Vibrational dynamics of a trinuclear oxo–bridged iron complex as studied by nuclear inelastic scattering, Mössbauer spectroscopy and DFT calculations

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Abstract. We have applied nuclear inelastic scattering (NIS) and computational predictions based on density functional theory (DFT) to explore the vibrational dynamics of $^{57}$Fe in a trinuclear oxo-bridged iron(III) complex. Quantitative comparison of the experimentally measured vibrational dynamics of the Mössbauer nuclei $^{57}$Fe, with normal mode analysis, calculated via quantum chemical calculation based on DFT methods generally yields a good overall agreement and enables the assignment of Fe vibrational modes. The oxidation and spin state of the complex were determined by $^{57}$Fe Mössbauer spectroscopy.

1. Introduction

There is a continuous interest in the search for selective metal complexes which serve as catalysts for the oxygenation of unactivated hydrocarbon substrates via polynuclear non-heme iron catalysts. The understanding on how such activation reactions work relies on the vibrational dynamics of the metal centre in the catalysts. Vibrational spectroscopy provides a sharp and clear probe of the structure, dynamics and reactivity of biological molecules. Identifying the active metal–site vibrations and relating them to the functional dynamics is of particular interest in enzymes. So far the published works by several authors were conducted on the vibrational properties of iron heme porphyrins [1] and non-heme Fe-S hydrogenase [2]. Recently, the mechanisms governing the spin crossover in Fe compounds were also reported in detail [3]. In this work, we report the first information about the vibrational dynamics of a trinuclear oxo-bridged iron complex (figure 1), investigated by NIS and DFT methods. The inhomogeneity of the iron coordination is determined by Mössbauer spectroscopy.

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2. Experiment

The trinuclear complex is prepared by the reaction of the deprotonated ligand 1 with iron(III) perchlorate (figure 1). On precipitation, the complex crystallizes out as red crystals [4]. An $^{57}$Fe transmission Mössbauer spectrum was measured at room temperature (RT) using a conventional constant–acceleration spectrometer equipped with a gas proportional counter and a $^{57}$Co/Rh source with a strength of 50 mCi. The resolution of the spectrometer was $\sim 0.24 \text{ mm s}^{-1}$ (full–width at half–maximum of the inner lines when measured with a $\alpha$–Fe foil at RT). The experimental data were fitted to Lorentzian profiles by the least–squares method, and the isomer shift is relative to the centroid (= zero mm s$^{-1}$) of the $\alpha$–Fe foil spectrum at RT. NIS is a new synchrotron based spectroscopic technique, which is used in the present work to study the vibrational dynamics of the Mössbauer nuclei, $^{57}$Fe. The method obeys very simple selection rules, as it senses only the $^{57}$Fe vibrational motion and thus measures the complete vibrational density of states (VDOS) for the Fe atoms including the mean square displacement (msd) of the Fe atom. The NIS experiments [5] were carried out at the nuclear resonance beamline ID18 of the European Synchrotron Radiation Facilities (ESRF) in Grenoble, with an energy bandwidth of 1.1 meV. Details of NIS theory, experimental procedure and data processing are described elsewhere [6, 7]. The unenriched crystalline sample is scanned at 3 s per point with a total of 36 scans (500 points per scan). In order to minimize the multiphonon contributions measurements were performed at 26.5 K (obtained from the ratio of anti-Stokes to Stokes intensities).

3. Computational details

The geometry optimizations and subsequent vibrational frequency calculations were carried out using the DFT B3LYP hybrid exchange correlation functional [8], as implemented in the GAUSSIAN03 program [9]. A correlation consistent polarized valence double–ζ basis set has been used for all atoms except Fe [10]. For the metal Fe atoms the 10 core electron wavefunctions was replaced by the scalar relativistic Stuttgart/Dresden effective core potential, which was combined with the corresponding basis set for the Fe valence shells as described in reference [11]. DFT calculations were performed on the complete structure including all the H atoms, thus in total 119 ($= N$) atoms. In the calculation, the spin state of each Fe atom was taken as 5/2 with a total multiplicity of the cluster of 16. The VDOS is extracted from the DFT calculated normal coordinates of all modes assuming the low temperature approximation according to [12]

$$g(E) = \frac{1}{3} \sum_{j=1}^{3N-6} \frac{m_{Fe}u_{Fe,j}^2}{\sum_{k=1}^{N} m_ku_{k,j}^2} \delta(E - E_j),$$

where $m_{Fe}$ (56.94 a.u.) is the mass of the resonant atom (Mössbauer nuclei), $u_{Fe,j}^2$ and $u_{k,j}^2$ are the msd of the Fe and $k^{th}$ atom, respectively, in the $j^{th}$ mode, $E$ is the difference between the incoming photon energy and the recoil–free resonance energy, and $E_j$ is the energy of the molecular vibration. The term $\delta(E - E_j)$ is a normalized Gaussian line shape function, which includes a width equal to 1.1 meV.

