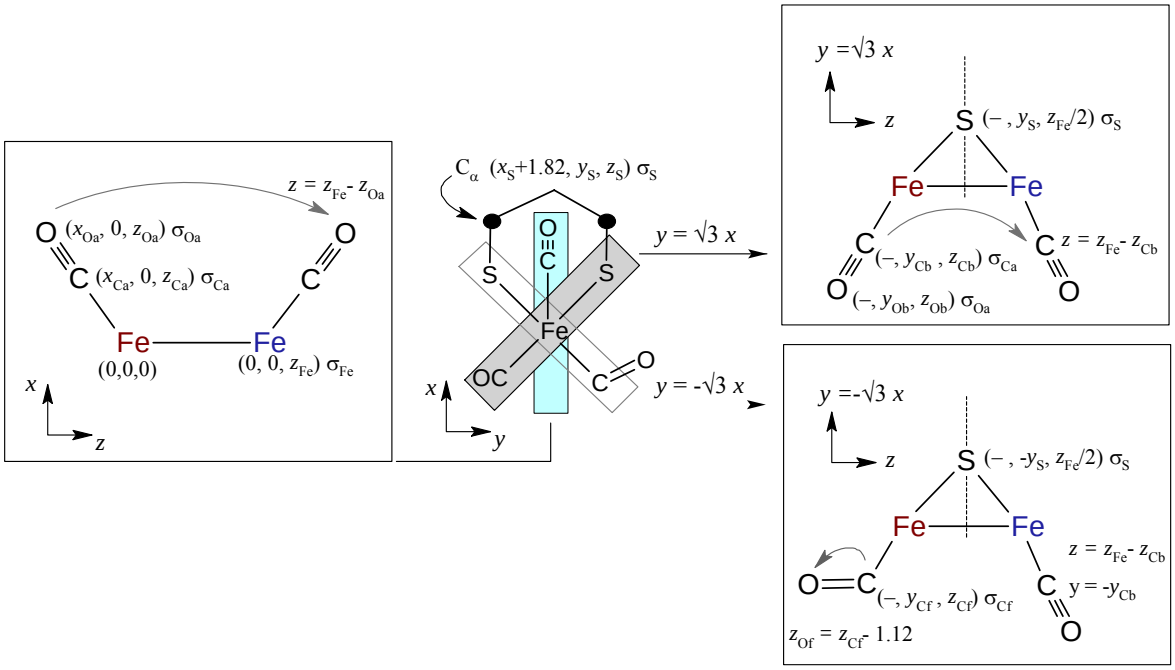
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_\alpha$	**Fe**	0	1	0, 0, 0	E_0, $E_0(1) > -15 \pm 1$
	Fe	1	1	0, 0, 2.53	E_0, $E_0(1) < 0 \pm 1$
	S	2	1	0.92, -1.59, 1.265	$E_0 = E_0(1)$
	S′	2	1	0.92, 1.59, 1.265	S_0^2, $S_0^2(1) > 0.5 \pm 0.1$
	P	3	1	0.9, 0, -2.05	S_0^2, $S_0^2(1) < 1 \pm 0.1$
	C_b	4	1	-0.88, -1.52, -0.19	$\sigma^2_{all} < 0.02 \pm 0.01$
	C_b'	4	1	-0.88, 1.52, -0.19	$\sigma^2_{all} > 0.001 \pm 0.001$
	C_b''	4	1	-0.88, -1.52, 2.73	$CO_{angle} \sim= 180 \pm 1°$
	C_b'''	4	1	-0.88, 1.52, 2.73	
	C_a	5	1	0.61, 0, 4.25	
	O_b	6	1	-1.45, -2.51, -0.32	
	O_b'	6	1	-1.45, 2.51, -0.32	
	O_b''	6	1	-1.45, -2.51, 2.85	
	O_b'''	6	1	-1.45, 2.51, 2.85	
	O_a	7	1	1.00, 0, 5.33	
	C_α	8	1	2.76, 1.57, 1.265	
	C_α'	8	1	2.76, -1.57, 1.265	

j. Model for **1P** two absorber basal



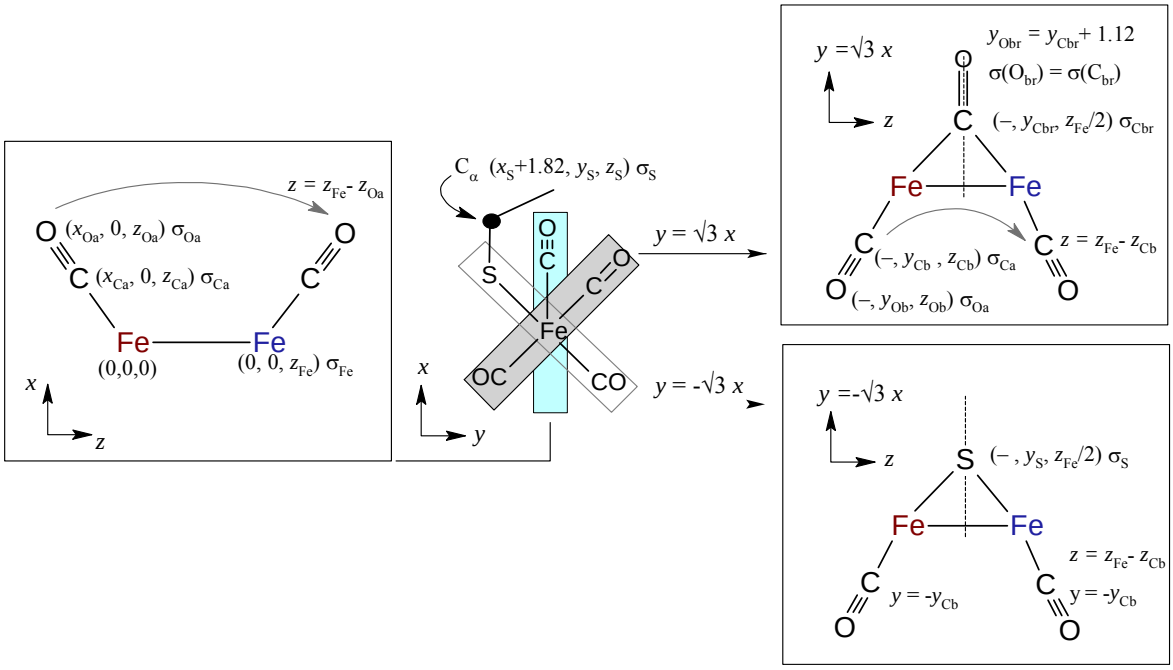
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_{\alpha}$	**Fe**	0	1	0, 0, 0	E_0, $E_0(1) > -15 \pm 1$
	Fe	1	1	0, 0, 2.53	E_0, $E_0(1) < 0 \pm 1$
	S	2	1	0.92, -1.59, 1.265	$E_0 = E_0(1)$
	S′	2	1	0.92, 1.59, 1.265	S_0^2, $S_0^2(1) > 0.5 \pm 0.1$
	P	3	1	-1.16, -2.02, -0.26	S_0^2, $S_0^2(1) < 1 \pm 0.1$
	C_b	4	1	-0.88, 1.52, -0.19	$\sigma^2_{all} < 0.02 \pm 0.01$
	C_b'	4	1	-0.88, -1.52, 2.73	$\sigma^2_{all} > 0.001 \pm 0.001$
	C_b''	4	1	-0.88, 1.52, 2.73	$CO_{angle} \sim= 180 \pm 1°$
	C_a	5	1	0.61, 0, -1.71	
	C_a'	5	1	0.61, 0, 4.25	
	O_b	6	1	-1.45, 2.51, -0.32	
	O_b'	6	1	-1.45, -2.51, 2.85	
	O_b''	6	1	-1.45, 2.51, 2.85	
	O_a	7	1	1.00, 0, -2.79	
	O_a'	7	1	1.00, 0, 5.33	
	C_{α}	8	1	2.76, 1.57, 1.265	
	C_{α}'	8	1	2.76, -1.57, 1.265	

