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WEAK PERTURBING RADIO-FREQUENCY FIELD EFFECTS IN NUCLEAR MAGNETIC DOUBLE RESONANCE. I

Line splittings and intensity changes in NMR spectra caused by an additional weak rf field H_2 have been investigated by several authors. Freeman and Anderson [1] have developed a theory for line splittings in terms of quantum transitions in a rotating frame. Kaiser [2] has discussed experiments where only changes of relative intensities of spectral lines are observed. Recently, the equations of motion of the density matrix of a nuclear spin system with nondegenerate energy levels and without accidental equalities in the differences of eigenvalues of the unperturbed Hamiltonian H_0 (nondegenerate systems) has been given in a simple form by Baldeschwieler [3].

Starting from these equations a density matrix description of effects caused by weak perturbing rf fields is presented in this paper. The laboratory coordinate system has been found useful in this case. We also assumed that all nuclei in the nuclear spin system of the molecule have the same positive magnetogyric ratio γ .

1. The Hamiltonian of the nuclear spin system of a molecule in an isotropic liquid interacting with external magnetic field

$$\mathbf{H} = H_0 \mathbf{k} + (2H_1 \cos \omega_1 t + 2H_2 \cos \omega_2 t) \mathbf{i} \quad (1)$$

is given by

$$\hat{h}\mathbf{H} = \hat{h}\mathbf{H}_0 + \hat{h}\mathbf{H}_1 + \hat{h}\mathbf{H}_2 + \hat{h}\mathbf{G}, \quad (2)$$

where

$$H_0 = - \left\{ \sum_j \omega_j I_{zj} + \sum_{j < k} J_{jk} (\mathbf{I}_j \cdot \mathbf{I}_k) \right\} \quad (3)$$

$$H_1 = D_{+1} e^{i\omega_1 t} + D_{-1} e^{-i\omega_1 t} \quad (4)$$

$$H_2 = D_{+2} e^{i\omega_2 t} + D_{-2} e^{-i\omega_2 t} \quad (5)$$

$$D_{\pm 1} = -\frac{1}{2} \gamma H_1 F_{\pm}$$

$$D_{\pm 2} = -\frac{1}{2} \gamma H_2 F_{\pm} \quad (6)$$

F is the total spin operator of the nuclear spin system and $\hat{h}\mathbf{G}$ represents random interaction with molecular surroundings. The eigenvalues and eigenvectors of the operator H_0 will be denoted according to the equation

$$H_0 |a\rangle = a |a\rangle. \quad (7)$$

Introducing the deviation matrix χ by the relation

$$\chi = \sigma - \sigma_0 \quad (8)$$

where σ is the density matrix and σ_0 its expression for thermal equilibrium, the equations of Baldeschwieler [3], in the representation in which H_0 is diagonal, are given by

$$\frac{d}{dt} \langle a|\chi|a' \rangle + \left\{ \frac{1}{T_{aa'2}} + i(a-a') \right\} \langle a|\chi|a' \rangle + i \langle a|[H_1+H_2, \chi]|a' \rangle = \\ = iq(a'-a) \langle a|H_1+H_2|a' \rangle \quad \text{if } a \neq a' \quad (9)$$

$$\frac{d}{dt} \langle a|\chi|a \rangle + i \langle a|[H_1+H_2, \chi]|a \rangle = \sum_{b=1}^p W_{ab} \{ \langle b|\chi|b \rangle - \langle a|\chi|a \rangle \}. \quad (10)$$

In the equations (9), (10) the quantities $\frac{1}{T_{aa'2}}$, W_{ab} , q are the same as used in [3].

