Dynamics of metal centers monitored by nuclear inelastic scattering

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Abstract Nuclear inelastic scattering of synchrotron radiation has been used now since 10 years as a tool for vibrational spectroscopy. This method has turned out especially useful in case of large molecules that contain a Mössbauer active metal center. Recent applications to iron–sulfur proteins, to iron(II) spin crossover complexes and to tin-DNA complexes are discussed. Special emphasis is given to the combination of nuclear inelastic scattering and density functional calculations.

Key words nuclear inelastic scattering · vibrational spectroscopy · iron–sulfur proteins · spin crossover complexes · density functional theory calculations
Abbreviations

NIS  nuclear inelastic scattering  
SCO  spin crossover  
DFT  density functional theory  
EXAFS  extended X-ray absorption fine structure  
msd  mean square displacement  
HS  high-spin  
LS  low-spin

1 Introduction

Nuclear inelastic scattering (NIS) of synchrotron radiation (also known as nuclear resonant vibrational spectroscopy, NRVS) can be regarded as an extension of the conventional, energy-resolved Mössbauer spectroscopy to energies of the order of molecular vibrations [1, 2]. NIS has similarity with resonance Raman spectroscopy: the energy of monochromatized synchrotron radiation is detuned from nuclear resonance by a certain amount of energy (several meV) that is sufficient to create or annihilate a phonon, or in terms of molecular spectroscopy, to excite or deexcite a molecular vibration. While the Raman intensity for a given molecular vibration depends on the change of polarizability with respect to the motion of the nuclei, the NIS intensity depends on the contribution of this particular vibration to the mean-square displacement (msd) of the Mössbauer nucleus. NIS is, therefore, a highly site-selective tool and it is as vibrational spectroscopy complementary to Raman or IR spectroscopy. The interpretation of measured NIS spectra is greatly facilitated due to the fact that the NIS intensity depends only on mechanical and not on electric properties of the investigated molecules. For example, iron-ligand bond stretching vibrations of an iron-containing molecule are normally easy to identify because of their relatively large contribution to the msd. The dependence on purely mechanical properties also facilitates the simulation of measured NIS spectra with the help of quantum chemical calculations, which are usually based on density functional theory (DFT). The calculation of IR or Raman intensities, which depend on electric properties like changes of dipole moment or polarizability tensor, is far less accurate. A quantitative analysis of this fact with the example of the ferrocene complex is given in Section 2.

The comparison of experimental and simulated spectra provides the possibility to assign peaks in the measured NIS spectrum with calculated normal modes of the molecule under study. This procedure has been applied first to small and medium-sized metal complexes (up to 100 atoms) [3, 4] but is now applied also to larger biological molecules like rubredoxin [5] or DNA with chelated metal ions [6] (in the latter two cases DFT calculations are restricted to a cluster of about 100 atoms around the iron center). First applications of NIS to problems of biological relevance were related to model hemes like tetraphenylporphyrins [7, 8] and to heme-based proteins like myoglobin [7–9] (see also references in [10]). Recently NIS measurements have been performed on model complexes of iron–sulfur proteins [11], on a rubredoxin-type iron–sulfur protein in the reduced and in the oxidized state [5], and on Benzoyl-CoA reductase [5], which contains [4Fe–4S]^{2+} centers. The NIS