COMMENTS AND ADDENDA

Mössbauer relaxation line shapes in the presence of complex hyperfine interactions*

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We have utilized a result of Clauser to evaluate the line shape of Mössbauer resonance spectra involving spin relaxation effects even in cases with nondiagonal hyperfine interactions. Compared to traditional methods for calculating the line shapes, this formulation saves computational time by approximately two orders of magnitude and thus makes possible consideration of many problems which were previously intractable. Examples are given for cases involving complicated hyperfine Hamiltonians, viz., hemoglobin cyanide, acid met myoglobin, and NpF_6.

The theory of resonance line shapes in Mössbauer experiments[1] involving spin relaxation effects is well known. In a few cases, closed-form expressions for the line shapes have been developed, for example, in problems involving adiabatic relaxation (diagonal hyperfine interaction) of an electronic Kramer's doublet, or in some special cases of nonadiabatic relaxation.[2,3] When closed forms are unavailable for describing the experimental data, as is frequently the case, the task of line shape calculation demands an inversion of a large super matrix (consisting of the matrix elements of a Liouville operator describing the static hyperfine interactions[4] and a matrix describing the relaxation processes[3,5]) at every energy point over the resonant part of the spectrum. Depending on the complexity of the problem at hand, a simple simulation of a spectrum by such a procedure required computational times on the order of tens to hundreds of minutes on the fastest machines available. Therefore, mere calculation of a spectrum was difficult, and least-squares fitting of the experimental data was impossible. A practical result of this situation has been that many problems of potential interest were never treated properly. Several years ago, Clauser presented a reformulation of the traditional expression for relaxation line shapes which requires in effect *only one* inversion of the super matrix.[6,7] Although the advantages are enormous, this procedure seems to have been largely overlooked. The purpose of the present article is to demonstrate the usefulness of this approach and to consider a number of problems which had previously been thought intractable.

The expression for Mössbauer line shapes in the presence of relaxation effects can in general be written as[3-5,8]

$$I(\omega) = \text{Re} \sum_m \underline{M}_{Lm}^\dagger \cdot \underline{A}^{-1} \cdot \underline{M}_{Lm} , \tag{1}$$

where $\underline{M}_{Lm}$ is an electromagnetic multipole operator of the order L, involving transitions of polarization m between various hyperfine levels, and

$$\underline{A} = (\Gamma - i\omega)\underline{1} - (i/\hbar)\mathcal{K}^* - \underline{R} . \tag{2}$$

Here, Γ is the natural width of the resonance, ω is the energy of the resonant γ ray, $\mathcal{K}^*$ is a Liouville operator describing the excited and ground-state hyperfine interactions,[4] and $\underline{R}$ delineates the relaxation processes involved in the problem.[3,5] If I_e and I_g are the excited and the ground-state nuclear spins, and S is the electron spin, the dimensionality of $\underline{A}$ is

$$n = (2I_e + 1)(2I_g + 1)(2S + 1)^2 .$$

Thus for the 14.4-keV resonance in ^{57}Fe, with $S = \frac{1}{2}$, we have $n = 32$. Computational complexities stated above arise in such cases since no closed-form inversions can be done for an $n = 32$ matrix.

In Clauser's formulation of the relaxation line-shape expression,[6] one recognizes the fact that the independent variable occupies a special position in the matrix $\underline{A}$: it enters only as a constant on the diagonal. Therefore, the eigenvectors of $\underline{A}$ will be the same whether ω is present or not, and the eigenvalues of $\underline{A}$ with ω removed will differ from those of $\underline{A}$ containing ω by only a constant. Thus, if $\underline{V}$ and $\overline{\lambda}$ represent the eigenvectors and eigenvalues of $\underline{A}$ with ω removed, then the line-shape expression reduces to

$$I(\omega) = \text{Re} \sum_m (\underline{M}_{Lm}^\dagger \cdot \underline{V}) \cdot (\underline{\lambda} - i\omega \underline{1})^{-1} \cdot (\underline{V}^{-1} \circ \underline{M}_{Lm}) \ . \quad (3)$$