Figure 1. Formation and structure of the trinuclear oxo–bridged Fe complex.
4. Results and discussion
The core structure can be well described as a central planar Fe$_3$O unit with three planar FeO$_4$ units perpendicular to the Fe–O–bonds of the Fe$_3$O (figure 1). Each unit of the Fe atoms is coordinated octahedrally by six O atoms, four of them are provided by the carboxylic acid groups of the ligand, the fifth O is the common central ion of the Fe$_3$O unit. For two of the Fe centers the sixth O is also provided by carboxylic ligand groups, but for the third Fe the sixth position is occupied by a H$_2$O molecule. This renders one of the three Fe centers slightly different from the other two. The Mössbauer spectrum of the complex at RT shown in figure 2 consists of an asymmetric broadened quadrupole doublet indicating the existence of two quadrupole doublets. While the doublet structure is in agreement with the expectation for inequivalent Fe sites and the isomer shift is typical for Fe$^{3+}$ the asymmetry is an immediate consequence of the inequivalence of the three Fe centers. Initial attempts to fit with two quadrupole doublets with isomer shift $\delta$, quadrupole splitting $\Delta E_Q$, line width $\Gamma$ and area ratios as free variables gave an area ratio far from the theoretically expected value of 2:1 [13]. Hence we fixed the area ratio as 2:1 (area ratio of inner doublet to outer doublet). A good fit is shown in figure 2 with values: inner doublet $\delta = (0.40 \pm 0.01)$ mm s$^{-1}$, $\Delta E_Q = (0.58 \pm 0.01)$ mm s$^{-1}$ and $\Gamma = (0.37 \pm 0.03)$ mm s$^{-1}$; outer doublet $\delta = (0.43 \pm 0.01)$ mm s$^{-1}$, $\Delta E_Q = (0.96 \pm 0.01)$ mm s$^{-1}$ and $\Gamma = (0.25 \pm 0.03)$ mm s$^{-1}$. The outer doublet, which has the large $\Delta E_Q$ and lower weight by area is attributed to the single Fe, which is coordinated to a H$_2$O molecule. The other two Fe sites, which are equivalent by coordination, can then be collectively attributed to inner doublet with large area. It should be noted that Mössbauer is a local probe technique which provides information about the spin state of the individual Fe centers, while magnetization and EPR measurements as reported by Rabe et al. [4] provides the spin state of the coupled Fe$_3$O cluster, and this was reported to have a spin 1/2 doublet ground state.

The experimental together with the DFT predicted VDOS of the trinuclear iron complex is shown in figure 2. In overall the DFT simulated spectrum for the $S = 15/2$ state is in agreement with the measured one. The calculation of the same structure for the $S = 1/2$ ground state yielded a completely different spectrum (not shown) and suffers from spin contamination. This discrepancy has to be further investigated. The acoustic modes in the spectrum extends up to $\sim 100$ cm$^{-1}$, which was estimated by the procedure prescribed by Chumakov et al. [14]. In this region, the calculated spectrum exhibits less than the measured number of peaks. This is because the calculation has been performed for a free single molecule. The Fe–O vibrations i.e. the skeletal modes comprising of the central FeO$_3$ unit, are generally present in the low frequency region, typically $< 700$ cm$^{-1}$. The measured and simulated VDOS displays a dominant peak at...
about 210 cm$^{-1}$ and a number of weaker peaks above 250 cm$^{-1}$. In a local $D_{3h}$ symmetry the central metal Fe$_3$O unit has six fundamental modes of vibration: $\nu_3$ and $\nu_2$ being nondegenerate while $\nu_1$ and $\nu_4$ are doubly degenerate [15]. By direct comparison of NIS with theory the stretching mode $\nu_3$ can be assigned to the peak at 244 cm$^{-1}$. Since this mode is Raman active we clarified by Raman analysis, where it appears at 245 cm$^{-1}$ (not shown). This is in contrast to the previously reported value of 148 cm$^{-1}$ [16]. One possible reason may a different spin state with larger force constant in our complex so that excitation of the stretching mode $\nu_3$ occurs at higher frequency, as the larger ligand mass would tend to the opposite effect. In the experimental spectrum we notice a broad dominant peak around 210 cm$^{-1}$. Since this peak is broad and intense, one may expect that it may be coupled with two or more unresolved modes. The complex has three planar FeO$_4$ units, $D_{3h}$ symmetry sites perpendicular to the Fe–O–bonds of the Fe$_3$O unit. Johnson et al. observed the O–Fe–O bending vibration $E_u$ of the planar FeO$_4$ units at 200 cm$^{-1}$ [16]. A similar feature is observed in our spectrum at 202 cm$^{-1}$ in the experimental as well as calculated VDOS and thus this mode should be assigned to the in-plane bend $E_u$ mode. On considering $D_{3h}$ symmetry of the Fe$_3$O unit interacting under the $D_{3h}$ symmetry of three FeO$_4$ units, the $E_u$ mode of the $D_{3h}$ symmetry leads to a rotational symmetry $A'_2$ of the Fe$_3$O unit. Thus $E_u$ as well as $A'_2$ contribute to the VDOS at 200 cm$^{-1}$.

5. Conclusion
The Mössbauer results show that the Fe$_3$O complex, which based on other methods was reported to have a spin doublet ground state, consists of high–spin Fe$^{3+}$ ions with two different inequivalent Fe sites. The vibrational dynamics obtained by NIS and DFT calculations are presented. Some of the vibrational modes of the central metal unit that are potentially important in the functional dynamics of the catalyst are assigned.

Acknowledgments
We thank Drs. A.I. Chumakov, I. Sergeev and R. Rüffer of ID 18 at ESRF for the assistance with NIS experiments. Financial support for this work by the Deutsche Forschungsgemeinschaft within the framework of SFB 706 and the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden–Württemberg is gratefully acknowledged.

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