

Installation of an IR microscope at the nuclear resonance beamline ID18 of ESRF

Sergej Rackwitz · Juliusz A. Wolny · Kai Muffler ·
Hans-Jörg Krüger · Sabine Reh · Harald Kelm ·
Alexander I. Chumakov · Volker Schünemann

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Abstract An IR microscope has been installed at the beamline ID18 at the ESRF in Grenoble, France in order to obtain nuclear inelastic scattering (NIS) data and IR spectra simultaneously. This setup combines the advantages of both spectroscopic methods. The applicability of the installed setup to the study of the spin crossover (SCO) phenomenon in polynuclear iron complexes has been shown.

Keywords Nuclear inelastic scattering · Density functional theory · Infrared spectroscopy · Spin crossover

1 Introduction

For the investigation of the vibrational properties of Mössbauer nuclei nuclear inelastic scattering (NIS), also called nuclear resonant vibrational spectroscopy (NRVS) has shown to be a powerful tool [1–3]. All vibrations with a contribution of a displacement of the Mössbauer nucleus parallel to the synchrotron beam can be detected. Due to the high brilliance of the synchrotron radiation of 3rd generation synchrotrons samples with micrometer dimensions can be used. The coupling of NIS with complementary techniques like IR- and Raman spectroscopy allows the assignment of the molecular modes, especially if the experimental data are compared

S. Rackwitz (✉) · J. A. Wolny · K. Muffler · V. Schünemann
Department of Physics, University of Kaiserslautern, Erwin-Schrödinger-Str. 46,
67663 Kaiserslautern, Germany
e-mail: rackwitz@physik.uni-kl.de

H. J. Krüger · S. Reh · H. Kelm
Department of Chemistry, University of Kaiserslautern, Erwin-Schrödinger-Str. 54,
67663 Kaiserslautern, Germany

A. I. Chumakov
ESRF, 38043 Grenoble Cedex, France

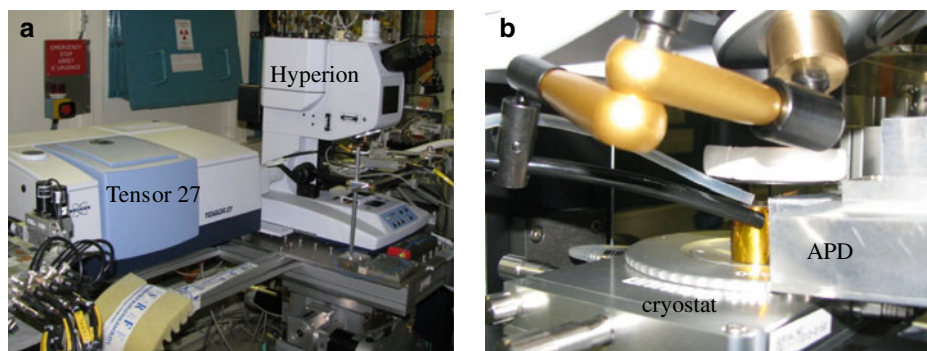


Fig. 1 **a** Installed setup of the IR microscope (Hyperion, Bruker AG) with the spectrometer (Tensor 27, Bruker AG) at ID18 of ESRF during beam time CH3079. **b** A closer look at the cryostat (Linkam station) and the avalanche photodiode (APD) for NIS detection. See also Fig. 2 for sample position within the cryostat

to simulations based on density functional theory (DFT) [4]. In this way a full understanding of the vibrational properties of the sample can be achieved. Here we report on the installation of an IR microscope at the beamline ID18 of the ESRF which enables combined NIS and Micro-IR investigations. The installation of a Raman microscope as a sample environment has been published in [5].

2 Materials and methods

The setup combines a Tensor 27 FTIR spectrometer and a confocal Hyperion microscope, both manufactured by Bruker AG. It allows taking IR data of sample areas down to $10 \times 10 \mu\text{m}^2$ within the region of 550 to 7500 cm^{-1} . The IR microscope was mounted on a self-constructed aluminum table (see Fig. 1a) which was fixed on a z stage (Huber 5103.2; $20 \times 20 \text{ cm}^2$) mounted on a goniometer (Huber goniometer heads 5202). The spectrometer needed to be shifted back to clear the synchrotron beam path and is placed on the left side of the microscope. For an accurate adjustment of all spatial directions and angles the center of mass of the aluminum table was aligned with the center of the z-stage.

Since the FTIR spectrometer is shifted considerably from the center of the z-stage a 60 kg counter mass was installed. The total weight of this construction is about 200 kg. In order to allow simultaneous Micro-IR and NIS measurements at varying temperatures a minicyostat (see Fig. 1b) dedicated to optical microscopy was modified (see Fig. 2 for details).

The temperature controlled surface of the cryostat was lifted up by placing a copper block onto it. For temperature isolation a plexiglass tube including a window for the NIS beam encased the block. In addition a combination of Kapton and Mylar foils was put around the tube. On top a BaF_2 glass was fixed, which is transparent for infrared light. The so modified cryostat was successfully operated in the temperature range from $\sim 160 \text{ K}$ to 300 K .

