# Narrowing of gamma resonance lines in crystals by continuous radio-frequency fields

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The narrowing of gamma resonance lines in crystals by a quasicontinuous rf field is considered. It is shown that the magnetic dipole-dipole and quadrupole interactions between nuclei and the chemical shift can be suppressed simultaneously.

In a previous paper[1] we proposed a method for reducing the width of gamma resonance lines due to the dipole-dipole interaction between nuclei and the interaction between the quadrupole moment of a nucleus and the electric-field gradient in a crystal. The method is based on the application of a series of $\pi/2$ pulses to the specimen. The pulses must be of very short length $\tau_p$ (in the limit, $\delta$ functions) and, consequently, the strength H of the rf field ($\gamma H\tau_p = \pi/2$) must be very high, since a finite pulse length reduces the efficiency of this method.[2] A different method of reducing the dipole linewidth was recently proposed in connection with NMR experiments, and is based on the use of quasiperiodic rf cycles.[3] This method can be used to obtain much shorter cyclic time T for the same rf power as in multipulse experiments, or the same cyclic times with much lower power. Let us consider the application of this method to gamma resonances.

The secular part of the Hamiltonian for the magnetic dipole-dipole interaction between nuclei in a strong static magnetic field is

$$\mathscr{H}_D=\sum_{i<j} b_{ij}(\mathbf{I}_i\mathbf{I}_j-3I_{iz}I_{jz})+\sum_{i'<j'} b_{i'j'}(\mathbf{I}_{i'}\mathbf{I}_{j'}-3I_{i'z}I_{j'z})-2\sum_{i'j} b_{i'j}I_{i'z}I_{jz},$$

$$b_{kl}=-\frac{\gamma_k\gamma_l\hbar^2}{r_{kl}^3}\frac{1-3\cos^2\theta_{kl}}{2};\qquad (1)$$

where $i'$ and $j'$ identify nuclei in the upper state and i, j those in the lower state. If we apply an rf field to the specimen, we generate in it an effective magnetic field at angle $\beta$ to the static field. The Hamiltonian is then a function of time:[1]

$$\tilde{\mathscr{H}}_D(t)=V_0^{-1}(t)\mathscr{H}_D V_0(t),\quad V_0(t)=\hat{T}\exp\left\{-\frac{i}{\hbar}\int_0^t \mathscr{H}_{nr}'(t')\,dt'\right\},\qquad (2)$$

where $\hat{T}$ is the Dyson time-ordering operator and $V_0(t)$ is the evolution operator which corresponds to the Hamiltonian for the interaction between the system and the rf field $\mathscr{H}'_{nr}$ in the interaction representation.

We shall consider a cyclic rf field with definite period T such that $V_0(T) = 1$. The period T must be such that $T \ll T_2$, where $1/T_2$ is the linewidth prior to the narrowing, which is determined by the interaction $\mathscr{H}_D$. In this case, the operator $\tilde{\mathscr{H}}_D(t)$ is replaced by the effective operator

$$\mathscr{H}_e=\mathscr{H}_e^{(0)}+\mathscr{H}_e^{(1)}+\mathscr{H}_e^{(2)}+\ldots,$$

$$\mathscr{H}_e^{(0)}=\frac{1}{T}\int_0^T \tilde{\mathscr{H}}_D(t)\,dt,$$

$$\mathscr{H}_e^{(1)}=-\frac{i}{2\hbar T}\int_0^T dt_2\int_0^{t_2} dt_1[\tilde{\mathscr{H}}_D(t_2),\tilde{\mathscr{H}}_D(t_1)],\qquad (3)$$

The formulas for the higher-order terms can be found in[4].

The gyromagnetic ratio for the excited and unexcited nuclei are different and, therefore, the amplitude and frequency of the rf field acting on the nucleus in the upper state should be different from the field on the nuclei in the lower state. We shall impose the following conditions on these quantities. Firstly, we shall demand that both the effective fields should be at the "magic" angle to the static field $H_0$. This angle is given by[2,3]

$$\beta_m=\operatorname{arctg}\frac{H^{(1)}}{\omega^{(1)}/\gamma^{(1)}-H_0}=\operatorname{arctg}\frac{H^{(2)}}{\omega^{(2)}/\gamma^{(2)}-H_0}=54^\circ 44';$$

where $H^{(i)}$, $\omega^{(i)}$ are the amplitude and frequency of the rf fields, and $\gamma^{(i)}$ are the gyromagnetic ratios for the upper and lower states of the nuclei. Secondly, we shall demand that the precession frequencies of the spin magnetic moments of the excited and unexcited nuclei about the direction of effective fields in the rotating frame be equal:

$$\omega_e=\gamma^{(1)}\left[\left(\frac{\omega^{(1)}}{\gamma^{(1)}}-H_0\right)^2+H^{(1)2}\right]^{1/2}=\gamma^{(2)}\left[\left(\frac{\omega^{(2)}}{\gamma^{(2)}}-H_0\right)^2+H^{(2)2}\right]^{1/2}.$$