The expression for the line shape given by Eq. (3) can be easily evaluated numerically by first obtaining the eigenvalues and eigenvectors of $\underline{A}$ without ω along its diagonal, then reintroducing ω in the simple algebraic way indicated. Thus the need to invert $\underline{A}$ at every value of ω is eliminated. In fact, when using Eq. (3), the computational time is largely dominated by the one eigenvalue problem and is fairly independent of the number of energy points in the spectrum. We shall now utilize Eq. (3) in discussing some actual data.
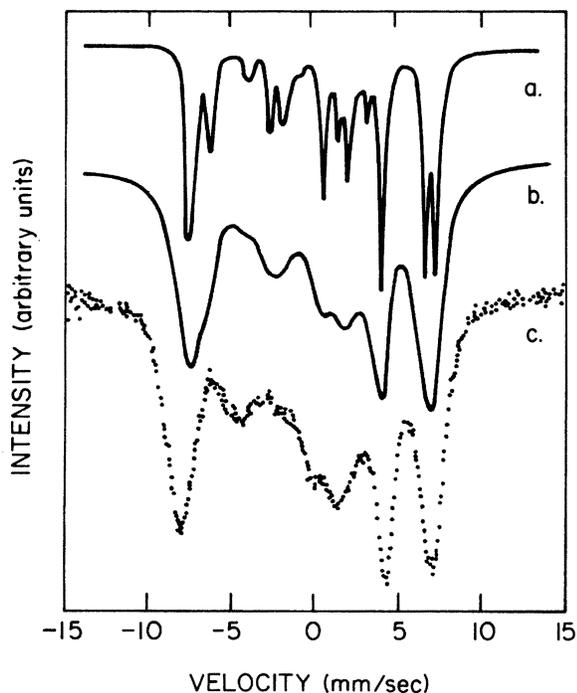
FIG. 1. Mössbauer resonance absorption of ^{57}Fe in hemoglobin cyanide. The experimental data (c) are from Ref. 6. The static pattern shown in (a) is calculated from hyperfine parameters given in Ref. 6 and a linewidth of 0.2 mm/sec. The simulation in (b) is obtained by assuming a spherical relaxation rate of 4.6 MHz, using the method given in the text.

Biological systems containing iron involve some of the most complex hyperfine interactions, and at the same time their elucidation using the Mössbauer effect in ^{57}Fe is of great interest. Lang and Marshall[9] have investigated hemoglobin cyanide in which iron has a low-spin ferric state with $S = \frac{1}{2}$. The hyperfine interaction for the excited state of ^{57}Fe in this low symmetry system is given by

$$\mathcal{H} = \underline{S} \cdot \underline{A}_0^* \cdot \underline{I} + \tfrac{1}{4} e^2 qQ[I_z^2 - \tfrac{5}{4} + \tfrac{1}{3}\eta(I_x^2 - I_y^2)] \ . \quad (4)$$

A similar expression is used for the ground state of ^{57}Fe by replacing A_0^* by A_0 and Q by 0. In Fig. 1(c) we have shown the experimental data of Lang and Marshall measured at 1.2 K, and in Fig. 1(a) the static hyperfine pattern devised by them using Griffith's model[10] is given. The observed spectrum can now be simulated using Eq. (3) by including spherical relaxation[3,5] in the problem, and the result is shown in Fig. 1(b). On an IBM 370/195 machine this spectrum was simulated in less than 1 sec. The curve reproduces the general trends in the data of Fig. 1(c) rather well, although there are some minor discrepancies in the line positions owing to uncertainty in the hyperfine parameters. It is sufficient to point out here that a least-squares fitting of such data now becomes very simple and could lead to a refinement of Griffith's model as applied to hemoglobin cyanide.

