

Nuclear Magnetic Spectra of Hindered Rotating CH₃ Group. I.

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1. Introduction

Many of the works have already been reported¹⁻⁵, as to the influence from a molecule or a part of it upon nuclear spin Zeeman levels of nuclei contained in the molecule, and its applications to the structural investigation. According to these authors, line width and fine-structures of nuclear spin Zeeman spectra of nuclei having effectively rigid structure, mainly originate from magnetic dipoles; and when the molecule or the part of it carries out a rotational motion, the fine-structures change and line width decreases. These influence of nuclear motion upon the nuclear magnetic spectra depend upon rate of the motion; be $\delta\nu$ a measure of fine-structure splitting or of line width, influence of motion reveals itself in the proximity of the reorientation rate of molecule in solids, ν_c , exceeding $\delta\nu$. Namely, for the case $\nu_c \ll \delta\nu$ the spectrum is essentially the same as that of the rigid case, and for the case $\nu_c \gg \delta\nu$ the spectrum may be explained as a fine-structure which is an average of dipolar interactions over the motion². Bloembergen, Purcell, and Pound¹ have calculated the influence, making a statistical assumption, and obtained

$$(\delta\nu)^2 = B^2 (2/\pi) \tan^{-1} [a(\delta\nu/\nu_c)] + C^2 \quad (1)$$

The expression cited is the one rewritten by Gutowsky and Pake². $A = (B^2 + C^2)^{1/2}$ is the line width in the case of rigid structure, C being that of free rotation. As for the transition of the shape of the spectrum, there is a result by Gutowsky and Saika^{6,7}.

Starting from the Bloch's semi-classical equation, they related the shape of nuclear magnetic spectrum of a nucleus exchanged between two chemically distinct states with the exchange rate between the two states. Although this work is a result on the nuclear magnetic spectrum of the liquid and is an analysis on the relation between chemical fine-structure and motion, it may be applicable to the fine-structure from dipolar interaction in solid. The results of Gutowsky and Saika⁶ show the transition of spectral shape or that of line width takes place in the proximity of $\zeta \cdot \delta\nu \sim 1$, where ζ denotes the life time of a chemical state or the reciprocal of the exchange rate, which corresponds to $1/\nu_c$ in a solid. $\delta\nu$ is the value of chemical shift, and in the case of nucleus in a solid it may be taken of the value of dipolar interaction in frequency scale.

From these results it was expected that the transition of the shape and the line width of the nuclear magnetic spectrum of a solid organic compound may provide useful

informations as to motions of a molecule or a part of it. Gutowsky and Pake² obtained the temperature dependence of ν_c in 1, 1, 1-trichloroethane employing Eq. (1), and assuming

$$\nu_c = \nu_0 e^{-V/RT}, \quad (2)$$

obtained the value of the hindering potential of CH₃ group in 1, 1, 1-trichloroethane, $V=7000$ cal./mole. Later, Powles and Gutowsky³ had obtained a value of $V=2700$ cal./mole for the same substance with the same method. It is the consequence of that the experimental plot of $\log \nu_c$ versus $1/T$ for finding the potential turns out to be a curved line instead of a linear one. Moreover, qualitatively many available results were obtained²⁻⁵; but there are many problems remained to be discussed about hindered rotation of a molecule or a part of it exactly according to these methods. First of all, as Gutowsky and Pake² had pointed, α of Equation (1) involves uncertainty of definition about line width and of statistical assumption about motion. And also, in case of the specified motion such as internal motion of a molecule. Eq. (42) of B. P. P¹. the starting point of Eq. (1), not always applies exactly.

Furthermore, Powles and Gutowsky⁴ have observed several transitions of line width corresponding to internal motion of CH₃ group in the proton magnetic spectrum of CH₃ groups, and found interesting changes of spectral line-shape in the transition region of line width. Although analyses of these line-shape change may promise further information about internal motion of CH₃ group, there is still no analysis of spectral line structure accomplished which is sufficient to interpret the experimental result.

