Inelastic X-Ray Scattering (IXS) of a Transition Metal Complex $(FeCl_4)^-$ – A Vibrational Spectroscopy for All Normal Modes

Hongxin Wang&,‡ Weibing Dong,&,† Marilyn M. Olmstead,& James C. Fettinger,& Jay Nix,‡ Hiroshi Uchiyama,¥ Satoshi Tsutsui,¥ Alfred Q. R. Baron,¥, § and Stephen P. Cramer *,&,‡.
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Department of Chemistry, University of California, Davis, CA 95616
‡
Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
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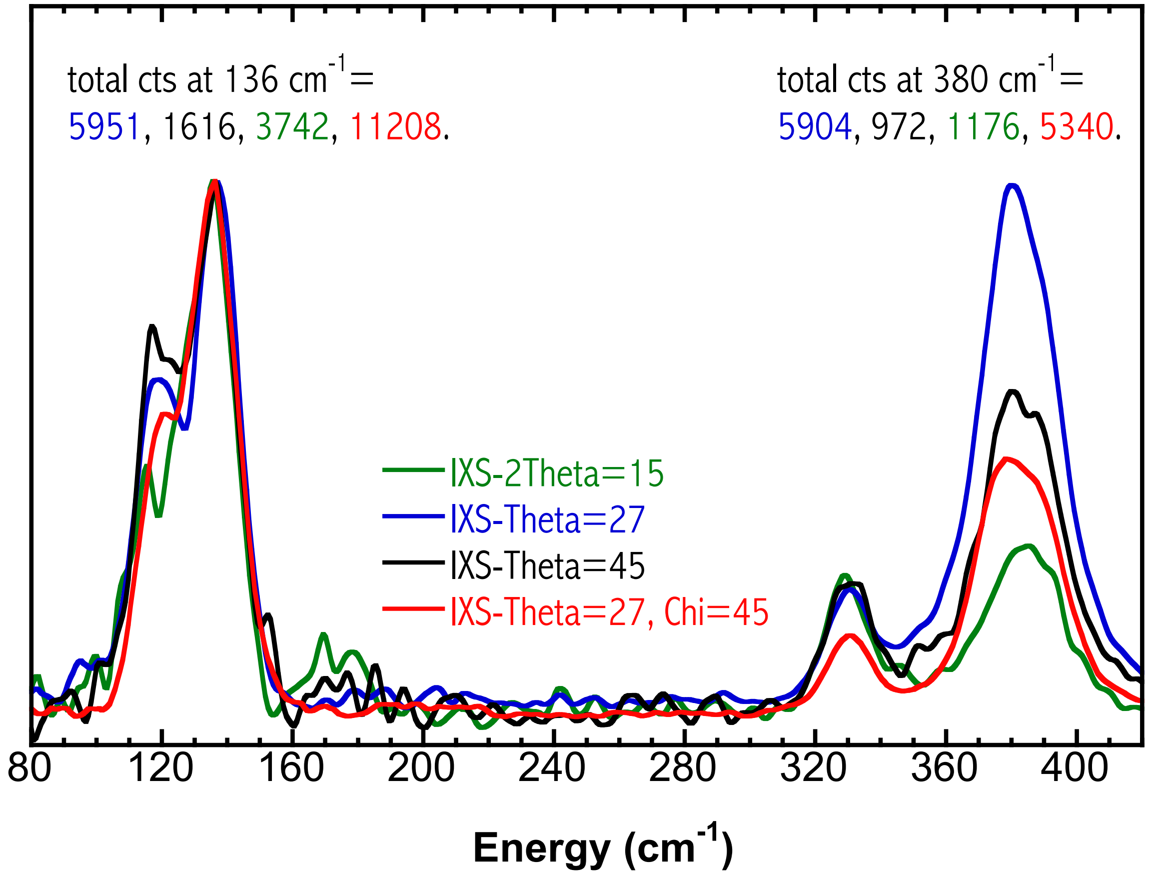
Department of Biochemistry & Molecular Biology, Pennsylvania State University, University Park, PA 16802
¥
Research and Utilization Division, SPring-8/JASRI, 1-1-1 Kouto, Sayo, Hyogo 679-5198, JAPAN
§
Materials Dynamics Laboratory, RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo, Hyogo 679-5148, JAPAN

Supporting Information

Preparation of $(NEt_4)(FeCl_4)$. A stoichiometric quantity of NEt_4Cl in 5mL of ethanol was added to a solution containing 5 mmol (0.81g) of $FeCl_3$ in 5mL of absolute ethanol. Upon mixing and stirring for 1 hour, an amorphous precipitate of $(NEt_4)(FeCl_4)$ appeared. In this experiment, 1.25 g of $(NEt_4)(FeCl_4)$ in the form of yellow powder was isolated after filtration of the amorphous precipitate. The powders were re-crystallized from a tetrahydrofuran (THF) solution at ambient temperature. After 5 days of re-crystallization, greenish-yellow colored crystals of various sizes were obtained**.** For this particular experiment, a hexagonal pyramid crystal of ~ 4 mm x 4 mm (base dimensions) x 5 mm height was selected for IXS measurement.

