Supporting Materials

Energy calibration issues in nuclear resonant vibrational spectroscopy: observing small spectral shifts and making fast calibrations

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S1 [Fe₄S₄Cl₄](Ph4P)₂ Sample Preparation

10%-^{57}Fe / 90%-^{54}Fe labeled [Fe₄S₄Cl₄](Ph4P)₂ samples was prepared by literature methods. Briefly metallic powder of 95 mg ^{54}Fe and 5 mg ^{57}Fe was weighted, mixed and reacted with HCl in methanol to prepare ^{57}Fe/^{54}Fe mix-labeled [Fe(MeOH)$_x$]Cl₂ as white crystals. Although the 5%-^{57}Fe / 95%-^{54}Fe were used in the initial reactants, the isotopic analysis for the final products were 10%-^{57}Fe / 90%-^{54}Fe, so we define it as 10%-^{57}Fe / 90%-^{54}Fe labeled [Fe₄S₄Cl₄](Ph4P)₂. The crystals were heated at 180 $^{\circ}$C in vacuo for several hours to a constant weight. A Schlenk flask was prepared with a mixture of anhydrous ^{57}Fe/^{54}Fe mix-labeled FeCl₂ (65 mg, 0.51 mmol), KSPh (112 mg, 0.76 mmol), (PPh₄)Cl (95 mg, 0.25 mmol), and elemental sulfur (20 mg, 0.63 mmol). Acetonitrile (5 mL) was then added with continuous stirring. After 45 min, the solution was filtered to remove KCl and the un-reacted sulfur, and to crystallize from ether. After several days, the solution exhibited deposition of a black crystalline solid. The product, 55 mg of ^{57}Fe/^{54}Fe mix-labeled (PPh₄)₂[Fe₄S₄Cl₄], was isolated by filtration, washed twice with ether, and dried in vacuo. Isotope analysis of ^{54}Fe and ^{57}Fe was done in plasma mass spectrometry in UC Davis Interdisciplinary Center and final ratio of ^{57}Fe vs ^{54}Fe in (PPh₄)₂[Fe₄S₄Cl₄] is 1:9 although the initial ^{57}Fe vs ^{54}Fe ratio is 5:95. Pure (Ph₄P)₂(^{57}Fe₄S₄Cl₄) was prepared in a similar way.

S2 Energy Shift Estimation: [Fe₄S₄Cl₄](Ph4P)₂

A simple estimation assuming a single diatomic Fe-S stretching predicted a 1% (0.477 meV or 3.85 cm^{-1}) shifts between ^{57}Fe-^{32}S and ^{54}Fe-^{32}S stretching peaks. The isotopic shift in Fe4S4 was estimated as 3.85 cm-1 adjusted with the ^{57}Fe/^{54}Fe ratio.

Assuming x ^{54}Fe and y ^{57}Fe (note: (x+y)=1)are inside the final products, then the ^{54}Fe/^{57}Fe labeled for iron sites inside the [Fe₄S₄Cl₄](Ph4P)₂ can have the following five combinations and

their probabilities are listed as in Table S1. The isotope analysis indicate a 1:9 (also consistent

with total NRVS cts/s of a 250:2350). If y is small (10%) and x is large (90%), most samples will

be at 1, 2, and 3 while 1 has no NRVS signal. Therefore most NRVS signal will come from 2

and 3 with a signal ratio of 3:1, means 25% NRVS signal is from a 2-^{57}Fe, and ~ 75% is from 1-

^{57}Fe. With a simple estimation, the energy shift between the fully enriched and (x vs. y) partially

enriched $(PPh_4)_2[Fe_4S_4Cl_4]$ could be (3*2.89+1*1.96)/4=2.65 cm-1 or 0.329 meV.

Table S1　Five combinations and their corresponding probabilities for the ^{54}Fe and y ^{57}Fe

labeled $[Fe_4S_4Cl_4](Ph4P)_2$

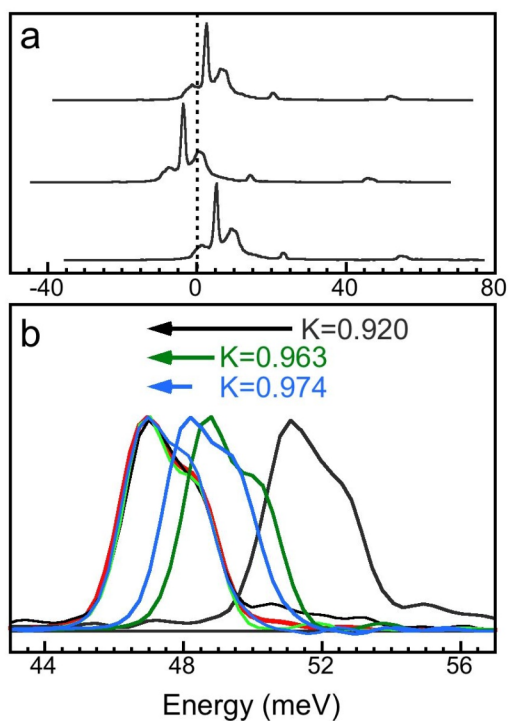| Combination	^{54}Fe	^{57}Fe	Amount	NRVS $\propto$	NRVS (x=0.1)	NRVS Ratio	Shifts * (cm^{-1})
1	4	0	x^4	0	0	0	3.85
2	3	1	$4x^3y$	$4x^3y$	0.292	3	2.89
3	2	2	$6x^2y^2$	$12x^2y^2$	0.096	1	1.93
4	1	3	$4xy^3$	$12xy^3$	0.011	0.33	0.96
5	0	4	y^4	$4y^4$	-	-	0

S3 Additional Figures

Figure S1

A conventional energy calibration procedure: (a) aligning spectral resonance peaks to E=0; (b) scaling the 47.0 meV peaks in $[Et_4N][^{57}FeCl_4]$ to match the published spectrum (thick red line). The energy scale factors (K) were thus obtained.
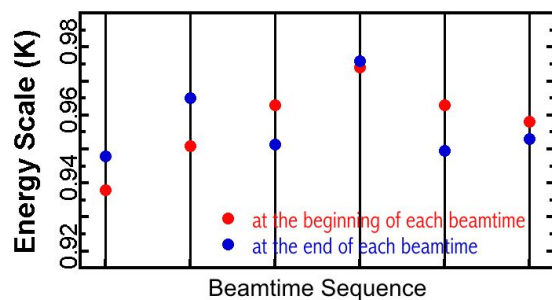

Figure S2

Energy scales (K values) obtained with $[Et_4N][FeCl_4]$ using conventional calibration procedures at the beginning (red) and the end (blue) of several beamtimes.