Authors intended to calculate fine structures of nuclear spin Zeeman levels attributable to magnetic dipolar interaction in the case of presence of motion, with rather proper quantum mechanical method instead of semi-classical method with Bloch's equation. Gutowsky and Pake² assumed that spin wave function and orbital wave function of hindered rotating group of nuclei are separable from each other, and then using

$$\psi = \sum_{\tau=-\infty}^{\infty} a_{\tau} e^{i\tau n\theta} \quad (n > 3) \quad (3)$$

as the orbital wave function with respect to the angle θ , about axis of internal rotation, where n is the numbers of period in 2π , they concluded that the expectation value of dipolar interaction energy over this wave function equals the classical average over θ . But it is expected that spin and orbital wave function are involved as non-product form in the consequence of perturbation term involving θ . Therefore, the wave function, Eq. (3), is to be regarded as an approximation which started from a wave function of free rotation and is taking account of tunnelling between hindering potential well; and therefore when the rotator is strongly bounded to a potential well, terms $\tau n \not\equiv 0 \pmod{3}$ (when $n=3$), the terms which is symmetric or anti-symmetric with respect to whole rotation, must be involved in summation in Eq. (3)⁸. On the assumption of hindering potential $\frac{H}{2}(1-\cos 3\theta)$, we started from wave functions for strongly bounded rotator⁸ and Andrew-Bersohn's equi-lateral triangular spin wave functions, and obtained the exact

solution of wave equation for rotating CH₃ group which involves orbital and spin part simultaneously. Rotational vibration levels of strongly bounded rotator split into tunnelling doublet which have splitting w corresponding to tunnelling frequency⁸. Our results of calculation show that the transition of fine structure of rotating triangular spin system occurs in the proximity of

$$w \sim \mu a, \quad (4)$$

where μ denotes nuclear magnetic moment, a denotes dipole-field factor, so (μa) is a measure of dipolar interaction energy. Writing $w = h \nu_c$, ν_c may be considered of tunnelling frequency or a sort of reorientation frequency, and so Eq. (4) agrees with former results $\nu_c \sim \delta\nu$. According to our results of calculation, the fine-structures transfer to Andrew-Bersohn's⁹ rigid case or rotating case, when $w \rightarrow 0$ or $m \rightarrow \infty$ (m is vibrational quantum number) respectively. We also computed the transition probability between Zeeman levels. If we average it over all possible orientations, of crystal powders, and take into account the influence from nuclei of neighbouring molecules by using appropriate broadening function, spectral line forms corresponding to each vibrational levels will be obtained, and combining several of them, we will obtain actual spectral line from at any temperature; thereby temperature dependence of line form will be explained from Boltzman-factor as the population of each vibrational levels. It is very interesting to calculate the line form actually, and to compare it with the experiments; but it may be left to following report.

2. Hamiltonian of Rotating Triangular Spin System.

When magnetic nuclei are involved in a rotating molecule or atomic group, total energy of it will consist of its kinetic energy of rotation together with the potential energy determined by its orientation in lattice, Zeeman energy of nuclei involved therein in the external magnetic field, and dipolar energy between nuclei²:

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{orb} + \mathcal{H}_{spin} \\ \mathcal{H}_{orb} &= \mathbf{p}^2 / 2F + V(\phi, \theta) \\ \mathcal{H}_{spin} &= -\sum_j g_j \beta \mathbf{H}_0 S_{zj} + \sum_{i>k} g_j g_k \beta^2 [\mathbf{S}_j \cdot \mathbf{S}_k r_{jk}^{-3} - 3 \mathbf{S}_j \cdot \mathbf{r}_{jk} \mathbf{S}_k \cdot \mathbf{r}_{jk} r_{jk}^{-5}] \\ &= \mathcal{H}_z + \mathcal{H}_D \end{aligned} \quad (5)$$

According to Van Vleck¹⁰, second term of \mathcal{H}_{spin} may be written

$$\mathcal{H}_D = \sum_{j>k} A_{jk} [\mathbf{S}_j \cdot \mathbf{S}_k - 3 S_{zj} S_{zk}] \quad (6)$$

$$A_{jk} = \frac{1}{2} g_j g_k \beta^2 r_{jk}^{-3} (3 \cos^2 \theta_{jk} - 1)$$

where g_j , \mathbf{S}_j and S_{zj} is the g -factor, spin operator and its z -component of j -th nucleus respectively, β is the nuclear magneton, r_{jk} is the distance between j - and k -th nuclei and θ_{jk} is the angle between its direction and z -axis.

