Suppression of the Mössbauer line broadening due to inhomogeneous isomeric shift

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Suppression of inhomogeneous broadening by using the sensitivity of the hyperfine structure to local changes in the density, and the possibility of regulating the scale of the change of the hfs by external parameter, are analyzed. It is possible to use for this purpose the external magnetic field H in the case of metals, the parameters H and T in the case of paramagnets, and the frequency shifts from resonance in the case of NMR with the excited and (or) ground level of the nucleus.

1. The possibility of observing ultranarrow Mössbauer lines and the problem of obtaining stimulated γ radiation by using long-lived isomer states encounters tremendous difficulties connected with the inhomogeneous line broadening due to various kinds of local distortions of the medium.[1] Particularly dangerous in this case is the isomeric shift, which is sensitive to the value of the local electron density

$$\delta\omega_i = \gamma\left|\frac{\Delta V_0}{V_0}\right| \tag{1}$$

($|\Delta V_0/V_0|$ is the relative change of the value of the unit cell). In particular, the broadening due to this shift is preserved also when use is made of those radio-frequency methods which are proposed for the suppression of the inhomogeneous broadening due to the hyperfine interactions.[2].

In the presence of a well resolved hyperfine structure, however, it is possible in principle to compensate for the inhomogeneous shift, by recognizing that the very value of the level splitting in the excited ("1") and ground ("0") states depends on $|\Delta V_0/V_0|$ via the distribution of the spin density of the electrons (for example, of the d and f electrons or of the s electrons in contact interaction) or in terms of the electric-field gradient, i. e.,

$$\delta\omega_h^{(s)} = \xi^{(s)}\left|\frac{\Delta V_0}{V_0}\right|, \qquad s = 0,1. \tag{2}$$

It is then possible to obtain suppression by creating conditions under which $\xi^{(s)}$ varies continuously with variation of the external parameters, so that for a fixed component of the transition we have

$$\gamma + \xi^{(1)} - \xi^{(0)} = 0. \tag{3}$$

The first to point out the possibility connected with the utilization of the radio-frequency method were Gol'danskiĭ, Karyagin, and Namiot.[3]

2. Such a compensation can be obtained in the simplest and physically most lucid manner, at least in principle, in nontransition metals placed in strong magnetic fields. The components of the Zeeman splitting of the nuclear levels experience in this case shifts that are proportional to the density of the magnetized conduction electrons at the nucleus (the Knight shift in NMR—see, e. g.,[4]), and thus behave in accordance with (2). Then

$$\xi^{(s)} \sim \zeta\mu_{\text{nuc}}H \tag{4}$$

($\zeta = |\Delta H/H|$ is the relative Knight shift in the given metal), and we can continuously vary the coefficients in (2) by varying the magnetic field H. Unfortunately, the coefficients ζ are not large (10^{-2} for the heaviest metals), so that this method can be used only in extremely strong fields and for nuclei with limited values of the isomeric shift.

Another possibility arises when a paramagnet is used in an external magnetic field under conditions of rapid electron-spin relaxation. In this case the hyperfine splitting is the Zeeman splitting in an effective field $\mathbf{H}_{\text{eff}}$ proportional to the average value of the electron moment $\langle\mu_s\rangle$; this splitting is determined by the values of the field H and of the temperature T. The change of the Zeeman splitting upon local variation of the density is obviously also proportional to $\langle\mu_s\rangle$. As a result we have

$$\xi^{(s)} = \xi^{(s)}(H, T) \tag{5}$$

and by varying the field and temperature we can satisfy the condition (3) if, as is the situation in most cases, we have at saturation

$$\xi_{max}^{(s)} > \gamma \tag{6}$$

(for one or both values of s).

3. When inequality (6) is satisfied, an interesting possibility of suppressing the broadening appears when an alternating magnetic field is used, with a frequency ω close to the resonant frequency for the excited or ground state of the nucleus. It is assumed here that the Zeeman splitting is produced by the effective magnetic field as a result of the hyperfine interaction in magnetically ordered crystals or in paramagnets, under the conditions considered above. It is possible in principle to use also quadrupole splitting, provided that condition (6) is valid for the corresponding ξ.