k. Model for **1F** two absorber



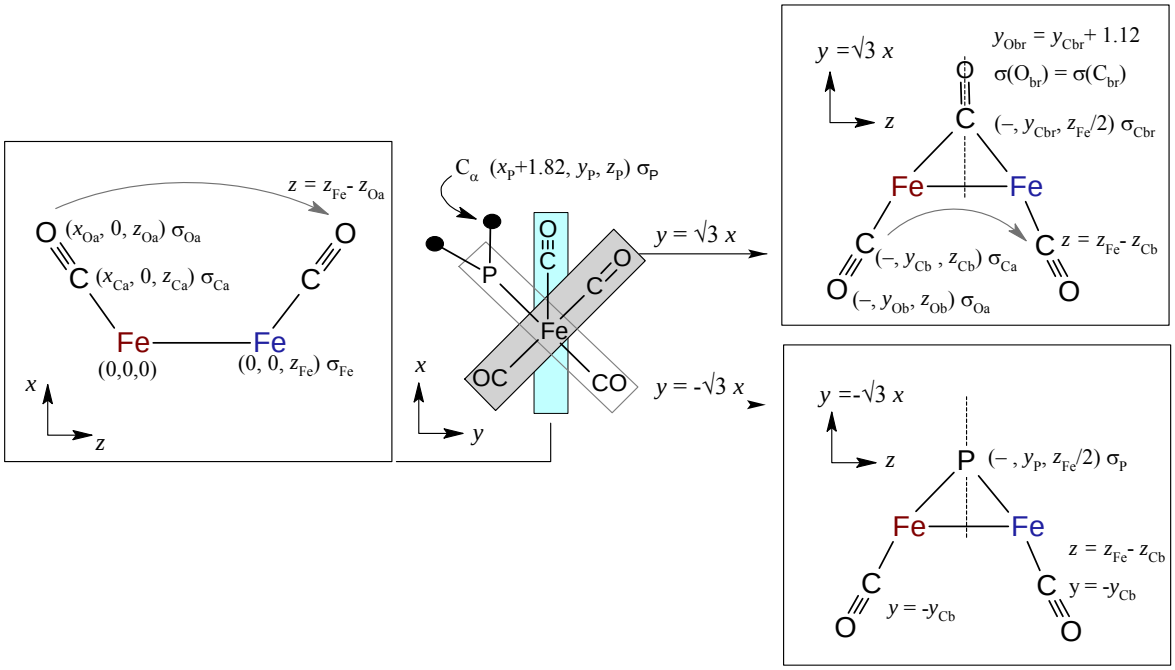
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_{\alpha}$	**Fe**	0	1	0, 0, 0	E_0, $E_0(1)$ > -15 ± 1
	Fe	1	1	0, 0, 2.53	E_0, $E_0(1)$ < 0 ± 1
	S	2	1	0.92, -1.59, 1.265	$E_0 = E_0(1)$
	S′	2	1	0.92, 1.59, 1.265	S_0^2, $S_0^2(1)$ > 0.5 ± 0.1
	C_a	3	1	0.61, 0, 4.25	S_0^2, S_0^2 (1) < 1 ± 0.1
	C_b	4	1	-0.88, -1.52, -0.19	σ^2 all < 0.02 ± 0.01
	C_b'	4	1	-0.88, 1.52, -0.19	σ^2all > 0.001 ± 0.001
	C_b''	4	1	-0.88, -1.52, 2.73	CO_{angle} ~= 180 ± 1°
	C_b'''	4	1	-0.88, 1.52, 2.73	
	O	5	1	1.00, 0, 5.33	
	O_b	6	1	-1.45, -2.51, -0.32	
	O_b'	6	1	-1.45, 2.51, -0.32	
	O_b''	6	1	-1.45, -2.51, 2.85	
	O_b'''	6	1	-1.45, 2.51, 2.85	
	C(f)	7	1	0.7, 0, -1.65	
	O(f)	8	1	1.90, 0, -1.65	
	C_{α}	9	1	2.76, -1.57, 1.265	
	C_{α}'	9	1	2.76, 1.57, 1.265	

l. Model for **4S** two absorber



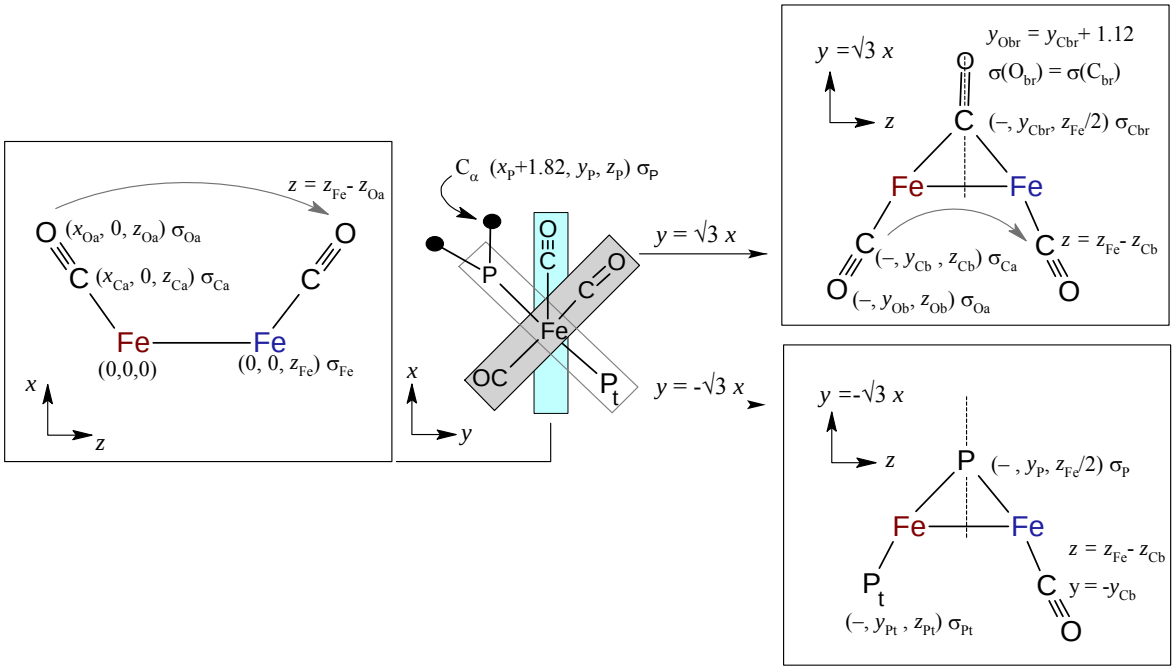
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_{\alpha}$	**Fe**	0	1	0, 0, 0	E_0, $E_0(1) > -15 \pm 1$
	Fe	1	1	0, 0, 2.53	E_0, $E_0(1) < 0 \pm 1$
	S	2	1	0.92, -1.59, 1.265	$E_0 = E_0(1)$
	$\mathbf{C_a}$	3	1	0.61, 0, -1.71	S_0^2, $S_0^2(1) > 0.5 \pm 0.1$
	$\mathbf{C_a}'$	3	1	0.61, 0, 4.25	S_0^2, $S_0^2(1) < 1 \pm 0.1$
	$\mathbf{C_b}$	4	1	-0.88, -1.52, -0.19	$\sigma^2_{all} < 0.02 \pm 0.01$
	$\mathbf{C_b}'$	4	1	-0.88, 1.52, -0.19	$\sigma^2_{all} > 0.001 \pm 0.001$
	$\mathbf{C_b}''$	4	1	-0.88, -1.52, 2.73	$CO_{angle} \sim= 180 \pm 1°$
	$\mathbf{C_b}'''$	4	1	-0.88, 1.52, 2.73	
	$\mathbf{O_a}$	5	1	1.00, 0, -2.79	
	$\mathbf{O_a}'$	5	1	1.00, 0, 5.33	
	$\mathbf{O_b}$	6	1	-1.45, -2.51, -0.32	
	$\mathbf{O_b}'$	6	1	-1.45, 2.51, -0.32	
	$\mathbf{O_b}''$	6	1	-1.45, -2.51, 2.85	
	$\mathbf{O_b}'''$	6	1	-1.45, 2.51, 2.85	
	$\mathbf{C_{br}}$	7	1	0.6, 1.04, 1.265	
	$\mathbf{O_{br}}$	8	1	1.90, 0, 1.265	
	$\mathbf{C_{\alpha}}$	9	1	2.76, -1.57, 1.265	