\mathcal{H}_D is now to be calculated for three equal nuclei of spin $\frac{1}{2}$ arranged in equi-lateral triangle and rotating about its C₃-axis. According to Andrew and Bersohn⁹, if we write,

$$\mathbf{S}_1 + \mathbf{S}_2 = \mathbf{S}, \quad \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 = \mathbf{S}, \quad S_{1z} + S_{2z} + S_{3z} = S_z,$$

matrix of \mathcal{H}_D expressed by system of spin wave functions which make S^2 , S^2 and S_z

stationary, may be written as follows :

$$\mathcal{H}_p = \begin{pmatrix} -2x & 0 & 0 & 0 \\ 0 & 2x & b & a \\ 0 & b & 0 & 0 \\ 0 & a & 0 & 0 \end{pmatrix} \begin{matrix} \text{wave function} \\ \text{Ms} \\ \text{S} \\ \text{S} \end{matrix} \left. \begin{matrix} \dots I^o \\ \dots I^a \\ \dots I^b \\ \dots I^c \end{matrix} \right\} \begin{matrix} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{matrix} \begin{matrix} 1 \\ 1 \\ 0 \end{matrix} \quad (7)$$

where

$$\begin{aligned} x &= \frac{1}{4} (A_{12} + A_{23} + A_{13}), & a &= \frac{\sqrt{6}}{4} (A_{13} - A_{23}), \\ y^2 &= x^2 + a^2 + b^2, & b &= \frac{\sqrt{2}}{4} (2A_{12} - A_{13} - A_{23}), \end{aligned} \quad (8)$$

and, denoting the angle between C_3 -axis and z -axis ϕ , the angle of rotation of the first nucleus about C_3 -axis θ ,

$$\begin{aligned} x &= \mu \alpha \left(\frac{1}{2} - \frac{3}{2} \cos^2 \phi \right), \\ a &= \mu \alpha \frac{3\sqrt{2}}{2} \sin^2 \phi \sin 2\theta, & y &= \mu \alpha \frac{3\sqrt{2}}{2} \sin^2 \phi, \\ b &= \mu \alpha \frac{3\sqrt{2}}{2} \sin^2 \phi \cos 2\theta, \end{aligned} \quad (9)$$

where μ is the nuclear magnetic moment, $\mu = \frac{1}{2} g \beta$; $a = \mu r^{-3}$ where r is the side of equilateral triangle.

3. Hindered Rotation Without Magnetic Interaction.

Putting the moment of inertia of triangle about their C_3 -axis I , Schrödinger's equation of this plane rotor in the hindering potential, $V = (H/2)(1 - \cos 3\theta)$, is

$$\frac{d^2 \psi}{d\theta^2} + \frac{2I}{\hbar^2} \left[W - \frac{H}{2} (1 - \cos 3\theta) \right] \psi = 0 \quad (10)$$

If we approximate V with $V' = (H/2)\frac{1}{2}(3\theta)^2$, Eq. (10) reduced to the wave equation of simple harmonic motion

$$\frac{d^2 \psi'}{d\theta^2} + (\lambda \xi - \xi^2 \theta^2) \psi' = 0 \quad (11)$$

where

$$\begin{aligned} \lambda \xi &= \frac{2I}{\hbar^2} W \\ \xi^2 &= \frac{2I}{\hbar^2} \cdot \frac{H}{2} \cdot \frac{9}{2}. \end{aligned} \quad (12)$$