2. We introduce new matrices $z^{(k)}(t)$, $k=0, 1, 2, \dots, 2F$ by the following relations

$$\langle a|\chi|a' \rangle = \begin{cases} z_{aa'}^{(k)}(t) e^{ik\omega_2 t} & , \text{ if } M_a - M_{a'} = k \\ 0 & , \text{ if } M_a - M_{a'} \neq k. \end{cases} \quad (11)$$

In the definition (11) F denotes the quantum number of operator F^2 and M_a the eigenvalue of operator F_z in state "a".

$$\text{Since } \chi \text{ is Hermitian,} \quad z_{a'a}^{(k)} = \bar{z}_{aa'}^{(k)}. \quad (12)$$

$$\text{Using further the abbreviation} \quad \langle a|\chi|a \rangle = \chi_a. \quad (13)$$

and taking into account the selection rules for the matrix elements of the operators $D_{\pm 1}$ and $D_{\pm 2}$, one obtains with the use of Eq. (11) from equations (9) and (10)

$$\frac{d\chi_a}{dt} + i \langle a|[B_+ + B_-, z^{(1)}]|a \rangle = \sum_b W_{ab} (\chi_b - \chi_a) \quad (14)$$

$$\sum_b \chi_b = 0 \quad (15)$$

$$\frac{dz_{aa'}^{(0)}}{dt} + \left\{ \frac{1}{T_{aa'2}} + i(a-a') \right\} z_{aa'}^{(0)} + i \langle a|[B_+ + B_-, z^{(1)}]|a' \rangle = 0 \quad (16)$$

$$\frac{dz_{aa'}^{(1)}}{dt} + \left\{ \frac{1}{T_{aa'2}} + i(a-a'+\omega_1) \right\} z_{aa'}^{(1)} + i \langle a|[B_+, z^{(0)}]|a' \rangle +$$

$$+ i \langle a|[B_-, z^{(2)}]|a' \rangle = i \langle a|B_+|a' \rangle \{ q(a'-a) - (\chi_{a'} - \chi_a) \} \quad (17)$$

$$\frac{dz_{aa'}^{(k)}}{dt} + \left\{ \frac{1}{T_{aa'2}} + i(a-a'+k\omega_2) \right\} z_{aa'}^{(k)} + i \langle a|[B_+, z^{(k-1)}]|a' \rangle + \\ + i \langle a|[B_-, z^{(k+1)}]|a' \rangle = 0 \quad \text{if } k > 1, \quad (18)$$

$$\text{where} \quad B_{\pm} = D_{\pm 2} + D_{\pm 1} e^{\pm i2t} \quad (19)$$

$$\Omega = \omega_1 - \omega_2 \quad (20)$$

The x component of the macroscopic nuclear polarization vector is now given by

$$M_x = \sum_{a < b} \sum \operatorname{Re} \{ \langle b | \mathbf{M}_- | a \rangle z_{ab}^{(1)} \} \cos \omega_2 t - \operatorname{Im} \{ \langle b | \mathbf{M}_- | a \rangle z_{ab}^{(1)} \} \sin \omega_2 t, \quad (21)$$

where

$$\mathbf{M}_\pm = N_0 \gamma \hbar \mathbf{F}_\pm \quad (22)$$

and N_0 denotes the number of nuclear spin systems per unit volume.

3. Steady-state solutions of equations (14) — (18) can be obtained in the case of weak rf fields by expressing all the matrix elements as Fourier series

$$\chi_a(t) = \sum_n \chi_{an} e^{in\Omega t} \quad (23)$$

$$z_{aa'}^{(k)}(t) = \sum_n Y_{aa'n}^{(k)} e^{in\Omega t}. \quad (24)$$

Because of the relation (12) and since χ is Hermitian

$$\chi_{a, -n} = \overline{\chi_{an}} \quad (25)$$

$$Y_{aa', -n}^{(k)} = \overline{Y_{a'an}^{(k)}}. \quad (26)$$

Inserting (23) and (24) into equations (14) — (18) and selecting terms of equal order in Ω one obtains