m. Model for **4P** two absorber



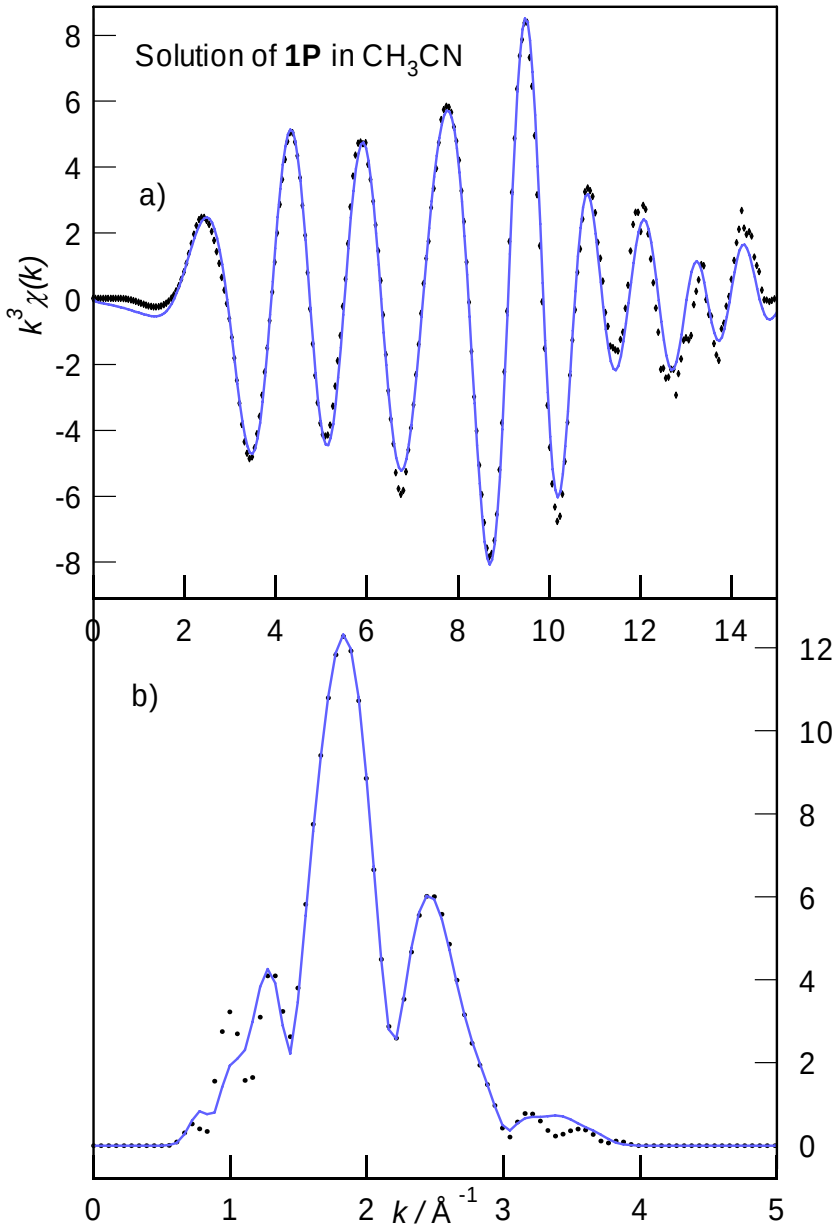
Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_{\alpha}$	**Fe**	0	1	0, 0, 0	E_0, $E_0(1) > -15 \pm 1$
	Fe	1	1	0, 0, 2.53	E_0, $E_0(1) < 0 \pm 1$
	P	2	1	0.92, -1.59, 1.265	$E_0 = E_0(1)$
	$\mathbf{C_a}$	3	1	0.61, 0, -1.71	S_0^2, $S_0^2(1) > 0.5 \pm 0.1$
	$\mathbf{C_a}'$	3	1	0.61, 0, 4.25	S_0^2, $S_0^2(1) < 1 \pm 0.1$
	$\mathbf{C_b}$	4	1	-0.88, -1.52, -0.19	$\sigma^2_{all} < 0.02 \pm 0.01$
	$\mathbf{C_b}'$	4	1	-0.88, 1.52, -0.19	$\sigma^2_{all} > 0.001 \pm 0.001$
	$\mathbf{C_b}''$	4	1	-0.88, -1.52, 2.73	$CO_{angle} \sim= 180 \pm 1°$
	$\mathbf{C_b}'''$	4	1	-0.88, 1.52, 2.73	
	$\mathbf{O_a}$	5	1	1.00, 0, -2.79	
	$\mathbf{O_a}'$	5	1	1.00, 0, 5.33	
	$\mathbf{O_b}$	6	1	-1.45, -2.51, -0.32	
	$\mathbf{O_b}'$	6	1	-1.45, 2.51, -0.32	
	$\mathbf{O_b}''$	6	1	-1.45, -2.51, 2.85	
	$\mathbf{O_b}'''$	6	1	-1.45, 2.51, 2.85	
	$\mathbf{C_{br}}$	7	1	0.6, 1.04, 1.265	
	$\mathbf{O_{br}}$	8	1	1.90, 0, 1.265	
	$\mathbf{C_{\alpha}}$	9	1	2.76, -1.57, 1.265	