The set-up was tested by investigating a single crystal of a dimeric Fe(II) complex $[\{\text{Fe}(\text{L})_2(\text{bbim})\}(\text{ClO}_4)_2 \cdot 2\text{EtCN}]$ ($\text{L} = \text{N}, \text{N}'\text{-dimethyl-2,11-diaza}[3.3](2,6)$ pyridine-

Fig. 2 Modified setup of the cryostat (Linkam station)

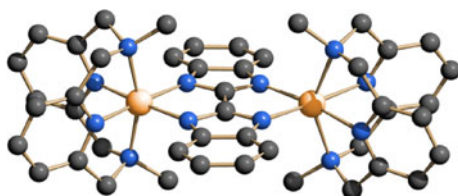
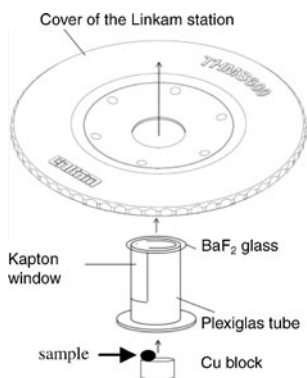


Fig. 3 X-ray structure of the dimeric Fe(II) complex $[\{\text{Fe(II)(L)}\}_2(\text{bbim})]^{+2}$ investigated in this study obtained at 150 K. The iron atoms are depicted in orange, carbon is black and nitrogen is blue [6]

ophane; bbim = 2,2'-Bibenzimidazolate) (see Fig. 3). One iron of this complex undergoes an abrupt spin crossover (SCO) from high spin (HS; $S = 2$) to low spin (LS; $S = 0$) at 175 K, whereas the other iron stays in its HS state [6].

3 Results and discussion

Figure 4a shows experimental NIS data of $[\{\text{Fe(L)}\}_2(\text{bbim})](\text{ClO}_4)_2 \cdot 2\text{EtCN}$ taken at 300 K. A DFT based simulation assuming both irons being in the HS state (Fig. 4b) reproduces the experimental data well. The broadening of the NIS data at 300 K is due to multi-phonon excitations which are not included in the simulations presented in this study [7, 8]. The simulation of the experimental NIS data obtained at 160 K (Fig. 4c) shows that only one iron site has switched to the LS state (Fig. 4d). The Fe-N modes in Fig. 4d within $185\text{--}220\text{ cm}^{-1}$ arise only from the HS iron of the HS-LS dimer, whereas the modes in between $380\text{--}610\text{ cm}^{-1}$ are those of the LS iron only. These LS modes have Fe-N stretching character whereas the modes within $270\text{--}300\text{ cm}^{-1}$ are Fe-N bending modes arising from both irons [4]. Figure 4e includes the IR data of the same sample, taken simultaneously. The most pronounced changes due to the spin crossover effect are observed within the energy region from 850 to 1050 cm^{-1} . According to our DFT analysis these modes include $\text{CH}_2\text{-N}_{sp^3}$ or aromatic ring stretching. Since these modes also have Fe-N stretching character they are sensitive to the spin state of the iron and serve as spin marker bands.

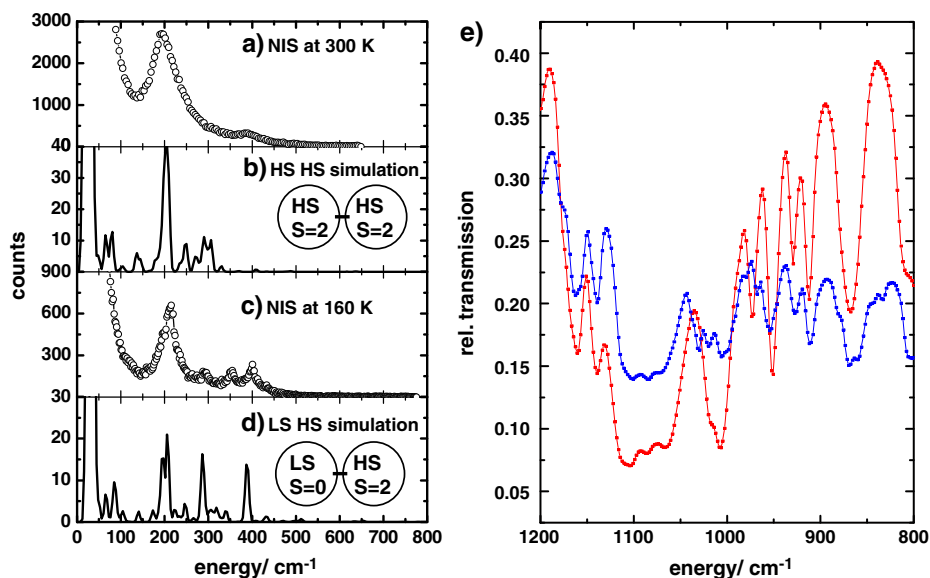


Fig. 4 Exp. (o) (a at 300 K, c at 160 K) and sim. (-) (b for HS-HS sim., d for LS-HS sim.) NIS spectra of $[\{\text{Fe}(\text{L})_2(\text{bbim})\}(\text{ClO}_4)_2 \cdot 2\text{EtCN}]$ and e IR spectra of $[\{\text{Fe}(\text{L})_2(\text{bbim})\}(\text{ClO}_4)_2 \cdot 2\text{EtCN}]$ taken at 300 K (red) and 160 K (blue)

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