IXS Measurements. IXS spectra were recorded on a $(NEt_4)(FeCl_4)$ single crystal using standard procedures at the SPring-8 high-resolution IXS beamline, BL35-XU [1] [2]. The photon flux on the sample was $\sim 10^{10}$ photons/sec in a 0.8 meV bandwidth at 21.75 keV with a spot size of ~0.1 mm diameter (FWHM) from a backscattering (89.8°) Si(11 11 11) monochromator. The scattered radiation was collected by a 2-dimensional array of 12 analyzer crystals. Each analyzer has an independent detector, allowing 12 spectra to be collected simultaneously, and the over-all (analyzer plus monchromator) energy resolution was 1.5 to 1.8 meV (different analyzers behaved differently). The energy scale was determined as discussed in [13] (?) and is expected to be accurate to better then 0.5%. The Q resolution was 0.48 nm^{-1}, where $Q = 4\pi / \lambda \sin\theta$, 2θ is the scattering angle and λ is the wavelength of x-rays. During the IXS measurements, the sample crystal was maintained at ~27K using a closed cycle He cryostat. The inelastically scattered radiation from each of the 12 analyzers was recorded with a separate CdZnTe detector. For $(NEt_4)(FeCl_4)$, the typical total signal count rate on the 380 cm^{-1} peak was ~0.2-0.9 cps.

The actual counts in each spectrum are shown below.



IXS Data Analysis and Normal Mode Calculations. The IXS signal was extracted from the raw averaged spectra by subtracting a combination of Lorentzian and Gaussian background lineshape functions. No smoothing was used for any of the spectra. Normal mode calculations were done using a modification of the program Vibratz [3] and a Urey-Bradley force field [4]. The parameters for this force field determine the potential energy V as previously described [5]. The Vibratz program was used to calculate the relevant phonon polarization eigenvectors (complex phonon polarization) including the Fe and Cl motion in a given normal mode from the normal mode eigenvectors. The calculations used the Evans *et al.*, *Acta Cryst*. 46, 1818 (1990) CSD structure file TABPIV, with a slightly larger force constant for the shorter Fe-Cl bond. To simulate the IXS, Gaussian components were generated at the calculated frequencies, with an amplitude determined by the relative dynamic structure for a particular normal mode and scattering geometry and a FWHM determined by the 14 cm^{-1} instrumental resolution. We note that there are no adjustable scale factors in these simulations.

X-Ray Crystallography. The tetrahedral $[FeCl_4]^-$ ion was chosen for its extremely simple set of well-studied normal modes , as well as the straightforward arrangement of the $(FeCl_4)^-$ ions in the crystal with $(NEt_4)^+$ counterions . An additional complication discovered *ex post facto* is that, with flash cooling, NEt_4FeCl_4 undergoes a first order phase transition at ~229 K that changes the space group from *P6₃mc*(Phase I) to *P*31*c* (Phase III). In Phase I there is one Fe in the asymmetric unit and the Fe resides on a site with crystallographic 3m symmetry. In Phase III there are five Fe's in the asymmetric unit, two of which have no crystallographic symmetry and three of which have 3-fold symmetry. As a consequence of the low temperature phase, the structure is not as simple, although the structure bears the same relationship with respect to the *c* axis as in the room temperature phase. The most noticable change is that two of the $(FeCl_4)^-$ units are tipped by 6.7° and 8.0°, respectively, with respect to *c*. With slow cooling, an intermediate phase is observed (Phase II) both Phase II and Phase III show less disorder in the $(NEt_4)^+$ group than in Phase I.

Table S1. Crystal data for three phases of $(NEt_4)(FeCl_4)$

	Phase I$^{\text{ref [1]}}$	Phase II$^{\text{slow cooling}}$	Phase III$^{\text{flash cooling}}$
Crystal system	hexagonal	orthorhombic	trigonal
Space group	$P6_3mc$ (No. 186)	$Pca2_1$ (No. 29)	$P31c$ (No. 159)
a, Å	8.198(1)	13.9690(3)	24.3337(9)
b, Å		8.1116(3)	
c, Å	13.183(3)	12.7889(5)	12.8909(5)
V, Å^3	767.3(2)	1449.12(10)	6610.4(6)
Z	2	4	18
T, K	295(2)	90(2)	90(2)
		3 component twin	inversion twin
R_1 $[I > 2\sigma(I)]$	0.053	0.015	0.031

Fe cryst symm, tilt to *c* axis, °			
Fe1	3m· (C_{3v}), 0	1 (*C1*), 4.0	1 (*C1*), 6.7
Fe2			1 (*C1*), 8.0
Fe3			3 (*C3*), 0
Fe4			3 (*C3*), 0
Fe5			3 (*C3*), 0

[1] Warnke, Z.; Styczeń, E.; Wyrzykowski, D.; Sikorski, A.; Kłak, J.; Mroziński, J. *Struct. Chem.* 2010, 21, 285-289.

1. Baron, A. Q. R., Phonons in Crystals using Inelastic X-Ray Scattering. *Journal of the Spectroscopical Society of Japan* **2009,** 58, (5), 205-214 (Japanese) arXiv 0910.5764 (English).
2. Baron, A. Q. R.; Tanaka, Y.; Goto, S.; Takeshita, K.; Matsushita, T.; Ishikawa, T., An X-ray scattering beamline for studying dynamics. *Journal of Physics and Chemistry of Solids* **2000,** 61, 461-465.
3. Dowty, E., Vibrational interactions of tetrahedra in silicate glasses and crystals: 2. Calculations on melilites, pyroxenes, silica polymorphs and feldspars. *Physics and Chemistry of Minerals* **1987,** 14, 122-138.
4. Simanouti, T., The Normal Vibrations of Polyatomic Molecules as Treated by Urey-Bradley Field. *Journal of Chemical Physics* **1949,** 17, (3), 245-248.
5. Smith, M. C.; Xiao, Y.; Wang, H.; George, S. J.; Coucovanis, D.; Koutmos, M.; Sturhahn, W.; Alp, E. E.; Zhao, J.; Cramer, S. P., Normal Mode Analysis of $[FeCl_4]^-$ and $[Fe_2S_2Cl_4]^{2-}$ *via* Vibrational Mössbauer, Resonance Raman, and FT-IR Spectroscopy. *Inorganic Chemistry* **2005,** 44, (16), 5562-5570.