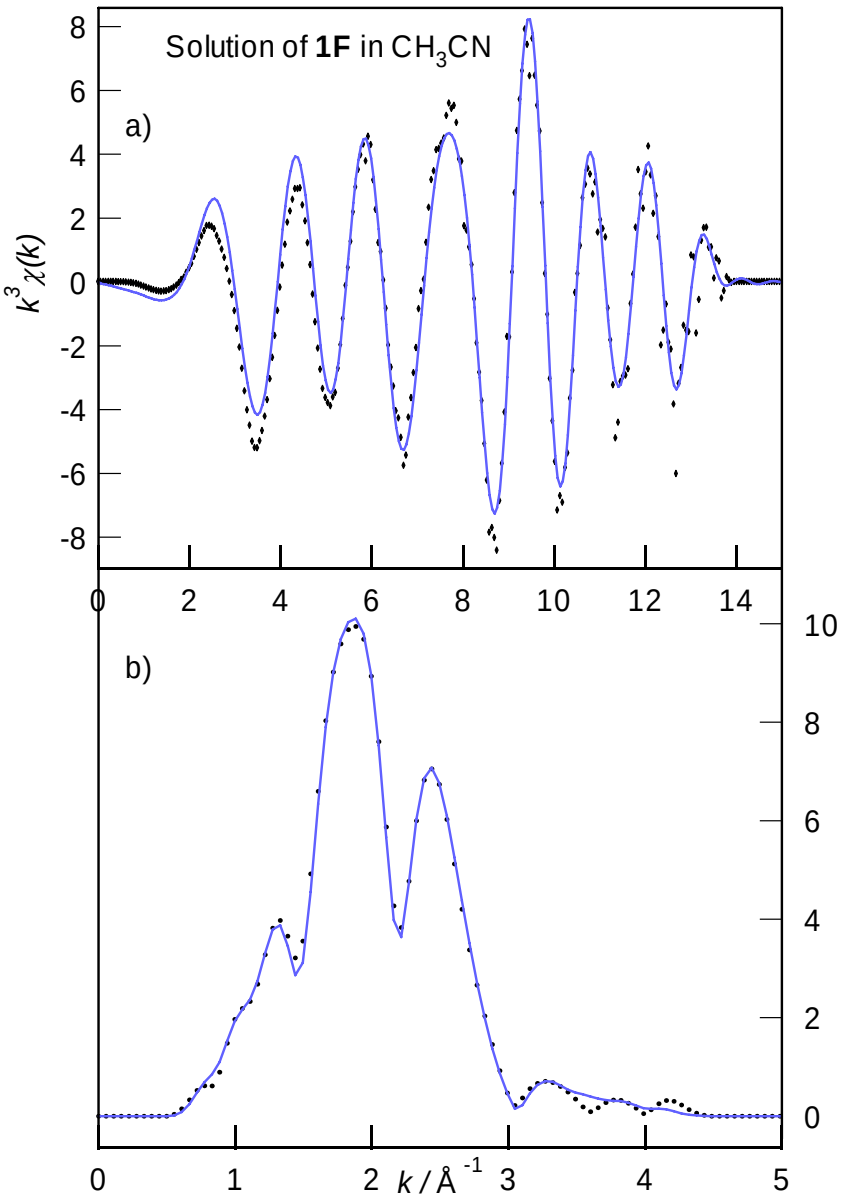
n. Model for **4PP** two absorber

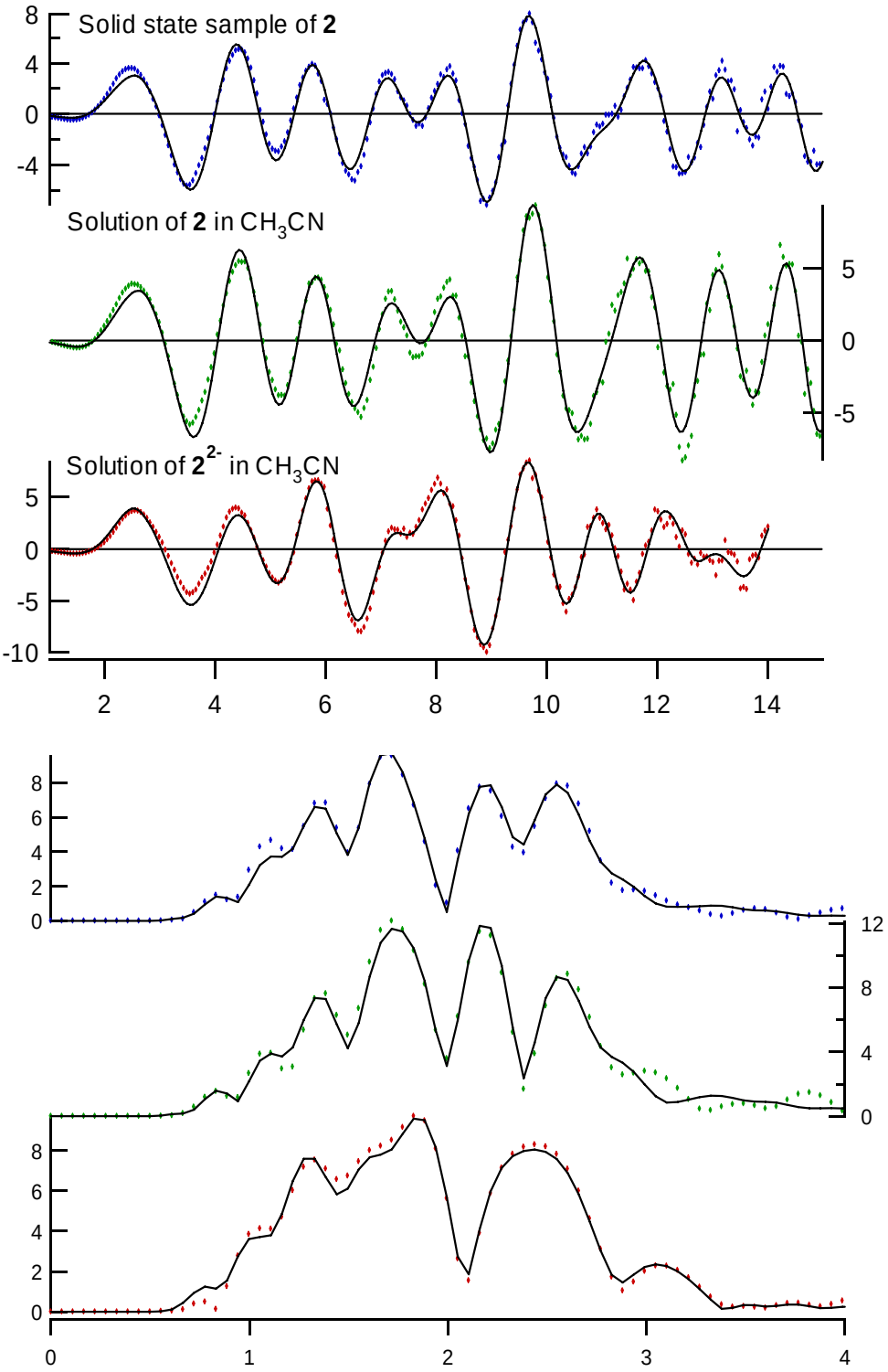


Model	Scatterer	POT	N_s	Starting coordinates (x, y, z)	Restraints
$C_{2v}P_{16}C_{\alpha}$	**Fe**	0	1	0, 0, 0	E_0, $E_0(1) > -15 \pm 1$
	Fe	1	1	0, 0, 2.53	E_0, $E_0(1) < 0 \pm 1$
	P	2	1	0.92, -1.59, 1.265	$E_0 = E_0(1)$
	C_a	3	1	0.61, 0, -1.71	S_0^2, $S_0^2(1) > 0.5 \pm 0.1$
	C_a'	3	1	0.61, 0, 4.25	S_0^2, $S_0^2(1) < 1 \pm 0.1$
	C_b	4	1	-0.88, -1.52, -0.19	$\sigma^2_{all} < 0.02 \pm 0.01$
	C_b'	4	1	-0.88, -1.52, 2.73	$\sigma^2_{all} > 0.001 \pm 0.001$
	C_b''	4	1	-0.88, 1.52, 2.73	$CO_{angle} \sim= 180 \pm 1°$
	O_a	5	1	1.00, 0, -2.79	
	O_a'	5	1	1.00, 0, 5.33	
	O_b	6	1	-1.45, -2.51, -0.32	
	O_b'	6	1	-1.45, -2.51, 2.85	
	O_b''	6	1	-1.45, 2.51, 2.85	
	P	7	1	-1.13, 1.95, -0.19	
	$C_{P\alpha}$	8	1	-2.96, 1.95, -0.19	
	C_{br}	9	1	0.6, 1.04, 1.265	
	O_{br}	10	1	1.90, 0, 1.265	
	C_{α}	11	2	2.76, -1.57, 1.265	

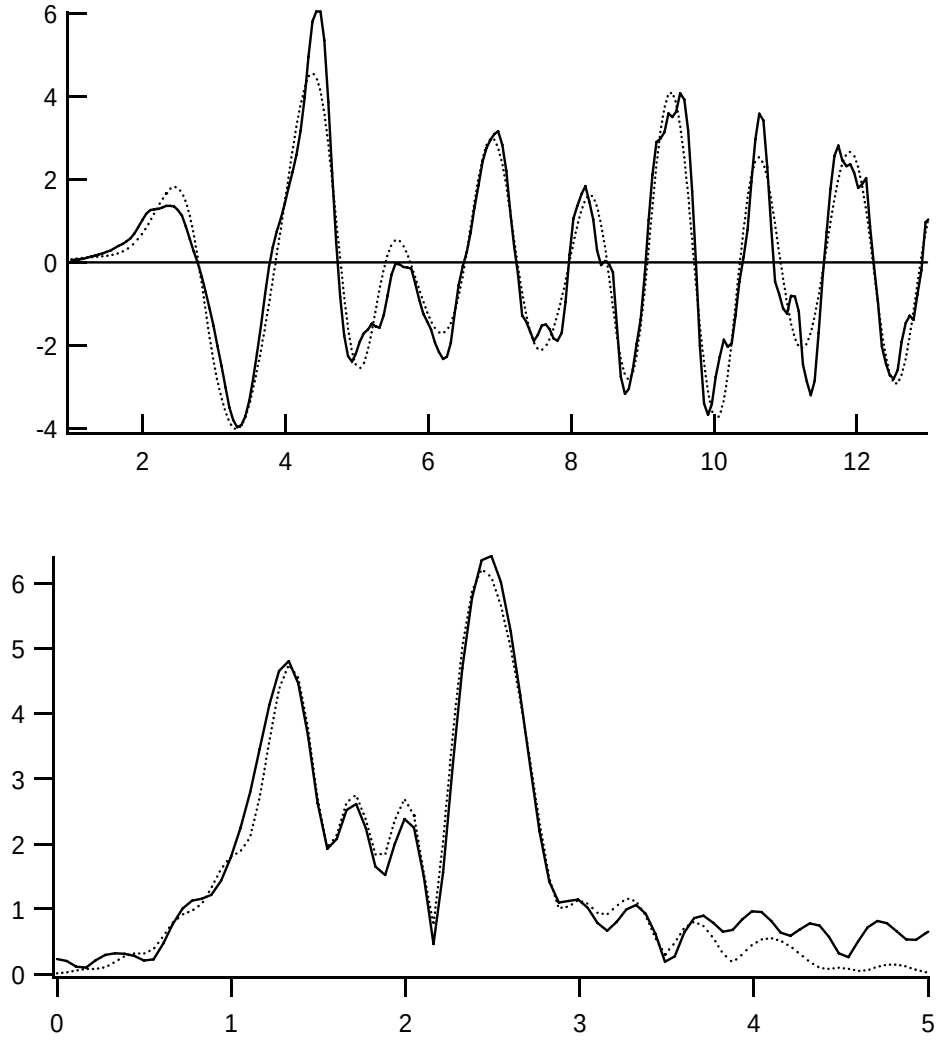
2. Fits of the XAFS of **1P**, **1F**, **2**, $\mathbf{2}^{2-}$, **3**, **4S**, **4P** and **4PP**.

