Journal of Radioanalytical and Nuclear Chemistry, Vol. 246, No. 1 (2000) 97–100

Nuclear inelastic scattering of synchrotron radiation on solutions of ^{57}Fe complexes

Gy. Vankó,[1] L. Bottyán,[2] D. L. Nagy,[2] E. Szilágyi,[2] A. Vértes[1]

[1] *Research Group for Nuclear Techniques in Structural Chemistry, Hungarian Academy of Sciences at Eötvös L. University Budapest, H–1518 Budapest, P.O. Box 32, Hungary*
[2] *KFKI Research Institute for Particle and Nuclear Physics, H–1525 Budapest, P.O. Box 49, Hungary*

(Received May 8, 2000)

Nuclear inelastic resonant scattering of synchrotron radiation was applied to the study solutions of ^{57}Fe complexes. In order to reveal different inelastic contributions solutions of two different ^{57}Fe complexes of different molecular dimensions with solvents of substantially different viscosities were studied. We argue that the only former experiment available in the literature overestimates the role of the diffusivity in affecting the spectrum. The first direct observation of an intramolecular vibrational transition assisting the nuclear resonance absorption in a liquid is reported.

Introduction

Experimental techniques based on nuclear elastic resonant scattering, i.e., the Mössbauer effect, provide information on the electronic and magnetic properties of the local environment of iron (or other elements with Mössbauer active isotopes) in solid samples. Since the characterisation of solutions containing transition metal complexes is of high importance, numerous efforts were made to apply the power of Mössbauer spectroscopy to study such solutions containing iron. Except for experiments performed under extreme conditions,[1,2] however, the Mössbauer effect cannot be achieved in liquids. Therefore, efforts in studying such solutions with Mössbauer spectroscopy were restricted to frozen solutions by applying a rapid freezing technique.[3]

Recent developments in the use of synchrotron radiation as an X-ray source for nuclear resonant scattering experiments[4,5] not only made an extension to conventional Mössbauer spectroscopy, but allowed also for a development of new experimental techniques, such as nuclear inelastic scattering (hereafter NIS). In a NIS experiment the energy spectrum of the nuclear absorption is taken around the energy of the nuclear resonance. This technique gives detailed information about those events when the resonance absorption is accompanied by some kind of inelastic process (e.g. phonon excitation). The probability of such "events with recoil" is $1-f_{LM}$, where f_{LM} is the Lamb-Mössbauer factor, the probability for the Mössbauer effect to take place. Actually, Mössbauer spectroscopy cannot provide information about the dynamics of the studied system, beyond this probability (related to the mean squared vibrational amplitude of the probe atom).

As opposed to Mössbauer-spectroscopy, NIS of synchrotron radiation, following the first observations,[6] soon became a powerful tool in studying lattice dynamics of solids. In addition to the direct measurement of the phonon density of phonon states, this method provides information on characteristics of phase transitions, vibrational anisotropy and dynamics of nanoparticles and macromolecules.[7,8]

However, it remains unclear, whether NIS can be used to study the structure and/or the dynamics of solutions. The only publication known to us on this topic[9] reports a shift and a broadening of the resonance line in the NIS spectrum of a hydrochloric acid solution of ^{57}Fe. The authors concluded that the spectrum reflects the recoil and the diffusional motion of the dissolved species. Accordingly, the recoil energy and the diffusional coefficient was derived from the experiment. Nuclear quasielastic scattering of synchrotron radiation has been further studied in very recent experiments and preliminary data was presented in favour of diffusion.[15]

Nonetheless, other inelastic processes may also contribute to the NIS spectra. Namely, intramolecular vibrations can be excited or annihilated, collective excitations (density fluctuations) of the liquid[10] can be excited and even electronic scattering can affect the spectra.[11] Moreover, the dynamics of complex equilibria might appear among the inelastic processes in solutions of kinetically labile complexes. As a first step in separating the above contributions here we present NIS studies of solutions of different ^{57}Fe complexes of different molecular dimensions and with solvents of different viscosities. We find indications of intramolecular vibrations rather than diffusional broadening in the spectra.