Solution of Eq. (11) is

$$\begin{aligned} \psi'_n &= N_n e^{-\frac{\xi}{2}\theta^2}, & \left(N_n = \frac{1}{2^n n!} \sqrt{\frac{\xi}{\pi}} \right) \\ \lambda &= 2n + 1, \end{aligned} \quad (13)$$

where ψ'_n 's make a normalized orthogonal set, and the second equation gives energies

$$W'_n = \frac{\hbar^2}{2I} 2\xi \left(n + \frac{1}{2} \right). \quad (14)$$

Then, if $\Delta W'_n$ denotes the interval between these vibrational energies, it turns out to be

$$\xi \Delta W'_n = \frac{9}{2} H, \tag{14a}$$

where ξ is large, the degree of approximation of solution Eq. (13) and (14) for Eq.(10) is good. Taking $I = 5.328 \times 10^{-40}$ gr cm² for the value of I of the CH₃ group¹⁰, and using $h = 6.624 \times 10^{-27}$ erg sec, and $c = 2.998 \times 10^{10}$ cm/sec we obtain ξ in terms of H in cm⁻¹,

$$\xi = 0.6545 \times H^{\frac{1}{2}} \tag{15}$$

Denoting the new approximate solution of differential equation (10), modified for the true potential, $V = (H/2)(1 - \cos 3\theta)$

$$\psi_n(\theta) \quad \text{and} \quad W_n$$

these solutions are not yet to be said proper wave functions and eigen-values, because, besides the given

$$H^{(1)} = \psi_n(\theta),$$

$$H^{(2)} = \psi_n(\theta - \frac{2}{3}\pi)$$

and

$$H^{(3)} = \psi_n(\theta + \frac{2}{3}\pi)$$

are also solutions of Eq. (10) for the same W_n . The consideration on the symmetry permit us to write the proper solution of Eq. (10), which is mutually orthogonal, as follows :

$$\phi_n^a = \frac{1}{\sqrt{3}}(H^{(1)} + H^{(2)} + H^{(3)}),$$

$$\phi_n^b = \frac{1}{\sqrt{6}}(2H^{(1)} - H^{(2)} - H^{(3)}), \tag{16}$$

$$\phi_n^c = \frac{1}{\sqrt{2}}(H^{(2)} - H^{(3)}).$$

Using these solutions, the energy values are calculated to be

$$W_n^a = \int_{-\pi}^{\pi} \phi_n^a \mathfrak{C}_{orb} \phi_n^a d\theta = \int_{-\pi}^{\pi} H^{(1)} \mathfrak{C}_{orb} H^{(1)} d\theta + 2 \int_{-\pi}^{\pi} H^{(1)} \mathfrak{C}_{orb} H^{(2)} d\theta,$$

and

$$W_n^b = W_n^c = \int_{-\pi}^{\pi} \phi_n^b \mathfrak{C}_{orb} \phi_n^b d\theta = \int_{-\pi}^{\pi} H^{(1)} \mathfrak{C}_{orb} H^{(1)} d\theta - \int_{-\pi}^{\pi} H^{(1)} \mathfrak{C}_{orb} H^{(2)} d\theta.$$

The three-fold degenerated level splits into a single level and a two-fold degenerated level separated by the amount

$$W_n^a - W_n^b = 3 \int_{-\pi}^{\pi} H^{(1)} \mathfrak{C}_{orb} H^{(2)} d\theta \equiv w_n \tag{17}$$

w_n 's are found to be the energies corresponding to the tunnelling frequencies, from the form of Eq. (17).

w_n 's have a factor $e^{-\xi(\frac{\pi}{3})^2}$ in their asymptotic forms. Namely,

$$w_n \sim H e^{-\xi(\frac{\pi}{3})^2},$$

and

$$\Delta W_n \sim H \cdot \frac{1}{\xi}$$

and therefore, if ξ is large, there can be a situation where vibrational levels split sufficiently with one another, and the splitting between the tunnelling doublets is the same order of the dipolar interaction energies, for which x , a , and b are measures of the order of magnitude.