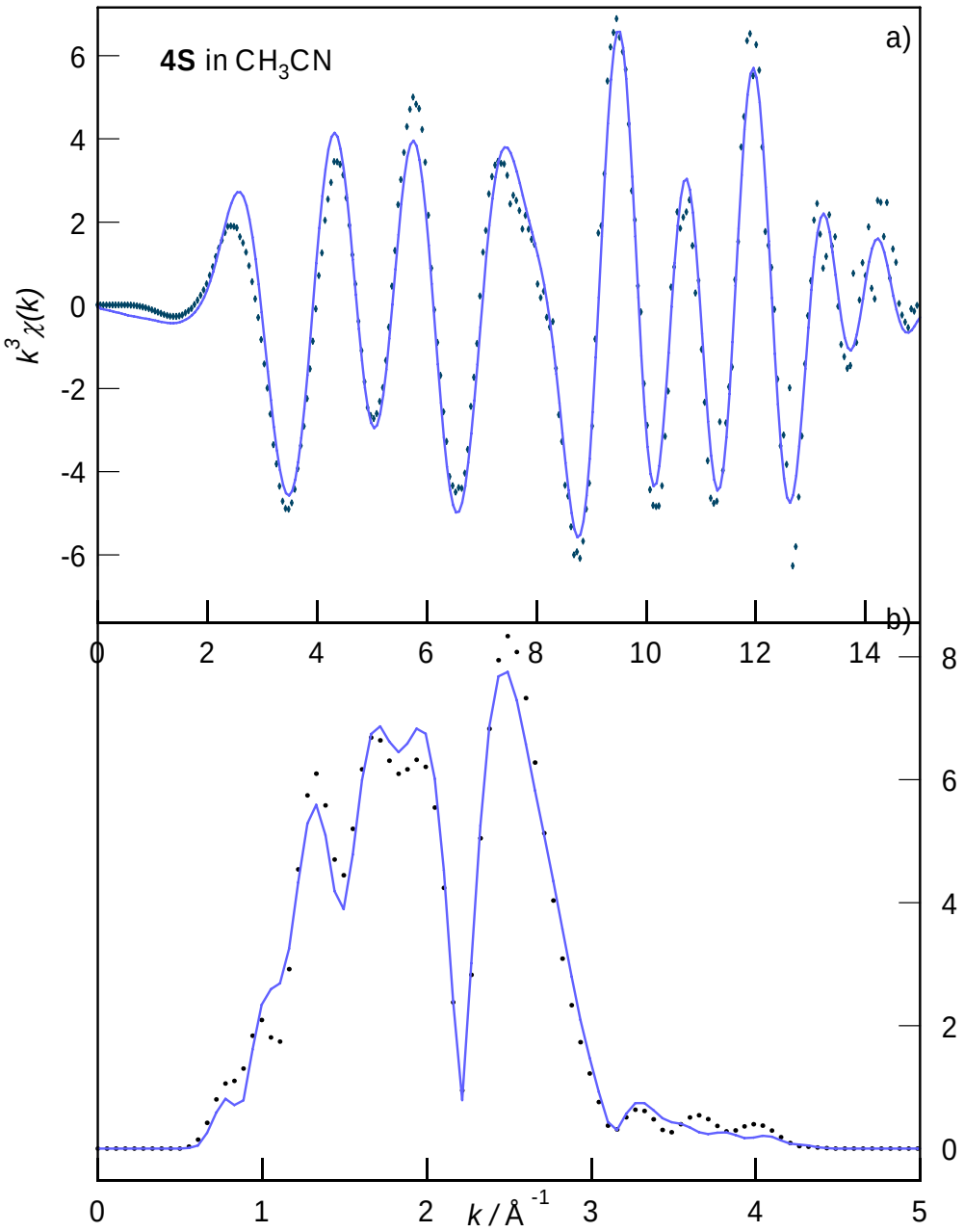


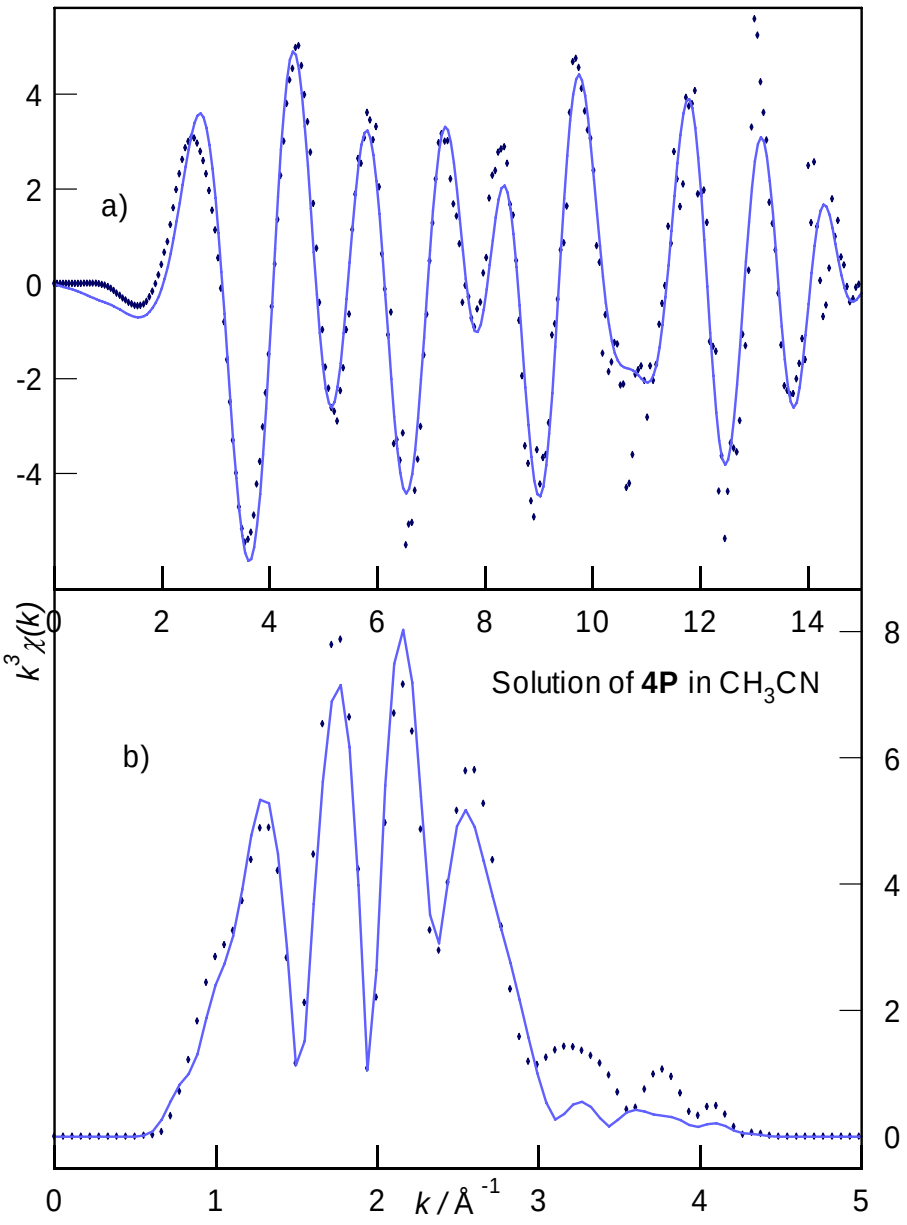

Solution of 1F in CH3CN
a)
b)
k3χ(k)
k / Å-1

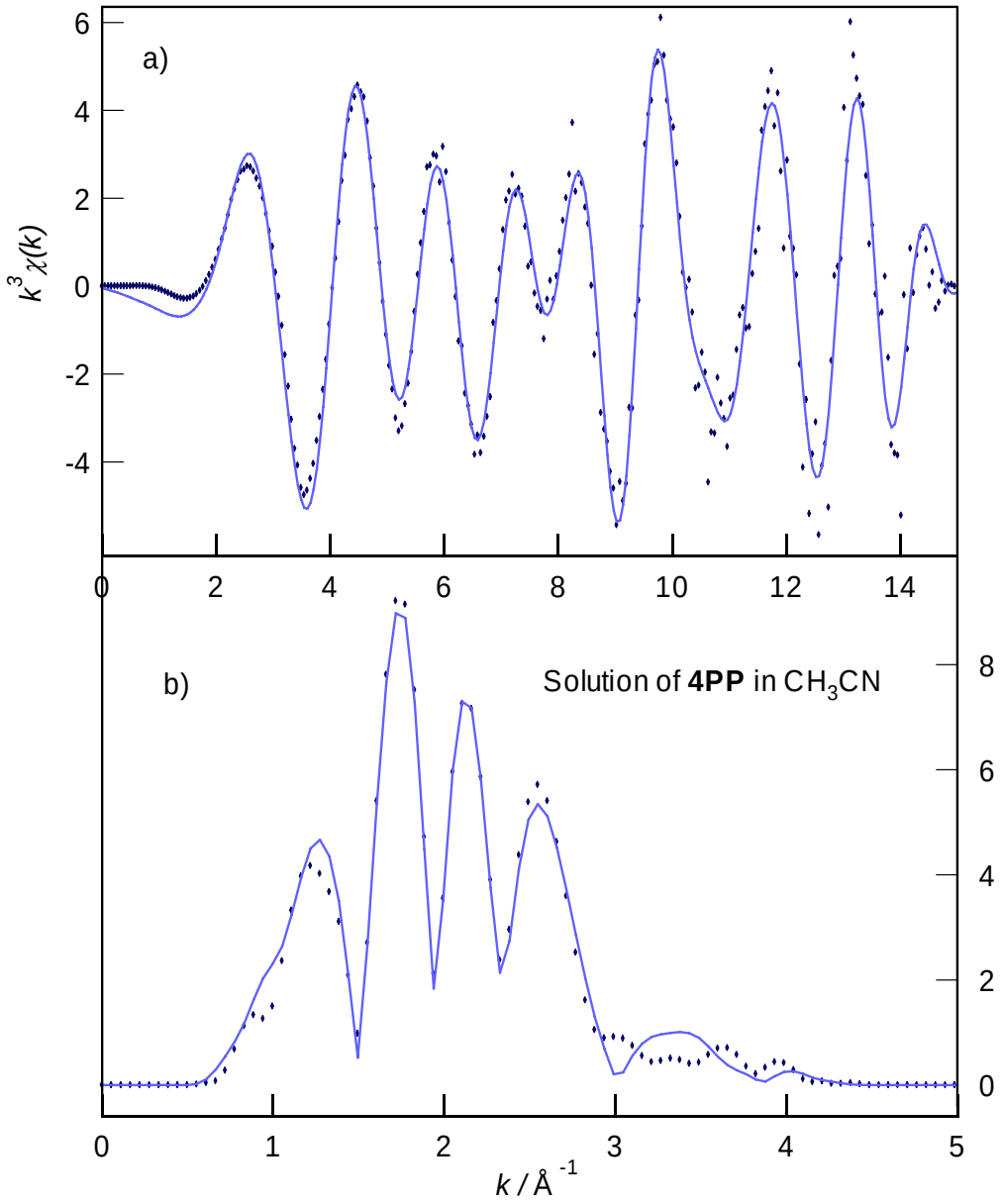

Solid state sample of 2
Solution of 2 in CH3CN
Solution of 2 2- in CH3CN

$Fe_2(CO)_9$, **3**




4S in CH3CN
a)
b)
k3χ(k)
k / Å-1


a)
b)
Solution of 4P in CH3CN
k3χ(k)
k / Å-1


a)
b)
Solution of 4PP in CH3CN
k3χ(k)
k / Å-1

3. Cartesian coordinates of optimised vacuum phase structures

a. **1F** (basal formyl)