As another example, we consider acid met myoglobin. Although the Hamiltonian of Eq. (4) is axial,[11] and $S_z = \pm\frac{1}{2}$ state alone is occupied at low temperatures, there are additional complications arising from the coupling of the iron spin with the ligand nuclear moments. In Fig. 2(d) we give the experimental spectrum measured by Lang et al.[11] The Fe single-ion hyperfine parameters have been obtained by Lang et al., by applying an external field sufficiently large that the Zeeman interaction predominated over hyperfine effects. The static (slow relaxation) spectrum obtained in zero field from those derived parameters is shown in Fig. 2(a). Our attempts to reproduce Fig. 2(d) merely by introducing relaxation into the problem, as in the previous example, was not fruitful, showing the necessity of including the ligand coupling with the iron spin. Following Viccaro et al.,[12] we have approximated the influence of the ligands by an interaction $\underline{H} \cdot \underline{g} \cdot \underline{S}$ where $\underline{H}$ represents the average magnetic field set up by the ligand nuclear moments. As has been shown,[12] such a "random-field" model improves the fit to the experimental data [see Fig. 2(b)] even without the inclusion of relaxation. The introduction of spherical relaxation in addition to this then reproduces the data almost exactly [Fig. 2(c)]. Because one has to perform numerous integrations over angles in the "random-field" model, the computational time was on the order of tens of seconds.
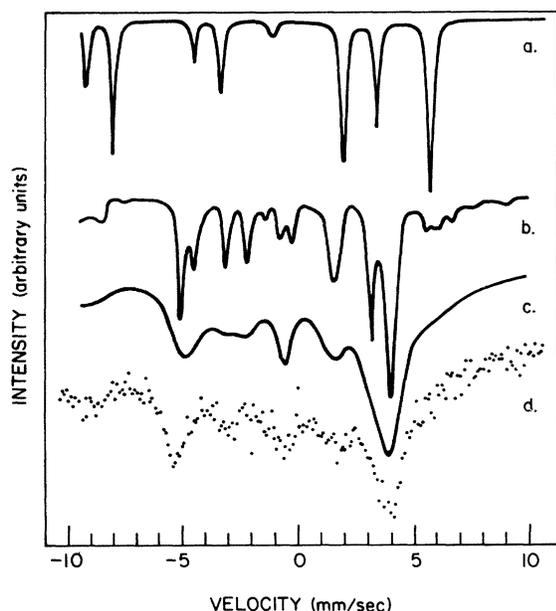
FIG. 2. Mössbauer resonance absorption of ^{57}Fe in acid met myoglobin. The experimental data (d) are from Ref. 8. The static pattern shown in (a) is calculated using the hyperfine parameters given in Ref. 8. The spectrum in (b) is obtained using the "random-field" model described in Ref. 9 with an average field of 10 G to describe the ligand nuclear coupling with the electron spin on iron. The relaxation superposed on this (relaxation rate of 5.8 MHz) produces the curve in (c), which exactly reproduces the experiment.

In the work of Gonzalez-Jimenez *et al.*,[3] a closed form-expression for the line shape of a relaxation spectrum for the $0 \rightarrow 2$ transition with $S = \frac{1}{2}$ has been given. In that case, the hyperfine interaction was assumed to be axially symmetric. A closed-form expression for the line shape was achieved since the matrix $\underline{A}$ could then be conveniently factored into submatrices, the largest having a dimensionality of 4. If we consider a Hamiltonian of a more general nature describing lower symmetry hyperfine interactions, namely

$$\mathcal{3C} = \underline{S} \cdot \underline{A_0} \cdot \underline{I} + \underline{I} \cdot \underline{P} \cdot \underline{I} \tag{5}$$

(where $\underline{P}$ is the quadrupole tensor), the factorization is not possible. However, using Eq. (3) we can readily calculate relaxation line shapes even in such cases.

Finally in Fig. 3(b) we show our own experimental data for NpF$_6$, measured with the 59.6-keV $\frac{5}{2} \rightarrow \frac{5}{2}$ transition in ^{237}Np. The spectrum is a broad asymmetric line which arises from the spin relaxation effects. The ground state of Np^{6+} in cubic NpF$_6$ is a doublet[13] and hence hyperfine interactions can be accounted for by a Hamiltonian of the type $A_0 \vec{\mathrm{I}} \cdot \vec{\mathrm{S}}$ with $S = \frac{1}{2}$. The super matrix has the dimensionality $n = 144$, but using Eq. (3) a

relaxation spectrum can be simulated in about 12 sec on our computer. Some of the simulated curves are shown in Fig. 3(a) along with the one that fits the experimental data in Fig. 3(b).