Let us assume for simplicity that the spin of the considered state of the nucleus is 1/2. Let an alternating field of amplitude $H_\perp$ ($\omega_\perp = \mu_{\text{nuc}}\mathbf{H}_\perp/\hbar$) rotate with frequency ω in a plane perpendicular to $\mathbf{H}_{\text{eff}}$ ($\omega_h = \mu_{\text{nuc}}H_{\text{eff}}/\hbar$). We then have for the spin part of the wave function of the nucleus the well known solution (see[5])

$$\psi_{1/2} = e^{-i\omega t/2}[A_1 e^{i\Omega t} + A_2 e^{-i\Omega t}], \tag{7}$$

$$\psi_{-1/2} = e^{i\omega t/2}\left[A_1 \frac{\omega_\perp}{\frac{\omega}{2} + \omega_h + \Omega} e^{i\Omega t} + A_2 \frac{\omega_\perp}{\frac{\omega}{2} + \omega_h - \Omega} e^{-i\Omega t}\right], \tag{8}$$

$$\Omega = \sqrt{(\omega/2 + \omega_h)^2 + \omega_\perp^2}\,.$$

The phase difference between the wave function in (7), for a definite spin projection, and of the corresponding function in the second state of the nucleus determines in fact the energy of the fixed hyperfine component of the γ transition. The transition energy shift due to the variation of H_{eff} is determined entirely by the change of Ω. We denote the mean value of ω_h, corresponding to the regular value of H_{eff}, by $\tilde{\omega}_h$. Then, under the condition

$$|\delta\omega_h| \ll |\Delta|, \quad |\Delta| \ll \omega_\perp, \qquad \Delta = \frac{\omega}{2} + \tilde{\omega}_h \tag{9}$$

we have

$$\delta\Omega = \omega_\perp + \frac{\Delta}{\omega_\perp}\delta\omega_h\,. \tag{10}$$

It follows therefore that by moving away from exact resonance ($\Delta = 0$), i. e., by varying Δ, we continuously vary one of the coefficients $\xi^{(s)}$, and if the resonance corresponds to a level with a large magnetic moment, then at a definite Δ we reach the compensation condition (3). The necessary linear dependence of $\delta\Omega$ on $\delta\omega_h$ takes place only if the inequality (9) is satisfied. Therefore only the broadening due to small shifts $|\delta\omega_h| \ll \omega_\perp$ can be suppressed, but it is precisely the small shifts which offer the greatest danger for the entire problem of obtaining ultranarrow lines.[1] Naturally, it is desirable to have the maximum value of $H_\perp$, and there exists simultaneously a requirement $\omega_\perp \tau_{nuc} \gg 1$ on the relaxation time τ_{nuc} of the nuclear spin.

4. In those cases when the states corresponding to the hyperfine structure have at least in part a mixed electron-nuclear character, an appreciable increase of $(\omega_\perp)_{eff}$ is possible, because the transitions are realized by a rotation of the electron spin.[4] The large $(H_\perp)_{eff}$, which is necessary in order for the results of[3] to be correct, should apparently be obtained precisely in this manner. In this case, however, there exists a difficulty connected with the need of having a very long relaxation time, but in this case for the electron spin.

5. If simultaneous resonance is realized separately in the excited and in the ground states, then two independent external parameters appear

$$\Delta^{(0)}/\omega_\perp^{(0)} \text{ and } \Delta^{(1)}/\omega_\perp^{(1)}.$$

Now, besides mutual cancellation of the shifts (1) and (2) due to the local changes of the density, it is possible to suppress simultaneously the shifts $\delta\omega_h^{(s)\prime}$ due, e. g., to the most pronounced type of distortion of the shape of the unit cell or of a definite field component produced by a defect at large distances. It is assumed only that $\delta\omega_h^{(0)\prime}$ is proportional to $\delta\omega_h^{(1)\prime}$,

$$\delta\omega_h^{(0)\prime} = \eta\,\delta\omega_h^{(1)\prime}. \tag{11}$$

The idea is to make the shifts in $\delta\Omega^{(s)}$ equal, by deviation from resonance, for the excited and ground state of the nucleus, i. e., to satisfy simultaneously with (3) the condition

$$\frac{\Delta^{(1)}}{\omega_\perp^{(1)}} = \eta\frac{\Delta^{(0)}}{\omega_\perp^{(0)}}\,. \tag{12}$$

The relation between the coefficients $\xi^{(0)}/\gamma$, $\xi^{(1)}/\gamma$, and η are subject to limitations that can be easily obtained directly by taking (9) into account. This leads to a limitation on the transitions variants, for which two-parameter suppression of the broadening is possible.

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