$$\sum_b W_{ab} (\chi_{bn} - \chi_{an}) = in\Omega \chi_{an} + i \langle a | [\mathbf{D}_{-2} + \mathbf{D}_{+2}, Y_n^{(1)}] | a \rangle + i \langle a | [\mathbf{D}_{-1}, Y_{n+1}^{(1)}] | a \rangle + i \langle a | [\mathbf{D}_{+1}, Y_{n-1}^{(1)}] | a \rangle \quad (27)$$

$$\sum_b \chi_{bn} = 0 \quad (28)$$

$$Y_{aa'n}^{(0)} = -i \frac{\langle a | [\mathbf{D}_{+2} + \mathbf{D}_{-2}, Y_n^{(1)}] | a' \rangle + \langle a | [\mathbf{D}_{+1}, Y_{n-1}^{(1)}] | a' \rangle + \langle a | [\mathbf{D}_{-1}, Y_{n+1}^{(1)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + n\Omega)} \quad (29)$$

$$Y_{aa'0}^{(1)} = +i \frac{\langle a | \mathbf{D}_{+2} | a' \rangle \{ q(a' - a) - (\chi_{a'0} - \chi_{a0}) \} + \langle a | \mathbf{D}_{+1} | a' \rangle (\chi_{a,-1} - \chi_{a',-1})}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_2)}$$

$$-i \frac{\langle a | [\mathbf{D}_{+2}, Y_0^{(0)}] | a' \rangle + \langle a | [\mathbf{D}_{-2}, Y_0^{(2)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_2)}$$

$$-i \frac{\langle a | [\mathbf{D}_{+1}, Y_{-1}^{(0)}] | a' \rangle + \langle a | [\mathbf{D}_{-1}, Y_{+1}^{(2)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_2)} \quad (30)$$

$$\begin{aligned}
 Y_{aa',+1}^{(1)} = & + i \frac{\langle a | D_{+1} | a' \rangle \{ q(a' - a) - (\chi_{a'0} - \chi_{a0}) \} + \langle a | D_{+2} | a' \rangle (\chi_{a1} - \chi_{a'1})}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_1)} \\
 & - i \frac{\langle a | [D_{+1}, Y_0^{(0)}] | a' \rangle + \langle a | [D_{-1}, Y_2^{(2)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_1)} \\
 & - i \frac{\langle a | [D_{+2}, Y_1^{(0)}] | a' \rangle + \langle a | [D_{-2}, Y_1^{(2)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_1)} \quad (31)
 \end{aligned}$$

$$\begin{aligned}
 Y_{aa'n}^{(1)} = & + i \frac{\langle a | D_{+2} | a' \rangle (\chi_{an} - \chi_{a'n}) + \langle a | D_{+1} | a' \rangle (\chi_{a,n-1} - \chi_{a',n-1})}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_2 + n\Omega)} \\
 & - i \frac{\langle a | [D_{+2}, Y_n^{(0)}] | a' \rangle + \langle a | [D_{-2}, Y_n^{(2)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_2 + n\Omega)} \\
 & - i \frac{\langle a | [D_{+1}, Y_{n-1}^{(0)}] | a' \rangle + \langle a | [D_{-1}, Y_{n+1}^{(2)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + \omega_2 + n\Omega)} \quad (32)
 \end{aligned}$$

$$\begin{aligned}
 Y_{aa'n}^{(k)} = & - i \frac{\langle a | [D_{+2}, Y_n^{(k-1)}] | a' \rangle + \langle a | [D_{-2}, Y_n^{(k+1)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + k\omega_2 + n\Omega)} \\
 & - i \frac{\langle a | [D_{+1}, Y_{n-1}^{(k-1)}] | a' \rangle + \langle a | [D_{-1}, Y_{n+1}^{(k+1)}] | a' \rangle}{\frac{1}{T_{aa'2}} + i(a - a' + k\omega_2 + n\Omega)} \quad \text{if } k > 1. \quad (33)
 \end{aligned}$$