4. Hindered Rotation with Magnetic Interaction

Now, it is necessary to solve the Schrödinger's Equation which involves $\mathfrak{H}_{\text{orb}}$ and $\mathfrak{H}_{\text{spin}}$ spin simultaneously under the condition that $\Delta W_n \gg w_n$ and $w_n \sim x$, a , and b . Under this condition, it is sufficient to seek the approximate solution of Schrödinger's Equation among the possible combinations of orbital wave functions of the previous section belonging to a specified n multiplied by Andrew-Bersohn's spin wave functions.

Orbital wave functions are

$$\psi_n^a, \quad \psi_n^b, \quad \text{and} \quad \psi_n^c$$

and spin wave functions are

$$I^o, \quad I^a, \quad I^b, \quad \text{and} \quad I^c;$$

and

$$\bar{I}^o, \quad \bar{I}^a, \quad \bar{I}^b, \quad \text{and} \quad \bar{I}^c,$$

in which only the sign of M_s is changed compared with I^o , I^a , I^b , and I^c respectively. Therefore, there are 24 of these products of orbital and spin wave functions. We must calculate matrix elements of \mathfrak{H}_D for these wave functions. In the course of the calculation, among the matrix element of \mathfrak{H}_D of rigid case, b and a , which involves $\cos 2\theta$ and $\sin 2\theta$ respectively, will be affected by the motion. Writing briefly,

$$a = D \sin 2\theta, \quad b = D \cos 2\theta, \quad D = \frac{3\sqrt{2}}{2} (\mu\alpha) \sin^2 \phi \quad (18)$$

there exist only the component $(\psi^b | a | \psi^a)$ for p and q which have the different odd-even characters, and only the component $(\psi^b | b | \psi^q)$ for p and q which have the same odd-even characters. Then the results of the calculation are

$$\begin{aligned} -(\psi_n^a | a | \psi_n^c) &= (\psi_n^a | b | \psi_n^b) = (\gamma_n - \delta_n) \frac{D}{\sqrt{2}}, \\ (\psi_n^b | a | \psi_n^c) &= (\psi_n^b | b | \psi_n^b) = -(\psi_n^c | b | \psi_n^c) = \left(\frac{\gamma_n}{\sqrt{2}} - \sqrt{2} \delta_n \right) \frac{D}{\sqrt{2}}, \\ (\psi_n^a | a | \psi_n^a) &= (\psi_n^a | a | \psi_n^b) = (\psi_n^b | a | \psi_n^b) = (\psi_n^c | a | \psi_n^c) = 0, \\ (\psi_n^a | b | \psi_n^c) &= (\psi_n^b | b | \psi_n^c) = (\psi_n^a | b | \psi_n^a) = 0 \end{aligned} \quad (19)$$

where

$$\gamma_n \equiv \int_{-\pi}^{\pi} (H_n^{(1)})^2 \cos 2\theta \cdot d\theta, \quad \delta_n \equiv \int_{-\pi}^{\pi} H_n^{(1)} \left(\theta - \frac{\pi}{3} \right) H_n^{(1)} \left(\theta + \frac{\pi}{3} \right) \cos 2\theta \cdot d\theta, \quad (20)$$

We see from the forms of Eq. (20)

$$r_n \sim 1, \quad \delta_n \sim e^{-\xi \left(\frac{\pi}{3}\right)^2}, \quad \text{if } \xi \gg 1.$$