0236–5731/2000/USD 17.00
© 2000 Akadémiai Kiadó, Budapest

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

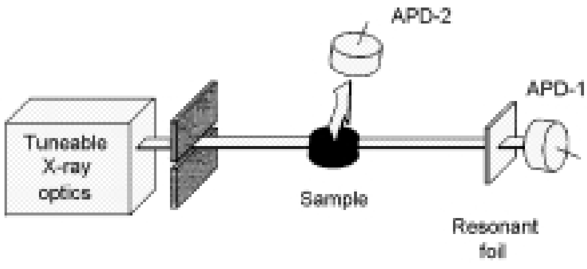

Fig. 1. Experimental setup of a NIS experiment; for more details see Reference 8. APD stands for avalanche photo diode. The delayed quanta detected by APD-1 gives the instrumental function, those detected by APD-2 gives the NIS spectra

Experimental

Hydrochloric acid solutions of ^{57}Fe

^{57}Fe was dissolved in a concentrated solution of HCl; the final pH value was kept below 1.0, thus the iron was present in the form of Fe^{3+} monomers. A fraction of this master solution was separated and, by adding $NaHCO_3$, the pH was increased to pH 2.3, a value at which majority formation of iron dimers (i.e., binuclear aquocomplexes) is expected.[16]

Solutions of [^{57}Fe(bipy)$_3$]Cl$_2$ ("bipy complex")

Hydrazine was added to the HCl acid solution of ^{57}Fe to reduce Fe^{3+} to Fe^{2+}. 2,2'-bipyridine (bipy: $C_{10}N_2H_8$) was then added in small excess to the solution for complex formation. Part of the solution was separated, crystallised and dissolved in glycerol at 330 K.

The yellow solutions of Fe^{3+} (iron concentration: 30 mg ^{57}Fe/cm^3) as well as the dark red solutions of the bipy complex (iron concentration: 6 mg ^{57}Fe/cm^3) were sealed in thin cylindrical plastic bags transparent for the synchrotron radiation.

The NIS experiments were performed at the BW4 beamline of HASYLAB, Hamburg.[17] The experimental setup, schematically shown in Fig. 1, was basically the same as in Reference 9. The experiments were done at room temperature. A nested high resolution monochromator was used with asymmetric (422) and symmetric (12 2 2) reflections. The studied energy range was set to ±100 meV around the resonance energy of the ^{57}Fe nucleus ($E_0 = 14.413$ keV).

Two avalanche photodiodes (APD) were used to count the delayed quanta (Fig. 1). APD-1 counted the delayed quanta coherently forward scattered on an iron foil situated in front of the detector: this curve was taken as the instrumental function of the high resolution monochromator. An aluminium foil was inserted between the iron foil and the detector to absorb the X-ray radiation emitted following the inelastic absorption so that those could not reach the detector. Consequently, the spectra of the counted elastic events led to symmetrical (Gaussian) resolution function with a linewidth of 9 MeV.

APD 2, which was mounted above the sample, detected the delayed quanta stemming from the liquid sample in the plastic container, thus the delayed quanta inelastically scattered into the resonant channel were recorded. For a more detailed description of the setup of a NIS experiment, see Reference 8.

In order to minimise the effect of the variations in the intensity of the beam on the spectra after the high resolution monochromator, a number of relatively fast scans of the inner crystal were performed. The inch worm, which moves the high resolution monochromator, showed individuality and did not always find the perfect position required for the next step in the energy scan. These deviations were considered and the encoder positions, which reflect the actual energy of the radiation through the monochromator, were recorded. The spectra were then corrected to have a common linear energy scale and added up to improve statistics.

Results

Figure 2 shows the NIS spectra. Each spectrum has a large peak around $E–E_0 \cong 0$ that comes from quasielastic scattering. None of the spectra is symmetrical around the center of the quasielastic peak: the spectra of the bipy complex have a separate low-intensity peak at 50 MeV, while those of the two HCl solutions of ^{57}Fe either have a peak around 20 MeV or the quasielastic peak shows high asymmetry. The widths of the quasielastic peaks are more or less the same in the two HCl solutions of ^{57}Fe.

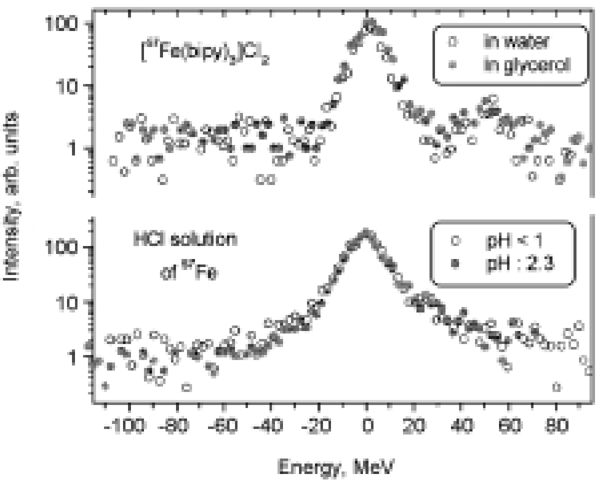

Fig. 2. NIS spectra of $^{57}Fe^{3+}$ in hydrochloric acid solution with different pH values (lower part), and [^{57}Fe(2,2'-bipyridil)$_3$]$^{2+}$ in water and glycerol solution (upper part)

The same holds for the two solutions of the bipy complex of different solvents: the widths are nearly the same in the spectra of the aqueous and glycerol solutions. Nevertheless, the widths (FWHMs) are somewhat larger in the case of the HCl solutions (ca. 13 MeV) than in the bipy complex (ca. 11 MeV).

