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NMR LINESHAPES IN SOLIDS WITH MOLECULAR MOBILITY

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Abstract: The new approach to the calculation of the NMR line shapes in solids has been discussed. This approach has been applied to simple model of quadrupolar nucleus with spin $I = 1$ (or isolate water molecule) jumping between two positions in crystal.

The problem of the NMR lineshapes or free induction decays (FID) in solids with molecular mobility is well known although still unsolved [1-3]. At present time a variety of approaches have been proposed in order to resolve this problem. One from these approaches is the moment method proposed in the papers [4, 5]. In this method the shape of FID $G(t)$ is approximated by a Taylor series

$$G(t) = \sum_{n=0}^{\infty} \frac{(-it)^n}{n!} a_n . \tag{1}$$

In the rigid lattices the coefficients are related to the Van-Vleck's moments [6]. In the solids with molecular mobility the first coefficients a_n can be also easily calculated. For example for simple model of the molecular motion in solids between discrete lattice sites it has been shown that [4, 5, 7]

$$a_0 = 1, \quad a_1 = 0, \quad a_2 = M_2, \quad a_3 = i\frac{\Delta M_2}{\tau_c}, \quad a_4 = M_4 - \frac{\Delta M_2}{\tau_c^2}. \tag{2}$$

In Eq. (2) τ_c is the correlation time characterizing the molecular motion and

$$\Delta M_2 = M_2 - \bar{M}_2,$$

where M_2 is the second moment of NMR line in rigid lattice and $\bar{M}_2$ is the second moment of motionally narrowed NMR line.

The other approach has been proposed in [8, 9]. In this approach the NMR lineshape $f(\Delta)$ is represented in the form of an infinite fraction

$$f(\Delta) = \mathrm{Re}\cfrac{1}{i\Delta - i\omega_0 + \cfrac{\nu_0^2}{i\Delta - i\omega_1 + \cfrac{\nu_1^2}{i\Delta - i\omega_2 + \cfrac{\nu_2^2}{\ddots}}}}. \tag{3}$$

In Eq. (3) $\Delta = \omega - \omega_L$, where $\omega_L = \gamma B_0$ is the Larmor frequency (γ is the magnetogyric ration of nucleus).

The coefficients ν_n^2 and ω_n are connected with coefficients a_n [8, 9]:

$$\omega_0 \equiv a_1, \tag{4a}$$

$$\nu_0^2 = a_2 - a_1^2, \tag{4b}$$

$$\omega_1 \equiv \frac{a_3 - a_1 a_2}{\nu_0^2} - \omega_0 = \frac{a_3 - 2a_1 a_2 + a_1^3}{\nu_0^2}, \tag{4c}$$

$$\nu_1^2 = \frac{a_4 - a_2^2}{\nu_0^2} - (\omega_0 + \omega_1)^2. \tag{4d}$$

. . .

In the case of rigid lattice the well-known result follows from (3) [10].

In this report we consider the application of Eq. (3) to simple model of quadrupolar nucleus with spin $I = 1$ (or isolate water molecule) jumping between two positions in lattice for which the NMR resonance frequencies are ω_1 and ω_2. This simple model has the well-known exact solution [1, 11-13].

The so-called stochastic Liouville equation for this case has the form [11, 12]

$$\frac{d}{dt}\vec{I}_X(t) = -i\tilde{L}\cdot\vec{I}_X(t), \tag{5}$$

where Liouville superoperator $\tilde{L}$ is

$$\tilde{L} = \begin{pmatrix} \bar{\omega} + \delta - iW & iW \\ iW & \bar{\omega} - \delta - iW \end{pmatrix}, \tag{6}$$

and

$$\vec{I}_X(t) \equiv \begin{pmatrix} I_{X1}(t) \\ I_{X2}(t) \end{pmatrix}. \tag{7}$$

In Eq. (6)

$$\omega_1 = \bar{\omega} + \delta, \quad \omega_2 = \bar{\omega} - \delta$$

and W is the rate constant which describes the probability of the nucleus jump.
The formal solution of (5) can be written as