If we neglect δ_n compared with 1, and put

$$r_n \frac{D}{2} = d_n, \tag{21}$$

matrix of \mathfrak{H}_D becomes

$$\mathfrak{H}_D = \begin{array}{c|cccc} -2x & & & & \\ \hline & -2x & & & \\ & & 0 & & \\ & & & 0 & \\ & & & & 0 \\ \hline & & 2x & & \\ & & & \sqrt{2}d_n & -\sqrt{2}d_n \\ & 0 & 2x & \sqrt{2}d_n & d_n \\ & & & & -d_n \\ & & & & -\sqrt{2}d_n & d_n \\ \hline & & & \sqrt{2}d_n & & \\ & 0 & \sqrt{2}d_n & d_n & & \\ & & & & 0 & \\ & & & & & 0 \\ \hline & & & & -\sqrt{2}d_n & \\ & 0 & & & & d_n \\ & & & & & 0 \\ & & & & & -\sqrt{2}d_n & d_n \\ \hline \end{array} \tag{22}$$

Considering the symmetry, we transform the matrix as follows :

The New Wave Function	The Result of Operator $\mathfrak{H}_{orb} + \mathfrak{H}_D$ (Appart from the constant $W_n^b = W_n^c$)
$\Psi^I = \frac{1}{\sqrt{2}}(\Psi^b I^c + \Psi^c I^b)$	0
$\left\{ \begin{array}{l} \Psi^{\text{II}}_1 = \Psi^a I^a \\ \Psi^{\text{II}}_2 = \frac{1}{\sqrt{2}}(\Psi^b I^b - \Psi^c I^c) \end{array} \right.$	$(w_n + 2x)\Psi^{\text{II}}_1 + 2d_n \Psi^{\text{II}}_2$ $2d_n \Psi^{\text{II}}_1$
$\left\{ \begin{array}{l} \Psi^{\text{III}}_1 = \Psi^b I^a \\ \Psi^{\text{III}}_2 = \Psi^a I^b \end{array} \right.$	$2x \Psi^{\text{III}}_1 + \sqrt{2}d_n \Psi^{\text{III}}_2 + \sqrt{2}d_n \Psi^{\text{III}}_3$ $\sqrt{2}d_n \Psi^{\text{III}}_1 + w_n \Psi^{\text{III}}_2$
$\left\{ \begin{array}{l} \Psi^{\text{III}}_3 = \frac{1}{\sqrt{2}}(\Psi^b I^c + \Psi^c I^c) \\ \Psi^{\text{IV}}_1 = \Psi^c I^a \\ \Psi^{\text{IV}}_2 = -\Psi^a I^c \end{array} \right.$	$\sqrt{2}d_n \Psi^{\text{III}}_1$ $2x \Psi^{\text{IV}}_1 + \sqrt{2}d_n \Psi^{\text{IV}}_2 + \sqrt{2}d_n \Psi^{\text{IV}}_3$ $\sqrt{2}d_n \Psi^{\text{IV}}_1 + w_n \Psi^{\text{IV}}_2$
$\left\{ \begin{array}{l} \Psi^{\text{IV}}_3 = \frac{1}{\sqrt{2}}(\Psi^b I^c - \Psi^c I^a) \end{array} \right.$	$\sqrt{2}d_n \Psi^{\text{IV}}_1$

where the part of the matrix concerning to the spin wave function I^o are already diagonalized, and we have written the transformation only about the other part of the matrix. Therefore the matrix split into four groups. There it is to be noticed that \mathfrak{H}_z is a constant for each of these groups.

$$\mathcal{H}_{orb} + \mathcal{H}_D = \begin{vmatrix} 0 & & & & & & \dots \Psi^I \\ & \begin{vmatrix} w_n + 2x & 2d_n \\ 2d_n & 0 \end{vmatrix} & & & & & \dots \Psi^{\text{II}}_1 \\ & & \begin{vmatrix} 2x & \sqrt{2}d_n & \sqrt{2}d_n \\ \sqrt{2}d_n & w_n & 0 \\ \sqrt{2}d_n & 0 & 0 \end{vmatrix} & & & & \dots \Psi^{\text{II}}_2 \\ & & & \begin{vmatrix} 2x & \sqrt{2}d_n & \sqrt{2}d_n \\ \sqrt{2}d_n & w_n & 0 \\ \sqrt{2}d_n & 0 & 0 \end{vmatrix} & & & \dots \Psi^{\text{II}}_3 \\ & & & & \begin{vmatrix} 2x & \sqrt{2}d_n & \sqrt{2}d_n \\ \sqrt{2}d_n & w_n & 0 \\ \sqrt{2}d_n & 0 & 0 \end{vmatrix} & & \dots \Psi^{\text{III}}_1 \\ & & & & & & \dots \Psi^{\text{III}}_2 \\ & & & & & & \dots \Psi^{\text{III}}_3 \end{vmatrix} \quad (23)$$