Discussion

Diffusivities and intramolecular vibrations of the aquocomplexes of ^{57}Fe^{3+} in aqueous solution with two different pH values, and those of [^{57}Fe(2,2'-bipyridil)$_3$]$^{2+}$ in water and glycerol were expected to differ substantially. The explicite purpose in selecting the present solutions and complex salts of ^{57}Fe was to separate those two inelastic contributions in the NIS spectra. In what follows, first, we give account on the expected and observed differences in the NIS spectra which are due to the differences in diffusivities; secondly we report on the excitation of an intramolecular vibration apparent in the NIS spectra.

The pH of the ^{57}Fe^{3+} aqueous solutions were below 1.0 and 2.3, so that Fe^{3+} forms monomers and dimers, respectively. The monomers have six water molecules as ligands but sometimes chloride ions can replace water in the first coordination sphere leading to a general composition of $[Fe(H_2O)_{6-x}Cl_x]^{+3-x}$.[16] Note, that this solution was basically of the same composition as that studied in Reference 9. The dimers, which are formed in the less acidic solution (pH 2.3), have the composition of $[(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}$.[16] NIS spectra of monomers and dimers were expected to show different diffusional behavior due to their different sizes.

The other two solutions contained the very stable bipy complex of Fe^{2+}, in which the iron ion has a local environment with three bidentate bipy ligands in the first co-ordination sphere. In these solutions the viscosity of the solvents were much different: water and glycerol was used, with viscosities of 1 cPs and 500 cPs at room temperature, respectively. Since the diffusional coefficient is inversely proportional to the viscosity, a variation of two orders of magnitudes was expected in the diffusional coefficient of the complex in the two different solutions.

In addition, due to its larger dimensions, the diffusivity of the bipy complex was expected to be smaller than that of its monomer aquocomplex counterpart.

If the linewidths in the NIS spectra were indeed determined by the diffusional broadening, as argued in Reference 9, then, in accordance with the differences in diffusivities discussed above, we expect the linewidths to differ when the spectra of (a) the monomer and the dimer Fe^{3+}, (b) the glycerol and water solutions of the bipy complex, and (c) the monomer Fe^{3+} and the water solution of the bipy complex are compared.

However, our experimental results only meet the third expectation (c), but failed to meet the first two. In the NIS spectra of the different HCl solutions of iron no significant variations were observed in the widths of the spectral lines. This means that the spectra of the monomer and dimer Fe^{3+} were very similar and, consequently they could not reflect the effect of different diffusional behavior of the complexes of different size. It is worth mentioning that the monomers, beside the hexaquo complexes, include some that have Cl$^-$ ions as ligands besides water molecules.[16] Nevertheless, we still expect that the spectral widths of the monomer and dimer complexes should differ if the effect of diffusion would play a decisive role in the inelastic contributions.

With the solutions of the bipy complexes, similar conclusion can be drawn. The widths of the NIS spectral lines do not significantly differ in the case of the water and glycerol solutions. However, if the widths of the spectral lines were indeed determined by the diffusional broadening as stated in Reference 9, the difference should be clearly visible since the diffusivities should differ by two orders of magnitude.

The line widths in the spectra of the monomer Fe^{3+} are larger than that of the water solution of the bipy complex. However, after what we have just discussed above it can hardly be interpreted as an unambiguous sign of the expected effect of diffusion. Moreover, if we follow the practice of ZHAN et al.[9] and apply the Singwi-Sjölander formalism to calculate D diffusional coefficients from the diffusional broadening ($\Delta\varepsilon = 4\pi E_0{}^2 D/hc^2$) of the spectral lines,[12] we obtain values that are far too large. ZHAN and his coworkers obtain $1.2\cdot10^{-9}$ m^2/s for the diffusion coefficient of the Fe^{3+} monomers, and they note that this is two times larger than the literature value of the real diffusion coefficient of the Fe^{3+} ions in water ($0.6\cdot10^{-9}$ m^2/s). From our spectrum we obtain a similar value of $1.3\cdot10^{-9}$ m^2/s. However, since the line widths in the spectra of the monomer and dimer hardly differ, we obtain the very same value for the dimers as well. Curiously enough, the calculated diffusion coefficients for the bipy complex are still very large, $0.9\cdot10^{-9}$ m^2/s. In these solutions, when diffusing, the iron 'carries' the covalently bound large ligands (that comprise 30 carbon and 6 nitrogen atoms altogether); consequently, it is unlikely, that the diffusivity of this complex is still greater than that of the hydrated Fe^{3+} ion.