In view of (23) and (24) the expression for M_x is now given by

$$\begin{aligned}
 M_x = & \sum_n \sum_{a < b} \text{Re} \{ \langle b | \mathbf{M}_- | a \rangle Y_{abn}^{(1)} \} \cos(\omega_2 + n\Omega)t - \\
 & - \text{Im} \{ \langle b | \mathbf{M}_- | a \rangle Y_{abn}^{(1)} \} \sin(\omega_2 + n\Omega)t. \quad (34)
 \end{aligned}$$

4. The Fourier series (23) and (24) converge rapidly and most of the matrix elements can be neglected if for any different a, b, a', b'

$$1) \quad |a - b| \gg \frac{1}{T_2}, \quad \gamma H_2, \quad \gamma H_1. \quad (35)$$

$$2) \quad |(a' - a) - (b' - b)| \gg \frac{1}{T_2}, \quad \gamma H_2, \quad \gamma H_1 \quad (36)$$

$$3) \quad \Omega \gg \sum_{b=1}^p W_{ab}. \quad (37)$$

Actually the conditions (35) — (37) define the meaning of "weak rf fields" and "lack of approximate degeneracy of a spin system".

The condition (37) implies that the only nonvanishing diagonal elements are time independent ($n=0$) and the matrix elements χ_{a0} will be denoted simply by χ_a . It is apparent from equations (29) ÷ (33) and the

conditions (35), (36) that an appreciable contribution from the matrix elements of various harmonics such as $Y_{aa'n}^{(k)}$ only arises if the resonance condition $k\omega_2 + n\Omega \approx a' - a$ is fulfilled. It is further seen from equations (29) ÷ (33) that $Y_{aa'n}^{(k)}$ ($n \neq 0, 1$) may have an appreciable value only if either $Y_{bb'1}^{(1)} \neq 0$ or $Y_{bb'0}^{(1)} \neq 0$. Let us assume that the following resonance conditions are fulfilled

$$\omega_2 \approx c' - c \quad (38)$$

$$\omega_1 \approx d' - d \quad (39)$$

so that $Y_{cc'0}^{(1)} \neq 0$ and $Y_{dd'1}^{(1)} \neq 0$. Inserting these matrix elements (and corresponding elements given by (26)) into equations (29), (30) and taking into account the conditions (35), (36) and selection rules for matrix elements of $D_{\pm 1}$, $D_{\pm 2}$, one obtains the following three possible cases:

1) if $c, c' \neq d, d'$ the only significant off-diagonal matrix elements are $Y_{cc'0}^{(1)}$ and $Y_{dd'1}^{(1)}$

2) if $c = d$ (the $\Lambda = 0$ case in the notation of Freeman and Anderson), we get an additional nonvanishing matrix element

$$Y_{c'd'1}^{(0)} = -i \frac{\langle c' | D_{-2} | c \rangle Y_{cd'1}^{(1)} - \langle c | D_{+1} | d' \rangle \bar{Y}_{cc'0}^{(1)}}{\frac{1}{T_{c'd'2}} + i(c' - d' + \Omega)} \quad (40)$$

3) if $c' = d$ (the $\Lambda = 2$ case), the matrix element

$$Y_{cd'1}^{(2)} = -i \frac{\langle c | D_{+2} | c' \rangle Y_{c'd'1}^{(1)} - \langle c' | D_{+1} | d' \rangle \bar{Y}_{cc'0}^{(1)}}{\frac{1}{T_{cd'2}} + i(c - d' + \omega_2 + \omega_1)} \quad (41)$$

does not vanish (in addition to $Y_{cc'0}^{(1)}$ and $Y_{dd'1}^{(1)}$).

According to equation (34) $Y_{dd'1}^{(1)}$ is the only matrix element that contributes to the signal since the induction signal at frequency ω_1 is usually observed. As a consequence of Eq. (31), we find that M_x depends upon the strength and frequency of the field H_2 through diagonal matrix elements ($\chi_{d'} - \chi_d$) (nuclear Overhauser effect) and through off-diagonal elements $Y_{c'd'1}^{(0)}$ or $Y_{cd'1}^{(2)}$ (line splitting).