5. Solution of Wave Equation and Classification of Energy Levels.

For the each group of the Eq. (23), we work out the solution of the wave equation. The first group gives an unperturbed singlet; the second group gives two perturbed singlets; and the third and fourth give three perturbed doublets.

i) For the singlet group, eigen-values are obtained as follows :

$$\begin{vmatrix} w_n + 2x - \epsilon_n & 2d_n \\ 2d_n & 0 \end{vmatrix} = 0,$$

$$\epsilon_n = \begin{cases} \frac{w_n}{2} + x + \sqrt{\left(\frac{w_n}{2} + x\right)^2 + 4d_n^2} \equiv \epsilon_{n1} \\ \frac{w_n}{2} + x - \sqrt{\left(\frac{w_n}{2} + x\right)^2 + 4d_n^2} \equiv \epsilon_{n2} \end{cases} \quad (24)$$

Then as for the wave functions, putting

$$\begin{aligned}
 \Phi_1^{\text{II}} &= c_{n11} \Psi_1^{\text{II}} + c_{n12} \Psi_2^{\text{II}}, \\
 \Phi_2^{\text{II}} &= c_{n21} \Psi_1^{\text{II}} + c_{n22} \Psi_2^{\text{II}},
 \end{aligned} \quad (25)$$

$$\begin{aligned}
 c_{n11} &= \frac{\epsilon_{n1}}{\sqrt{\epsilon_{n1}^2 + 4d_n^2}}, & c_{n12} &= \frac{2d_n}{\sqrt{\epsilon_{n1}^2 + 4d_n^2}}, \\
 c_{n21} &= \frac{\epsilon_{n2}}{\sqrt{\epsilon_{n2}^2 + 4d_n^2}}, & c_{n22} &= \frac{2d_n}{\sqrt{\epsilon_{n2}^2 + 4d_n^2}}.
 \end{aligned} \quad (26)$$

ii) For the doublet group,

$$\begin{vmatrix} 2x - E_n & \sqrt{2}d_n & \sqrt{2}d_n \\ \sqrt{2}d_n & w_n - E_n & 0 \\ 0 & 0 & -E_n \end{vmatrix} = 0$$

We write the solution

$$E_n = E_{n1}, E_{n2}, \text{ and } E_{n3} \quad (27)$$

As for the wave functions putting

$$\begin{aligned}
 \Phi_1^{\text{III}} &= k_{n11} \Psi_1^{\text{III}} + k_{n12} \Psi_2^{\text{III}} + k_{n13} \Psi_3^{\text{III}}, \\
 \Phi_2^{\text{III}} &= k_{n21} \Psi_1^{\text{III}} + k_{n22} \Psi_2^{\text{III}} + k_{n23} \Psi_3^{\text{III}}, \\
 \Phi_3^{\text{III}} &= k_{n31} \Psi_1^{\text{III}} + k_{n32} \Psi_2^{\text{III}} + k_{n33} \Psi_3^{\text{III}},
 \end{aligned} \quad (28)$$

$$\begin{aligned}
 k_{ni1} &= \frac{(E_{ni} - w_n) E_{ni}}{\sqrt{(E_{ni} - w_n)^2 E_{ni}^2 + 2d_n^2 [E_{ni}^2 + (E_{ni} - w_n)^2]}}, \\
 k_{ni2} &= \frac{\sqrt{2} d_n E_{ni}}{\sqrt{(E_{ni} - w_n)^2 E_{ni}^2 + 2d_n^2 [E_{ni}^2 + (E_{ni} - w_n)^2]}}, \quad (i=1, 2, 3) \quad (29) \\
 k_{ni3} &= \frac{\sqrt{2} d_n (E_{ni} - w_n)}{\sqrt{(E_{ni} - w_n)^2 E_{ni}^2 + 2d_n^2 [E_{ni}^2 + (E_{ni} - w_n)^2]}}.
 \end{aligned}$$