$$\vec{I}_X(t) = \exp(-i\tilde{L}t)\cdot\vec{I}_X(0). \tag{8}$$

From Eq. (8) it follows

$$G(t) = \frac{\langle\vec{I}_X(t)\,|\,\vec{I}_X(0)\rangle}{\langle\vec{I}_X(0)\,|\,\vec{I}_X(0)\rangle} = \frac{\langle\vec{I}_X(0)\,|\,\exp(-i\tilde{L}t)\,|\,\vec{I}_X(0)\rangle}{\langle\vec{I}_X(0)\,|\,\vec{I}_X(0)\rangle} = \sum_{n=0}^{\infty}\frac{(-it)^n}{n!}\frac{\langle\vec{I}_X(0)\,|\,\tilde{L}^n\,|\,\vec{I}_X(0)\rangle}{\langle\vec{I}_X(0)\,|\,\vec{I}_X(0)\rangle} \tag{9}$$

and so the coefficients a_n are defined by equation

$$a_n = \frac{\langle \vec{I}_X(0) | \tilde{L}^n | \vec{I}_X(0) \rangle}{\langle \vec{I}_X(0) | \vec{I}_X(0) \rangle}. \tag{10}$$

Using Liouville superoperator (6) we obtain from Eq. (10)

(11)

$$a_2 = \bar{\omega}^2 + \delta^2, \tag{12}$$

$$a_3 = \bar{\omega}^3 + 3\bar{\omega}\delta^2 - i2W\delta^2, \tag{13}$$

$$a_4 = \bar{\omega}^4 + 6\bar{\omega}^2\delta^2 + \delta^4 + 4\delta^2 W^2. \tag{14}$$

Using Eqs. (11-14) we have from Eqs. (4)

$$\omega_0 = a_1 = \bar{\omega}, \tag{15}$$

$$\nu_0^2 = a_2 - a_1^2 = \delta^2, \tag{16}$$

$$\omega_1 \equiv \frac{a_3 - a_1 a_2}{\nu_0^2} - \omega_0, \quad = \bar{\omega} - i2W \tag{17}$$

$$\nu_1^2 = \frac{a_4 - a_2^2}{\nu_0^2} - (\omega_0 + \omega_1)^2 = 0. \tag{18}$$

Using these values we can write Eq. (3) in the form

$$f(\Delta) = \mathrm{Re}\,\frac{1}{i\Delta - i\bar{\omega} + \dfrac{\delta^2}{i\Delta - i\bar{\omega} - 2W}} = \mathrm{Re}\,\frac{i\Delta\omega - 2W}{-(\Delta\omega)^2 - i2W(\Delta\omega) + \delta^2}, \tag{19}$$

where $\Delta\omega = \Delta - \bar{\omega}$.
From Eq. (19) it follows

$$f(\Delta) = \frac{2W\delta^2}{\Delta\omega^4 + 2\Delta\omega^2(2W^2 - \delta^2) + \delta^4}. \tag{20}$$

The obtained expression (20) fully coincides with one obtained in [1, 11-13].

In conclusion, it should be note that in the considered model the dipolar interactions between different nuclei (intermolecular interactions) were neglected. Usually these interactions may be included in consideration by introducing the phenomenological parameter T_2 [12, 13]. We hope the Eq. (3) can be treated as the base for making further approximations in order to find the most convenient way of describing the intermolecular dipolar interaction in NMR spectra of mobile water molecules and ^2H nuclei.

References

[1] Abragam A., *The Principles of Nuclear Magnetism,* University Press, Oxford, 1961.
[2] Anderson P. W. and Weiss P. R., Rev. Mod. Phys. **25**, 269 (1953).
[3] Dattagupta S., *Relaxation Phenomena in Condensed Matter Physics*, Academic Press, 1987.
[4] Low I. J., Vollmers K. W. and Punkkinen M., *Proceedings of the Specialized Coloque AMPERE – Kraków*, 70 (1973).
[5] Low I. J., *Proceedings of the IV AMPERE International Summer School – Pula,* 343 (1977).
[6] Van Vleck J. H., Phys. Rev. **74**, 1148 (1948).
[7] Sergeev N. A. and Ryabushkin D. S., Izvest. Vuzov (Fizyka) **7**, 48 (1982) (in Russian).
[8] Sergeev N. A. and Ryabushkin D. S., *Abstracts of IX AMPERE School – Novosibirsk*, 291 (1987).
[9] Sergeev N. A. et al., Izvest. Vuzov (Fizyka) **11**, 15 (1989) (in Russian).
[10] Lado F., Memory J. D. and Parker G. W., Phys. Rev. **4**, 1406 (1971).
[11] Spiess H. W. and Sillescu H., J. Magn. Res. **42**, 381 (1981).
[12] Sergeev N. A. et al., J. Struct. Chem. **22**, 83 (1981).
[13] Sapiga A. V. and Sergeev N. A., Mol. Phys. Rep. **29**, 60 (2000).