As far as the role of the vibrations is concerned, our spectral data of the aquocomplexes do not allow for a conclusion. In addition to the poor resolution of spectral lines, another difficulty arises from the fact that the local environment (i.e., the coordination sphere) of the iron ion is not perfectly uniform as mentioned above.

However, the spectra of both $[^{57}Fe(bipy)_3]^{2+}$ solutions of a well-defined co-ordination sphere, show a separate peak at around $E–E_0 \cong 50$ MeV. This energy corresponds to an excitation of a transition of 400 cm^{-1} that accompanies the nuclear absorption. In the NIS spectra of crystalline form of similar complexes, i.e., low spin Fe^{2+} complexes with a FeN$_6$ core, similar peaks were observed at around 45–50 MeV besides the "normal" phonon spectrum. These "Einstein-frequencies" were attributed to intramolecular transitions of the complexes.[13] With a similar argument we suggest that such phenomenon can be observed in solutions of complexes where the iron is strongly bound to the ligands. The vibrational (IR) spectra of this complex seems to be in agreement with this hypothesis. Two Fe–N stretchings modes were reported in this frequency (energy) region: in the spectrum of $[^{57}Fe(bipy)_3](ClO_4)_2$ two bands at 380 cm^{-1} (↔47 MeV) and 371 cm^{-1} (↔ 46 MeV) were observed.[14] Therefore, we conclude that the 50 meV peaks in our spectra are the first direct observation of intramolecular vibrational transition assisted nuclear resonant absorption in a liquid state of a solution.

Experiments with variations in the size and strength of the coordinative bond in similar complexes are subject of accepted applications at a beamline of higher intensity and better energy resolution. Temperature dependence of the NIS spectra are also planned.

Conclusions

As opposed to the arguments in Reference 9, we conclude that diffusion, within the experimental error, does not effect the NIS spectra of the solutions of iron complexes. Quite as the reverse, we argue, that the inelastic contribution is of vibrational origin. The present experimental data appear to be the first direct observation of nuclear resonant absorption assisted by an intramolecular transition in the state of a solution.

*

The authors are indebted to Dr. Yurii SHVYD'KO and Dr. Olaf LEUPOLD for discussions and participation in the experiments. This work was supported by the Hungarian National Research Fund OTKA No. T 029409.

References

1. K. BURGER, A. VÉRTES, Nature (London), 306 (1983) 353.
2. D. St. P. BUNBURY, J. A. ELLIOTT, H. E. HALL, J. M. WILLIAMS, Phys. Lett., 8 (1963) 34.
3. A. VÉRTES, D. L. NAGY, Mössbauer Spectroscopy of Frozen Solutions, Akadémiai Kiadó, Budapest, 1990.
4. E. GERDAU, U. VAN BÜRCK, R. RÜFFER, Hyp. Int., 123/124 (1999) 3.
5. G.V. SMIRNOV, Hyp. Int., 123/124 (1999) 31.
6. M. SETO, Y. YODA, S. KIKUTA, X. W. ZHANG, M. ANDO, Phys. Rev. Lett., 74 (1995) 3828.
7. A. I. CHUMAKOV, R. RÜFFER, Hyp. Int., 113 (1998) 59.
8. A. I. CHUMAKOV, W. STURHAHN, Hyp. Int., 123/124 (1999) 781.
9. X. ZHANG, Y. YODA, M. SETO, Y. MAEDA, M. ANDO, S. KIKUTA, Japan J. Appl. Phys., 34 (1995) 330.
10. F. SETTE, G. RUOCCO, M. KIRSCH, U. BERGMANN, C. MASCIOVECCHIO, V. MAZZACURATI, G. SIGNORELLI, R. VERBENI, Phys. Rev. Lett., 75 (1995) 850.
11. A. I. CHUMAKOV, A. Q. R. BARON, R. RÜFFER, H. GRÜNSTEUDEL, H. F. GRÜNSTEUDEL, A. MEYER, Phys. Rev. Lett., 76 (1996) 4258.
12. K. S. SINGWI, A. SJÖLANDER, Phys. Rev., 120 (1960) 1093.
13. H. PAULSEN, H. WINKLER, A. X. TRAUTWEIN, H. GRÜNSTEUDEL, V. RUSANOV, H. TOFTLUND, Phys. Rev., B 120 (1999) 975.
14. Y. SAITO, J. TAKEMOTO, B. HUTCHINSON, K. NAKAMOTO, Inorg. Chem., 11 (1972) 2003.
15. R. HARUKI, S. KITAO, M. SETO, Yu. MAEDA, T. HARAMI, X. W. ZHANG, Y. YODA, S. KIKUTA, ICAME-99 poster T7/24.
16. A. VÉRTES, L. KORECZ, K. BURGER, Mössbauer Spectroscopy, Elsevier, Amsterdam, 1979, p. 296.
17. http://www-hasylab.desy.de/