From these two conditions we have the equation $|\gamma^{(1)}H^{(1)}| = |\gamma^{(2)}H^{(2)}| = \omega_1$. A good average of the resonance part of the Hamiltonian (1) is achieved by applying the symmetrized Lee-Goldburg cycle to the nucleus in the course of which the phase $\omega_e$ changes by $\pi$ at time $T/2$. In this case, $\mathscr{H}_e^{(0)} = \mathscr{H}_e^{(1)} = 0$. However, because of the presence of the nonresonant part, we can use it only for one of the states of the nuclei, for example, the excited state. The cycle acting on the unexcited nuclei must be such that there is simultaneous averaging of the nonresonant Hamiltonian. These requirements are satisfied only by the cycles shown in the figure, in which $H_x^{(1)}$ and $H_x^{(2)}$ are the amplitudes of the rf fields, which are resonant for the excited (1) and unexcited (2) nuclei. It is clear from the figure that the amplitudes change in sign

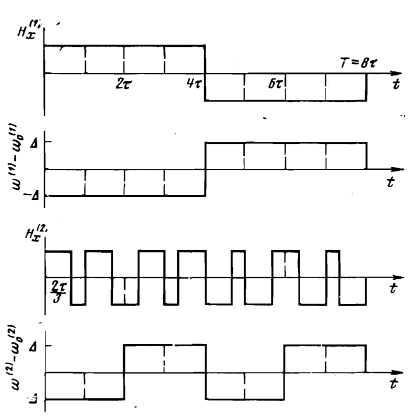


FIG. 1. Time variation of the rf-field parameters which results in the suppression of the dipole-dipole interaction $H_x^{(1)}$ and $H_x^{(2)}$ are the x-components of amplitudes which resonate with excited (1) and unexcited (2) nuclei in the rotating frame, and $\omega^{(1)}$ and $\omega^{(2)}$ are the corresponding frequencies; $\tau = 2\pi/\omega_e$ and $\Delta = \omega_1 \cot\beta_m$.

  

but not in magnitude, i.e., their phase changes by $\pi$. The frequencies $\omega^{(i)}$ of the rf field vary during the cycles by $\pm\Delta$ relative to the Larmor frequencies $\omega_0^{(i)} = \gamma^{(i)}H_0$. The cycle acting on the unexcited nuclei is chosen so that if the end point of the magnetization vector due to the spins of these nuclei describes the curve $\mathbf{M} = \mathbf{M}(t)$ in the interval $(0, \tau)$, then it describes the curve $\mathbf{M} = -\mathbf{M}(t-\tau)$ in the interval $(\tau, 2\tau)$, and so on. This procedure yields the average of the nonresonant part. These nuclei behave as a whole in the same way as under the action of the Lee-Goldburg cycle in the interval $(0, T/2)$, but the direction around which the magnetic moment precesses assumes four different values. To reduce to zero the term $\mathscr{H}_e^{(1)}$, one can use the symmetrization procedure $\tilde{\mathscr{H}}_D(t) = \tilde{\mathscr{H}}_D(T-t)$ proposed in,[3] and we did this by continuing the cycle from $T/2$ to $T$.

As noted earlier,[1] the spin dependence of the Hamiltonian for the interaction between the quadrupole moment of the nucleus and the electric-field gradient has the same form as the resonant part of the Hamiltonian (1), so that the quadrupole interaction $\mathscr{H}_Q$ is averaged together with $\mathscr{H}_D$.

In this way, the linewidth will be determined by the term $\mathscr{H}_e^{(2)}$ in (3), i.e., it will decrease approximately in the ratio $\mathscr{H}_e^{(2)}/\mathscr{H}_{D,Q} \sim 1/6(T/T_0)^2$, where $1/T_0$ is the linewidth set by the interactions $\mathscr{H}_D$ and $\mathscr{H}_Q$ prior to narrowing, and T is the length of the cycle, which can be much less than in single-pulse experiments. This enables us to reduce the gamma resonance linewidth by several orders of magnitude.

The quasicontinuous rf field can also be used to suppress at the same time the broadening due to random magnetic fields due to "foreign" nuclei, isotopes, and inhomogeneities in the static field $H_0$. For this one must use the same variation of $H_x^{(i)}$ as for the field $H_x^{(2)}$ in the figure, but with $T^{(1)}/T^{(2)} = 1/8$. A small deformation of the last cycle when the length ratio for the constant field-amplitude components differs from 1/3:2/3 can be used with a suitable amplitude ratio by the scheme proposed in[5, 6].

In this way, one can suppress the quadrupole interaction, the chemical shift, and the resonant part of the dipole dipole interaction, but there remains a small fraction of the nonresonant dipole-dipole interaction and also the interaction with the foreign nuclei, both of which produce broadening.

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