5. Let us suppose that

$$H_1 \ll H_2 \quad (42)$$

so that we can neglect terms with $D_{\pm 1}$ in equations (27) and (30). According to Bloch [4] one obtains the solutions of equations (27) in the form

$$\chi_{c'} - \chi_c = \frac{2|\langle c | D_{+2} | c' \rangle|^2 T_{c'c1} T_{cc'2} q(c' - c)}{1 + (\Delta\omega_2 T_{cc'2})^2 + 2|\langle c | D_{+2} | c' \rangle|^2 T_{c'c1} T_{cc'2}} \quad (43)$$

$$\chi_{d'} - \chi_d = \frac{T_{a'a1}}{T_{c'c1}} (\chi_{c'} - \chi_c), \quad (44)$$

where $\Delta\omega_2 = \omega_2 - (c' - c)$ (45)

$$T_{a'a1} = T_{a'a} = T_a \quad (46)$$

The quantities T_a depend only upon the relaxation coefficients and can be found from a system of equations that takes the form

$$\begin{aligned} \sum_b W_{cb} T_{bc1} &= 1 \\ \sum_b W_{c'b} T_{bc'1} &= -1 \\ \sum_b W_{ab} T_{ba1} &= 0, \quad \text{if } a \neq c, c' \\ \sum_b T_b &= 0. \end{aligned} \quad (47)$$

Inserting the solution (43) into equation (30) and taking into account the condition (42), we find

$$Y_{cc'0}^{(1)} = \frac{\langle c | D_{+2} | c' \rangle T_{cc'2} q (c' - c) (i + \Delta\omega_2 T_{cc'2})}{1 + (\Delta\omega_2 T_{cc'2})^2 + 2 \langle c | D_{+2} | c' \rangle^2 T_{c'c1} T_{cc'2}}. \quad (48)$$

Consequently

$$q(a' - a) - (\chi_{a'} - \chi_a) = q(c' - c) (1 - S_{a'a}) \quad (49)$$

since $(a' - a) \approx (c' - c)$. The saturation parameter $S_{a'a}$ in (48) and (49) is given by

$$S_{a'a} = \frac{T_{a'a1}}{T_{c'c1}} \cdot \frac{2 \langle c | D_{+2} | c' \rangle^2 T_{cc'2} T_{c'c1}}{1 + (\Delta\omega_2 T_{cc'2})^2 + 2 \langle c | D_{+2} | c' \rangle^2 T_{cc'2} T_{c'c1}}. \quad (50)$$

If there are no common energy levels ($c, c' \neq d, d'$), the second and third terms in equation (31) can be neglected and we get

$$Y_{dd'1}^{(1)} = \frac{\langle d | D_{+1} | d' \rangle T_{dd'2} q (c' - c) (1 - S_{d'd}) (i + \Delta\omega_1 T_{dd'2})}{1 + (\Delta\omega_1 T_{dd'2})^2}, \quad (51)$$

where

$$\Delta\omega_1 = \omega_1 - (d' - d). \quad (52)$$

Inserting Eq. (50) into Eq. (34) we obtain for the absorption signal

$$V_{dd'1} = \frac{\langle d | D_{+1} | d' \rangle \langle d' | M_- | d \rangle q (c' - c) T_{dd'2} (1 - S_{d'd})}{1 + (\Delta\omega_1 T_{dd'2})^2}. \quad (53)$$

As a consequence of Eq. (53) and Eq. (50) only changes of relative intensities of spectral lines can be observed in the case of frequency — swept ($\Delta\omega_2 = \text{const}$) spectra (pure Overhauser effect). The relative intensities depend upon H_2 , $\Delta\omega_2$, $T_{c'c1}$, $T_{d'd1}$, $T_{cc'2}$ and $T_{dd'2}$. The necessary relaxation times can be found from equations (47) which are similar to expressions of Kirchoff law and can be solved by dc electrical analogue circuits [4]. The saturation parameter $S_{a'a}$ can have positive or negative values, but always

$$0 \leq |S_{a'a}| \leq 1. \quad (54)$$

Possible changes of relative intensities of spectral lines by a pure Overhauser effect are given by inequalities (54).