Atom	x	y	z
Fe	-1.24544	0.00880	0.01826
Fe	1.25496	-0.54854	-0.03990
S	0.21027	0.89233	-1.57418
C	-2.62549	1.06789	-0.04364
S	0.33157	0.84095	1.64099
C	0.88142	2.58123	1.32958
H	0.57603	3.14521	2.22356
H	1.98101	2.58830	1.29451
C	0.74058	2.63558	-1.24542
H	1.83612	2.66388	-1.33844
H	0.32393	3.22464	-2.07584
C	0.29961	3.25547	0.08409
H	-0.79740	3.24985	0.14526
O	-2.35964	-1.81828	2.01403
O	1.21545	-2.68980	1.96033
C	-1.90654	-1.09857	1.22523
O	4.06604	0.30059	0.04535
O	1.41807	-2.50245	-2.21785
C	1.20340	-1.83933	1.16619
C	-2.00036	-1.09138	-1.38267
C	1.33424	-1.72875	-1.35422
C	2.94075	-0.00184	0.00387
H	0.61706	4.31530	0.08475
O	-3.55581	1.77099	-0.09089
H	-1.48581	-0.94792	-2.37780
O	-2.93078	-1.88859	-1.35604

1F (apical formyl)

Atom	x	y	z
Fe	1.23520	-0.18621	-0.06797
Fe	-1.35746	-0.42226	0.02377
S	-0.06961	0.82068	1.58116
C	2.78869	0.92812	-0.07919
S	-0.21978	0.85230	-1.62361
C	-0.52551	2.64815	-1.28156
H	-0.13080	3.18418	-2.15731
H	-1.61567	2.79462	-1.26845
C	-0.40941	2.62120	1.29823
H	-1.49800	2.75644	1.38356
H	0.06048	3.14168	2.14557
C	0.10576	3.22514	-0.01025
H	1.19716	3.11852	-0.05589
O	2.36020	-1.80687	-2.22466
O	2.27838	-1.99712	1.97813
O	-1.37123	-2.63183	-1.90139
C	1.89830	-1.16356	-1.37246
O	-4.03456	0.75482	-0.24023
O	-1.94473	-2.26026	2.22469
C	-1.32175	-1.75469	-1.13272
C	1.86904	-1.26977	1.17322
C	-1.69915	-1.53466	1.34756
C	-2.95150	0.33638	-0.11147
H	-0.10699	4.31038	0.01039
H	2.73707	1.72276	-0.88116
O	3.79182	0.91703	0.62140

4S

Atom	x	y	z
Fe	-0.78305	1.32234	0.00564
Fe	-1.29716	-1.19423	0.04084
S	0.68841	-0.27494	0.91689
S	6.33512	-0.12207	0.21002
C	-0.86997	0.00817	-1.45755
C	-1.18146	1.85749	1.68228
C	0.40427	2.42175	-0.68715
C	-2.19423	2.10420	-0.67409
C	-1.86364	-1.46510	1.73114
C	-0.61753	-2.68325	-0.59365
C	-2.90152	-1.39338	-0.63219
O	-1.43061	2.26657	2.74547
O	1.14469	3.20331	-1.13486
O	-3.13075	2.63016	-1.13431
O	-2.24323	-1.70577	2.80787
O	-0.21160	-3.70438	-0.99162
O	-3.96856	-1.53678	-1.08721
O	-0.77680	-0.02838	-2.64570
C	2.13073	-0.62401	-0.21820
C	3.46922	-0.14329	0.37742
C	4.67545	-0.54466	-0.50718
H	1.93035	-0.16894	-1.19539
H	2.15099	-1.71425	-0.35082
H	3.60856	-0.57918	1.37777
H	3.46333	0.94910	0.50472
H	4.56166	-0.05715	-1.49137
H	4.62103	-1.63368	-0.68619

4P

Atom	x	y	z
Fe	1.32925	0.23396	0.04136
Fe	-1.32915	0.23410	0.04090
P	-0.00013	-1.57887	-0.15481
O	2.22523	3.00912	0.35913
O	2.12165	-0.52379	2.78426
O	3.42531	-0.69467	-1.76262
O	-2.22181	3.01013	0.36049
O	-2.12755	-0.52599	2.78130
O	-3.42414	-0.69023	-1.76655
O	0.00085	1.47732	-2.31520
C	1.85649	1.91125	0.23802
C	1.77594	-0.21505	1.71185
C	2.56690	-0.31499	-1.06348
C	-1.85454	1.91185	0.23863

C	-1.77913	-0.21624	1.71003
C	-2.56608	-0.31243	-1.06599
C	0.00072	0.90062	-1.27258
C	0.00031	-2.53216	-1.75813
H	-0.89521	-3.16698	-1.83199
H	0.89571	-3.16722	-1.83142
H	0.00068	-1.82546	-2.59607
C	-0.00017	-2.97394	1.08131
H	-0.00114	-2.57384	2.10147
H	0.89426	-3.60037	0.94911
H	-0.89373	-3.60135	0.94780

4PP (terminal P basal opposite bridging P)

Atom	x	y	z
Fe	0.92342	-0.54962	-0.07138
O	0.08865	0.79523	-2.56655
O	1.62634	-0.91954	2.77362
C	-0.02660	0.40707	-1.44085
C	1.32281	-0.74543	1.65270
Fe	-1.46312	0.67457	0.00525
P	-1.06315	-1.53679	0.17124
P	2.56865	0.93531	-0.34005
C	1.66418	-1.81453	-0.99684
C	-1.90123	0.78931	1.72262
C	-1.19534	2.40273	-0.17426
C	-2.88542	0.52118	-0.99523
C	-1.67587	-2.66624	-1.18228
C	4.29807	0.35205	0.05164
O	2.17139	-2.70173	-1.58035
O	-1.02340	3.55341	-0.30079
O	-3.88046	0.43842	-1.61092
C	2.51025	2.56507	0.56214
H	2.77911	1.40900	-1.67340
C	-1.49786	-2.54297	1.68041
H	-0.97983	-3.51344	1.65729
H	-2.58264	-2.72256	1.72172
H	-1.19720	-2.00504	2.58670
H	-2.75940	-2.83455	-1.08901
H	-1.15803	-3.63649	-1.14530
H	-1.47538	-2.19671	-2.15244
H	2.47441	2.36962	1.64232
H	1.59195	3.09534	0.28514
H	3.38245	3.19526	0.33246
H	5.05149	1.12926	-0.14285
H	4.52293	-0.53384	-0.55614
H	4.34638	0.05847	1.10883
O	-2.26056	0.87794	2.83448

4PP (terminal P basal opposite bridging CO)

Atom	x	y	z
Fe	-0.94381	0.45807	-0.50212
O	0.98901	0.91285	-2.64804
O	-2.29660	3.01570	-0.80390
C	0.59740	0.53991	-1.58509
C	-1.75256	1.98159	-0.67817
Fe	1.49522	-0.48469	-0.00672
P	0.55115	1.29022	1.00011
P	-2.02313	-0.86371	1.00435
C	-1.75730	-0.36808	-1.81964
C	1.49616	-1.44593	1.47599
C	1.57467	-1.88059	-1.08171
C	3.09810	0.17891	-0.22752
C	1.23622	2.99297	0.65621
C	-2.11294	-2.69982	0.66842
O	-2.32588	-0.88099	-2.70441
O	1.63324	-2.80759	-1.79033
O	4.19573	0.57686	-0.32699
C	-3.82493	-0.49732	1.37893
H	-1.54523	-0.93007	2.35158
C	0.29555	1.42395	2.84734
H	-0.41869	2.22721	3.08333
H	1.25399	1.65263	3.33697
H	-0.07959	0.48090	3.26042
H	2.16785	3.15745	1.21829
H	0.50942	3.77169	0.93283
H	1.45211	3.07847	-0.41493
H	-4.39984	-0.55521	0.44434
H	-3.90929	0.52941	1.75899
H	-4.25836	-1.19488	2.11137
H	-2.67047	-3.24026	1.44737
H	-1.09057	-3.09112	0.60879
H	-2.59678	-2.86363	-0.30390
O	1.58281	-2.07704	2.46354

4PP (terminal P apical)

