

Review

Mössbauer studies of coordination compounds using synchrotron radiation

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Abstract

Nuclear resonant forward scattering (NFS) and nuclear inelastic scattering (NIS) of synchrotron radiation are fairly recent spectroscopic methods for the investigation of complexes containing Mössbauer-active transition metal ions. NFS, which can be regarded as Mössbauer spectroscopy in the time domain, overcomes some limitations of conventional Mössbauer spectroscopy as has been demonstrated especially for bioinorganic compounds. NIS extends the energy range of conventional Mössbauer spectroscopy to the range of molecular vibrations. Since NIS is sensitive only to the mean-square displacement of Mössbauer nuclei it can be used as site-selective vibrational

Abbreviations: APD, avalanche photo diode; bpp, 2,6-bis(pyrazol-3-yl)pyridine; DFT, density functional theory; efg, electric field gradient; EPR, electron paramagnetic resonance; HS, high spin; LS, low spin; MS_{1,2}, metastable states 1 and 2 of the nitroprusside anion; msd, mean-square displacement; NFS, nuclear resonant forward scattering; NIS, nuclear inelastic scattering; PDOS, partial phonon density of states; tpa, tris(2-pyridylmethyl)amine; tptMetame, 1,1,1-tris((N-(2-pyridylmethyl)-N-methylamino)methyl)ethane

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spectroscopy. It complements usefully comparable techniques such as IR or Raman spectroscopy. Examples are given for applications to spin crossover complexes, nitroprusside compounds, heme model complexes and myoglobin.

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1. Introduction

Mössbauer spectroscopy is based on the recoilless nuclear γ -resonance discovered by Mössbauer in 1958 [1]. A γ -quantum emitted by a Mössbauer nucleus can be absorbed in resonance by another nucleus of the same kind if the recoil energy of the absorbing nucleus is small compared to the linewidth of the nuclear transition ($\Gamma \sim 5 \times 10^{-9}$ eV for ^{57}Fe). This is the case if the recoil is transferred not to the absorbing nucleus alone ($E_{\text{R}} \sim 2$ meV) but to the embedding lattice as a whole ($E_{\text{R}} \sim 0$) and if the same holds for the emission of the γ -quantum. There is a finite probability for such a zero-phonon process that is given by the so called Lamb–Mössbauer factor f_{LM} . This factor increases with decreasing temperature. If the emitting and the absorbing nuclei do not have the same chemical environment, the nuclear resonance can be destroyed by small shifts of the nuclear energy levels due to hyperfine interactions between the Mössbauer nucleus and the surrounding nuclei and electrons and external fields. Such energy shifts can be detected by tuning the energy of the γ -quanta, and in this way valuable information can be obtained about the geometric and electronic structure of the molecule or crystal that hosts the Mössbauer nucleus.

In conventional Mössbauer spectroscopy a simple setup consists of a source, a detector for γ -quanta, and a sample that is mounted between source and detector (transmission geometry). The source, which can be moved with a tunable velocity of some millimeter per second, contains a radioactive precursor that decays to the excited state of the Mössbauer nucleus, which in turn relaxes into the ground state by emission of a γ -quantum (e.g. ^{57}Co decays to ^{57}Fe). Resonance can be observed if the velocity of the source is chosen in such a way that the Doppler shift of the γ -quantum compensates for the hyperfine interactions of the Mössbauer nucleus with its surroundings. As a consequence, a fraction of the γ -quanta emitted from the source are absorbed by the sample and the count rate of the detector decreases. In the last several decades, this method has developed into a powerful tool in solid-state physics and chemistry, including bioinorganic chemistry [2]. It has been applied to more than 80 so-called Mössbauer-active isotopes such as ^{40}K , ^{61}Ni , ^{67}Zn , and ^{57}Fe , to mention only those that are important in bioinorganic chemistry. From these ^{57}Fe is by far the most intensely investigated Mössbauer isotope. This is, among other reasons, due to the availability of a precursor (^{57}Co) with a lifetime (270 days) that is very suitable for most experimental purposes, and also due to, in most cases,

relatively high Lamb–Mössbauer factors, which mean short measurement times.

The resulting spectra can be used as fingerprints, or they can be rationalized by the spin-Hamiltonian formalism [3] (see also [4,5] for reviews). Within this formalism a variety of parameters that reflect the electronic structure of the molecule containing the Mössbauer nucleus are obtained by fitting a simulated spectrum to the experimental one. Among these parameters are the isomer shift (δ) which gives information about spin and oxidation state of the Mössbauer ion, and the quadrupole splitting, ΔE_{Q} , which describes (together with the asymmetry parameter η) the anisotropy of the electric field in the vicinity of the Mössbauer nucleus. If the Mössbauer ion is paramagnetic the degeneracy of its spin multiplet is usually lifted even in the absence of an external magnetic field, due to second-order spin–orbit coupling between different electronic states. The parameters that describe the splitting of the spin multiplet and the interactions between the electronic spin, the nuclear spin, and an external magnetic field in the framework of the spin-Hamiltonian formalism are the zero-field splitting D , the rhombicity E/D , the hyperfine tensor A and the tensor g [4,5]. These parameters which can be extracted from Mössbauer spectra reflect the character of the electronic ground state and the lowest excited states of the sample compound.

Mössbauer spectroscopy has become an indispensable tool in many fields of physics and chemistry, but there are limitations that cannot be overcome by the conventional technique, which can be regarded as Mössbauer spectroscopy in the energy domain. With the advent of third-generation synchrotron radiation sources the technique of nuclear resonant forward scattering (NFS) of synchrotron radiation has been developed [6–10] which can be regarded as Mössbauer spectroscopy in the time domain. Another related technique, nuclear inelastic scattering (NIS) of synchrotron radiation [11], can be regarded as an extension of the conventional, energy-resolved Mössbauer spectroscopy (in the range 10^{-9} to 10^{-7} eV) to energies of the order of molecular vibrations (in the range 10^{-3} to 10^{-1} eV).

The use of synchrotron radiation overcomes some of the limitations of the conventional technique. For instance, NFS allows the direct determination of the Lamb–Mössbauer factor (examples can be found in [12,13]). In addition, the high brilliance and the extremely collimated beam lead to a large flux of photons through the very small size of the sample (0.1 – 1 mm 2) that make it possible to measure extremely small samples of bioinorganic compounds or metalloproteins. Information about the anisotropy of a single crystal

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