We would like to point out that symmetries in the problem can often factorize the super matrix, as mentioned above for the $0 \rightarrow 2$ case. For example, in the present ^{237}Np problem, the $n = 144$ matrix can be subdivided into 13 matrices of dimensions 1, 1, 4, 4, 8, 8, 12, 12, 16, 16, 20, 20, 22. Calculation of the spectrum with repeated use of Eq. (3) on these submatrices further reduces the
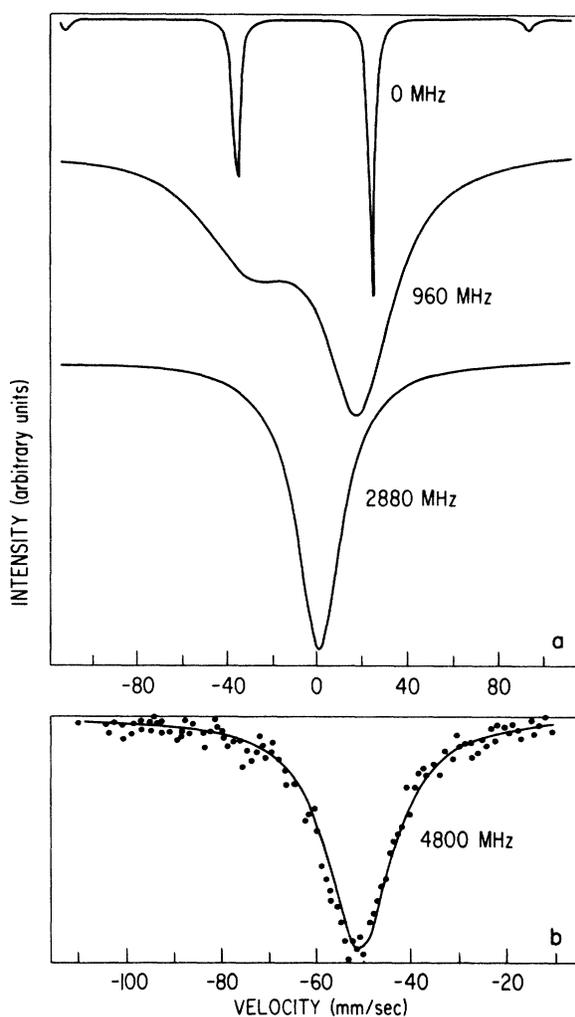
FIG. 3. Mössbauer resonance absorption of 59.6 keV $\frac{5}{2} \rightarrow \frac{5}{2}$ transition in ^{237}Np experiencing cubic hyperfine coupling in NpF$_6$. In the simulations and the analysis of the data we have used $A_0 = -43$ mm/sec and resonance width of 3.0 mm/sec. The experimental data (b) show an isomer shift of -51 mm/sec with respect to the Am source, while the isomer shift is presumed zero for sake of calculation in (a). Values for the spherical relaxation rates are shown.

computing time by about one order of magnitude. A similar Hamiltonian would also break up the super matrix in the $\frac{1}{2} \to \frac{3}{2}$ transition to eight submatrices.[14] The super matrix A for $S = \frac{3}{2}$ and for ^{57}Fe resonance has $n = 128$. In some cases this may also be subdivided. However, even for the complicated Hamiltonian of Eq. (5), a spectral simulation can be performed in about 9 sec. Such a Hamiltonian describes the spectra measured with some of the Fe^{3+} dithiocarbamates investigated by Wickman and Wagner.[15] In discussing their data, they have utilized the theory of Blume and Tjon[2] which is only an approximation for this problem. The time needed to simulate a spectrum in their case was larger by a factor of 20.

The usefulness of this formulation of the expression for the relaxation line shape is plain, and in fact, Eq. (3) is applicable to almost any spin relaxation problem or to problems involving quadrupolar relaxation. The perturbation model assumed in the examples to describe the relaxation processes,[3,5] and in particular the assumption of the spherical relaxation, may be a simplification; improvements over this can be done by least-squares fitting of the actual data, which now becomes possible in cases of interest. Finally we emphasize that the implications of this approach are not confined to Mössbauer spectroscopy, but in fact apply to EPR and NMR problems where one may be interested in determining line shapes.[8]

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