Atom	x	y	z
Fe	-0.94381	0.45807	-0.50212
O	0.98901	0.91285	-2.64804
O	-2.29660	3.01570	-0.80390
C	0.59740	0.53991	-1.58509
C	-1.75256	1.98159	-0.67817
Fe	1.49522	-0.48469	-0.00672
P	0.55115	1.29022	1.00011
P	-2.02313	-0.86371	1.00435
C	-1.75730	-0.36808	-1.81964
C	1.49616	-1.44593	1.47599
C	1.57467	-1.88059	-1.08171
C	3.09810	0.17891	-0.22752
C	1.23622	2.99297	0.65621
C	-2.11294	-2.69982	0.66842
O	-2.32588	-0.88099	-2.70441
O	1.63324	-2.80759	-1.79033
O	4.19573	0.57686	-0.32699
C	-3.82493	-0.49732	1.37893
H	-1.54523	-0.93007	2.35158
C	0.29555	1.42395	2.84734
H	-0.41869	2.22721	3.08333
H	1.25399	1.65263	3.33697
H	-0.07959	0.48090	3.26042
H	2.16785	3.15745	1.21829
H	0.50942	3.77169	0.93283

H	1.45211	3.07847	-0.41493
H	-4.39984	-0.55521	0.44434
H	-3.90929	0.52941	1.75899
H	-4.25836	-1.19488	2.11137
H	-2.67047	-3.24026	1.44737
H	-1.09057	-3.09112	0.60879
H	-2.59678	-2.86363	-0.30390
O	1.58281	-2.07704	2.46354

Cartesian coordinates of optimised structures using continuum solvation

1F (basal formyl)

Atom	x	y	z
Fe	-1.24655	0.01460	0.02587
Fe	1.24922	-0.54508	-0.03974
S	0.20453	0.88557	-1.54766
C	-2.64247	1.07604	-0.01864
S	0.31398	0.83359	1.61130
C	0.84591	2.58079	1.32334
H	0.52472	3.12522	2.21502
H	1.93925	2.59349	1.31348
C	0.72407	2.63210	-1.23803
H	1.81231	2.66194	-1.33810
H	0.30800	3.20231	-2.07244
C	0.28188	3.25384	0.08002
H	-0.81070	3.26679	0.13347
O	-2.30851	-1.87043	1.99422
O	1.31678	-2.64813	2.00670
C	-1.88175	-1.12680	1.22468
O	4.04262	0.37582	-0.03334
O	1.35385	-2.52554	-2.20514
C	1.27729	-1.82443	1.20164
C	-1.98403	-1.08871	-1.39546
C	1.30353	-1.75005	-1.35530
C	2.94016	0.04141	-0.03918
H	0.60389	4.30503	0.08261
O	-3.57989	1.75288	-0.05282
H	-1.50608	-0.90936	-2.39803
O	-2.87792	-1.92517	-1.37115

1F (apical formyl)

Atom	x	y	z
Fe	-1.23274	-0.18993	0.07644
Fe	1.35011	-0.42056	-0.03724
S	0.06066	0.83554	-1.54495
C	-2.79500	0.93456	0.13428
S	0.21961	0.82519	1.60561
C	0.51015	2.62828	1.30522
H	0.11299	3.13330	2.18921
H	1.59333	2.77828	1.30623
C	0.38772	2.63477	-1.25944
H	1.46789	2.77352	-1.35961
H	-0.08666	3.14797	-2.09954
C	-0.11712	3.22222	0.05050
H	-1.20530	3.13179	0.09881
O	-2.26493	-1.88532	2.22586
O	-2.29310	-1.96512	-1.99289
O	1.55340	-2.55709	1.96231
C	-1.85111	-1.21560	1.38236
O	4.01684	0.81579	0.04394
O	1.75335	-2.31680	-2.23664
C	1.45176	-1.72027	1.17143
C	-1.88103	-1.25961	-1.18183
C	1.58996	-1.57711	-1.36607
C	2.94970	0.37639	-0.00078
H	0.09877	4.30011	0.04331
H	-2.76556	1.70715	0.94888
O	-3.79324	0.93194	-0.56895

4S

Atom	x	y	z
Fe	-0.65283	1.32768	0.00157
Fe	-1.43321	-1.13066	0.04211
S	0.56045	-0.39515	0.99302
S	6.14122	-0.11755	0.12604
C	-0.81998	-0.00162	-1.44588
C	-1.07245	1.93898	1.66452
C	0.69200	2.27633	-0.65155
C	-1.95812	2.24044	-0.77078
C	-2.12453	-1.30756	1.71765
C	-0.85713	-2.70432	-0.52559
C	-3.02386	-1.18019	-0.73487
O	-1.31815	2.36255	2.70876
O	1.54575	2.92875	-1.07583
O	-2.80910	2.82144	-1.29177
O	-2.56363	-1.45957	2.77357
O	-0.50176	-3.74502	-0.88298
O	-4.05204	-1.20562	-1.25926
O	-0.68952	-0.06090	-2.62430
C	1.99188	-0.91028	-0.06639
C	3.31121	-0.29244	0.40108
C	4.50502	-0.78178	-0.42968
H	1.77318	-0.65452	-1.10347
H	2.03773	-2.00005	0.00495
H	3.48291	-0.54259	1.45429
H	3.25839	0.79926	0.34476
H	4.34215	-0.50856	-1.47788
H	4.53282	-1.87764	-0.39630
H	6.82642	-0.93351	0.39613

4P

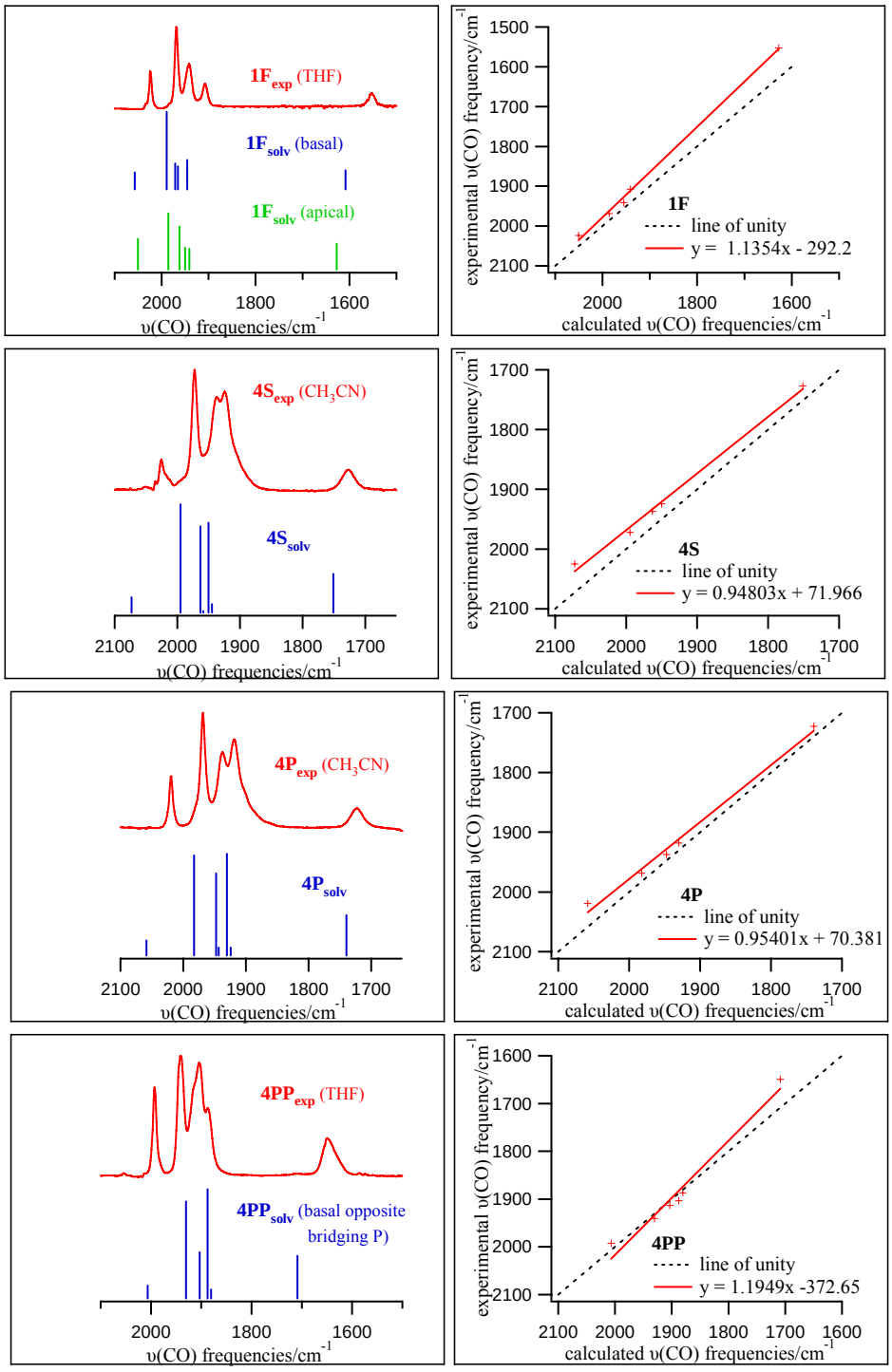
Atom	x	y	z
Fe	1.32729	0.22845	0.04241
Fe	-1.32691	0.22785	0.04125
P	0.00056	-1.57706	-0.15172
O	2.13984	3.03200	0.37530
O	2.13654	-0.54125	2.78060
O	3.41109	-0.66823	-1.79425