6. We shall further consider nuclear spin systems with a common energy level "l" for ω_1 and ω_2 (the $\Lambda=0; 2$ cases). Inserting the expressions (40), (41) and (49) into equation (31), we obtain

$$Y_{td'1}^{(1)} = i \frac{\langle t | \mathbf{D}_{+1} | d' \rangle q(c' - c) T_{td'2} (1 - S_{d't})}{1 + i\Delta\omega_1 T_{td'2} + \frac{|\langle c | \mathbf{D}_{+2} | c' \rangle|^2 T_{td'2} T_{rd'2}}{1 + i(\Delta\omega_1 \mp \Delta\omega_2) T_{rd'2}}} +$$

$$+ \frac{\langle t | \mathbf{D}_{+1} | d' \rangle \langle t | \mathbf{D}_{\pm 2} | r \rangle T_{td'2} T_{rd'2} Y_{rt0}^{(1)}}{(1 + i\Delta\omega_1 T_{td'2}) [1 + i(\Delta\omega_1 \mp \Delta\omega_2) T_{rd'2}] + |\langle c | \mathbf{D}_{+2} | c' \rangle|^2 T_{td'2} T_{rd'2}}. \quad (55)$$

If $\Lambda = 0$, then $t = c$, $r = c'$ and the upper signs hold.

If $\Lambda = 2$, then $t = c'$, $r = c$ and the lower signs hold.

Inserting Eq. (48) into Eq. (55) and the result into Eq. (34) we get the expression for the absorption signal $V_{td'1}$. Using the notations

$$\lambda_{td'} = \langle d' | \mathbf{M}_- | t \rangle \langle t | \mathbf{D}_{+1} | d' \rangle T_{td'2} q(c' - c) \quad (56)$$

$$h^2 = |\langle c | \mathbf{D}_{+2} | c' \rangle|^2 T_{rd'2}^2 \quad (57)$$

$$\alpha_1 = \Delta\omega_1 T_{rd'2} \quad (58)$$

$$\alpha_2 = \Delta\omega_2 T_{rd'2} \quad (59)$$

$$\tau_1 = \frac{T_{td'1}}{T_{c'c1}} \quad (60)$$

$$\tau_2 = \frac{T_{c'c1}}{T_{rd'2}} \quad (61)$$

$$v_1 = \frac{T_{td'2}}{T_{rd'2}} \quad (62)$$

$$v_2 = \frac{T_{c'c2}}{T_{rd'2}} \quad (63)$$

this expression takes the form

$$\frac{V_{td'1}}{\lambda_{td'}} = (1 \mp \tau_1 S) \frac{1 + \frac{h^2 v_1}{1 + (\alpha_1 \mp \alpha_2)^2}}{\left[1 + \frac{h^2 v_1}{1 + (\alpha_1 \mp \alpha_2)^2} \right]^2 + \left[v_1 \alpha_1 - \frac{v_1 h^2 (\alpha_1 \mp \alpha_2)}{1 + (\alpha_1 \mp \alpha_2)^2} \right]^2} \mp$$

$$\mp \frac{S}{\tau_2} \frac{[1 + v_1 h^2 - \alpha_1 (\alpha_1 \mp \alpha_2) v_1] \pm v_2 \alpha_2 [v_1 \alpha_1 + (\alpha_1 \mp \alpha_2)]}{[1 + v_1 h^2 - \alpha_1 (\alpha_1 \mp \alpha_2) v_1]^2 + [v_1 \alpha_1 + (\alpha_1 \mp \alpha_2)]^2}, \quad (64)$$

where

$$S = \frac{2h^2 v_2 \tau_2}{1 + v_2^2 \alpha_2^2 + 2h^2 v_2 \tau_2}. \quad (65)$$

In the formula (64) the same convention for signs and indices as in Eq. (55) has been used.

It should be noted that in case of a common energy level for ω_1 and ω_2 from the definition of $T_{rd'2}$ [3] and the electrical analogue, it follows that

$$0 \leq \tau_1 \leq 1 \quad (66)$$

$$0 \leq \frac{1}{\tau_2} \leq 1. \quad (67)$$

Formula (64) describes both line splittings and intensity changes that are caused by a weak perturbing field H_2 . Unlike the formula of Freeman and Anderson [1] it contains 4 relaxation parameters. An expression for the dispersion signal can similarly be derived from Eq. (55).

7. The expressions (53) and (64) hold for spin systems in a completely homogenous strong magnetic field H_0 . To compare these formulae with experimental data, the field inhomogeneities must be taken into account.

Because of the field inhomogeneities the resonance frequencies $\omega_{a'a} = (a' - a)$ for any two levels a, a' are somewhat different for various molecules. Let $g(\xi) d\xi$ denote the relative number of spin systems with resonance frequencies between $\omega_{a'a}$ and $\omega_{a'a} + d\omega_{a'a}$.

$$\xi = \omega_{a'a} - \langle \omega_{a'a} \rangle_{av}. \quad (68)$$

Let further
$$\Delta\omega_1^* = \omega_1 - \langle \omega_{d'd} \rangle_{av}. \quad (69)$$

$$\Delta\omega_2^* = \omega_2 - \langle \omega_{c'c} \rangle_{av}. \quad (70)$$

Noting that
$$\Delta\omega_1^* = \Delta\omega_1 + \xi \quad (71)$$

$$\Delta\omega_2^* = \Delta\omega_2 + \xi \quad (72)$$

we obtain for absorption signal in inhomogenous field

$$V_{dd'}^*(\Delta\omega_1^*, \Delta\omega_2^*) = \int_{-\infty}^{+\infty} V_{dd'}(\Delta\omega_1^* - \xi; \Delta\omega_2^* - \xi) g(\xi) d\xi. \quad (73)$$

Inserting one of the equations (53), (64) into the formula (73), we can calculate line shapes for various experimental conditions. For frequency — swept spectra $\Delta\omega_2^* = \text{const}$ and the signal $V(\Delta\omega_1^*)$ is observed. For field — swept spectra the condition $\Delta\omega_1^* = \Delta\omega_2^*$ is to be inserted into (73).

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NÕRGA RAADIOSAGEDUSLIKU HÄIREVÄLJA EFEKTID TUUMA MAGNETILISE TOPELTRESONANTSIS. I

Lähtudes Baldeschwieleri poolt antud võrrandeist tiheduse maatriksile kõdunemata süsteemide puhul, tuletatakse valemid, mis kirjeldavad spektraaljoonte lõhenemist ja intensiivsuse muutumist suure lahtuvusega tuuma magnetilise resonantsi spektrites nõrga kõrgsagedusliku lisamagnetvälja toimele.

В. СИНИВЕЕ, Э. ЛИППМАА

ЭФФЕКТЫ СЛАБОГО ВОЗМУЩАЮЩЕГО РАДИОЧАСТОТНОГО ПОЛЯ В ДВОЙНОМ ЯДЕРНОМ МАГНИТНОМ РЕЗОНАНСЕ. I

Исходя из уравнений движения для матрицы плотности, предложенных Бальдешвиером, выводятся формулы, описывающие расщепления и изменения интенсивностей спектральных линий в ЯМР спектрах высокого разрешения под воздействием слабого дополнительного высокочастотного магнитного поля.