O	-2.14193	3.03030	0.37745
O	-2.14156	-0.54329	2.77742
O	-3.40829	-0.66748	-1.79876
O	0.00082	1.45203	-2.31752
C	1.81812	1.92967	0.25466
C	1.79662	-0.23781	1.71792
C	2.57232	-0.31274	-1.07790
C	-1.81887	1.92857	0.25509
C	-1.79934	-0.23956	1.71557
C	-2.57052	-0.31264	-1.08094
C	0.00054	0.87871	-1.27758
C	0.00174	-2.52685	-1.73725
H	-0.88551	-3.16228	-1.80592
H	0.88929	-3.16201	-1.80473
H	0.00222	-1.83731	-2.58185
C	0.00005	-2.95359	1.08000
H	-0.00063	-2.56141	2.09662
H	0.88652	-3.57990	0.94906
H	-0.88609	-3.58014	0.94797

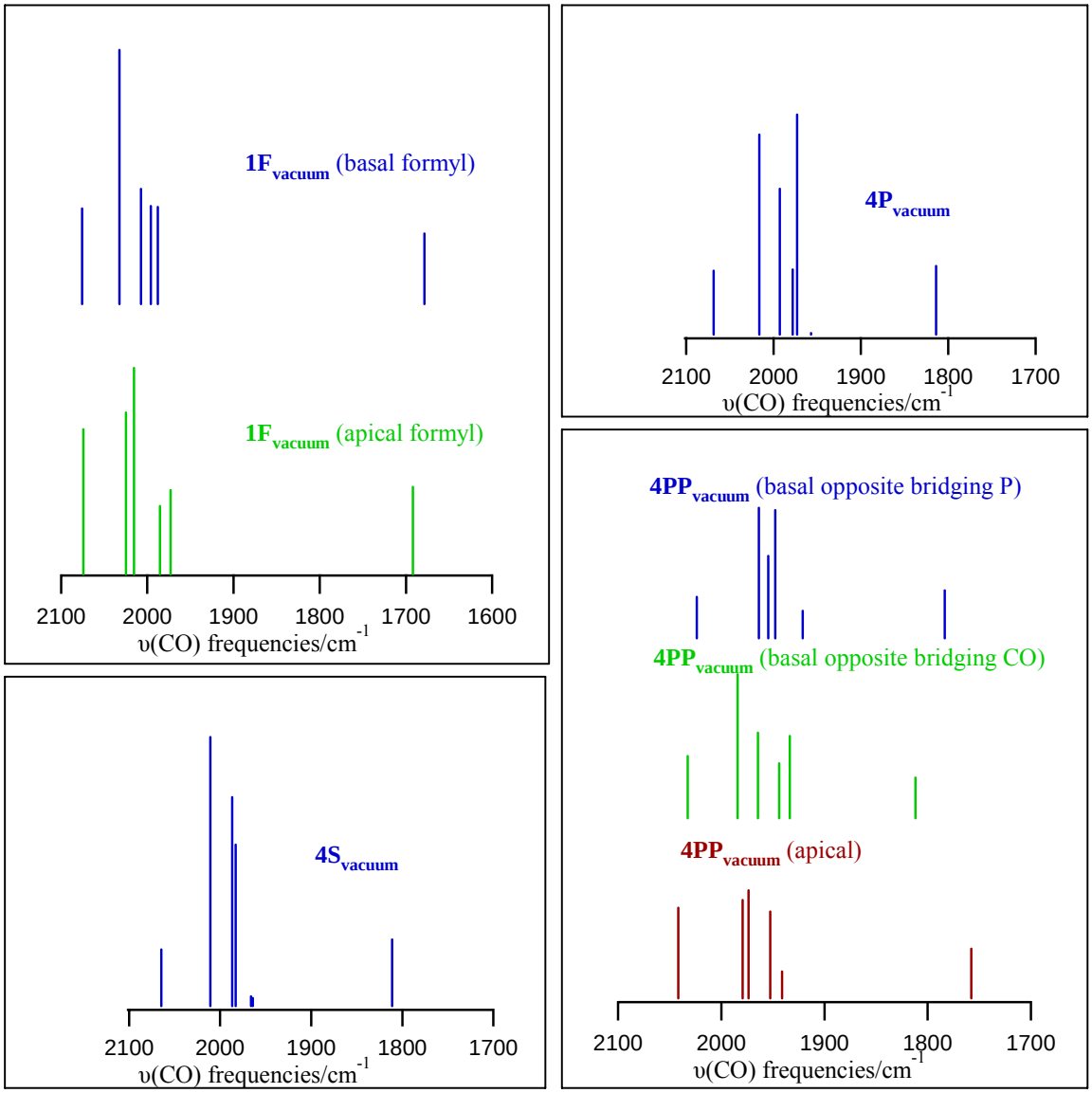
4PP (terminal P basal opposite bridging P)

Atom	x	y	z
Fe	0.91890	-0.54977	-0.07534
O	0.03976	0.72457	-2.58900
O	1.58937	-0.85788	2.78740
C	-0.02615	0.36793	-1.45375
C	1.31499	-0.71599	1.66703
Fe	-1.46675	0.68057	0.00861
P	-1.06621	-1.52158	0.19270
P	2.58134	0.92501	-0.35088
C	1.66057	-1.84566	-0.97408
C	-1.87174	0.82635	1.74146
C	-1.17803	2.41352	-0.22164
C	-2.89641	0.50289	-0.99024
C	-1.69620	-2.65375	-1.12856
C	4.29352	0.32866	0.00342
O	2.14238	-2.73790	-1.54983
O	-0.99822	3.54715	-0.39232
O	-3.87735	0.40936	-1.61128
C	2.54072	2.53048	0.56047
H	2.76044	1.40198	-1.67489
C	-1.49385	-2.49687	1.70501
H	-0.99001	-3.46750	1.69186
H	-2.57251	-2.67060	1.75503
H	-1.18840	-1.95955	2.60262
H	-2.77208	-2.81822	-1.01960
H	-1.19027	-3.62246	-1.08381
H	-1.51016	-2.20937	-2.10691
H	2.53695	2.33368	1.63475
H	1.62485	3.06821	0.31479
H	3.40240	3.15669	0.31610
H	5.04160	1.09783	-0.20153
H	4.50960	-0.54965	-0.60720
H	4.36707	0.03530	1.05284
O	-2.19427	0.94048	2.85241

4. Observed and calculated (B3LYP/6-311+G(d) and C-PCM continuum solvation) IR spectra in the ν(CO) region.

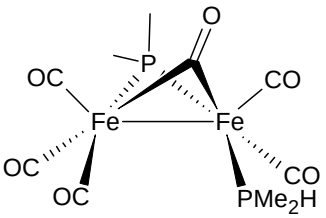


5. Observed and calculated (B3LYP/LanL2DZdp in vacuum phase) IR spectra in the ν(CO) region.

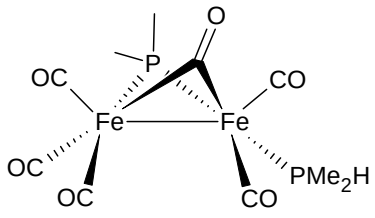


6. DFT calculated energies of the isomers of **4PP** and **1F**.

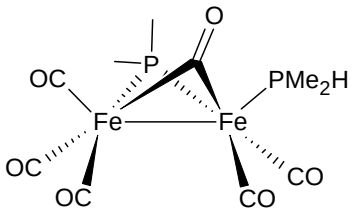
Calculated isomers of **4PP** in vacuum phase and relative energies



4PP (basal opposite bridging P)
0 kcal/mol

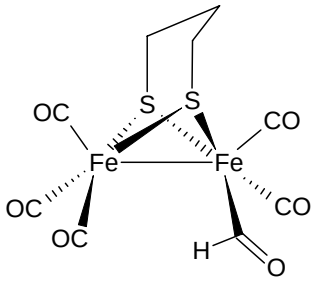


4PP (basal opposite bridging CO)
1.920 kcal/mol

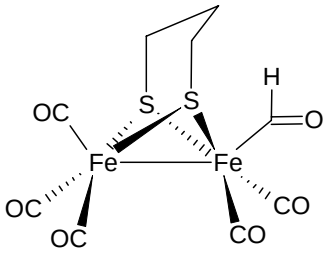


4PP (apical)
3.851 kcal/mol

Calculated isomers of **1F** in vacuum phase and continuum solvation model. Relative energies and relative free energies in solution given in brackets



1F (basal)
0 kcal/mol
(0 kcal/mol)



1F (apical)
1.126 kcal/mol
(2.385 kcal/mol)