Now we will see how do these energy levels change with the state of motion. If n increases or if ξ decreases, w_n increases and d_n decreases; these conditions correspond to an intense motion and in the extreme case the motion turns into the free rotation. On the contrary, if w_n is small or ξ is large, the motion is quiet and in the extreme case it turns into the rigid case.

i) Rigid case :

If $w_n \rightarrow 0$

as for the singlet levels,

$$\begin{aligned}
 \varepsilon_{n1} &= x + \frac{w_n}{2} + \sqrt{\left(x + \frac{w_n}{2}\right)^2 + 4d_n^2} \rightarrow x + \sqrt{x^2 + 4d_n^2} \\
 \varepsilon_{n2} &= x + \frac{w_n}{2} - \sqrt{\left(x + \frac{w_n}{2}\right)^2 + 4d_n^2} \rightarrow x - \sqrt{x^2 + 4d_n^2}
 \end{aligned}$$

and as for the doublet levels,

$$\begin{aligned}
 &E^3 - (2x + w_n)E^2 + (2xw_n - 4d_n^2)E + 2d_n^2 w_n \\
 &\rightarrow E^3 - 2xE^2 - 4d_n^2 E \\
 &= E(E^2 - 2xE - 4d_n^2) = 0
 \end{aligned}$$

Namely,

$$E_{n1} \rightarrow 0, \quad E_{n2} \rightarrow x + \sqrt{x^2 + 4d_n^2}, \quad E_{n3} \rightarrow x - \sqrt{x^2 + 4d_n^2}.$$

From Eqs. (21) and (18),

$$d_n = \frac{D}{2} r_n = \frac{1}{2} \sqrt{a^2 + b^2} r_n$$

and from Eq. (19) $r_n \rightarrow 1$ for $\xi \rightarrow \infty$, therefore

$$\sqrt{x^2 + 4d_n^2} \rightarrow \sqrt{x^2 + a^2 + b^2} = y$$

It confirms the solutions of Eq. (24) and Eq. (27) agree with energy levels of Andrew-Bersohn's rigid case.

ii) Free-rotational case :

If $w_n \gg x$, d_n

as for the singlet levels,

$$\begin{aligned}
 \varepsilon_{n1} &= x + \frac{w_n}{2} + \frac{w_n}{2} \left(1 + \frac{x}{w_n} + \dots\right) \rightarrow w_n + 2x \\
 \varepsilon_{n2} &= x + \frac{w_n}{2} - \frac{w_n}{2} \left(1 + \frac{x}{w_n} + \dots\right) \rightarrow 0
 \end{aligned}$$

and as for the doublet groups,

$$\begin{aligned}
 & E^3 - (2x + w_n)E^2 + (2xw_n - 4d_n^2)E + 2d_n^2 w_n \\
 &= \left(\frac{E}{w_n}\right)^3 - \left(1 + \frac{2x}{w_n}\right)\left(\frac{E}{w_n}\right)^2 + \left(\frac{2x}{w_n} - \frac{4d_n^2}{w_n^2}\right)\left(\frac{E}{w_n}\right) + \frac{2d_n^2}{w_n^2} \\
 &\rightarrow \left(\frac{E}{w_n}\right)^3 - \left(1 + \frac{2x}{w_n}\right)\left(\frac{E}{w_n}\right)^2 + \frac{2x}{w_n}\left(\frac{E}{w_n}\right) = 0 \\
 &\quad \frac{E}{w_n} \cdot \left(\frac{E}{w_n} - 1\right)\left(\frac{E}{w_n} - \frac{2x}{w_n}\right) = 0
 \end{aligned}$$

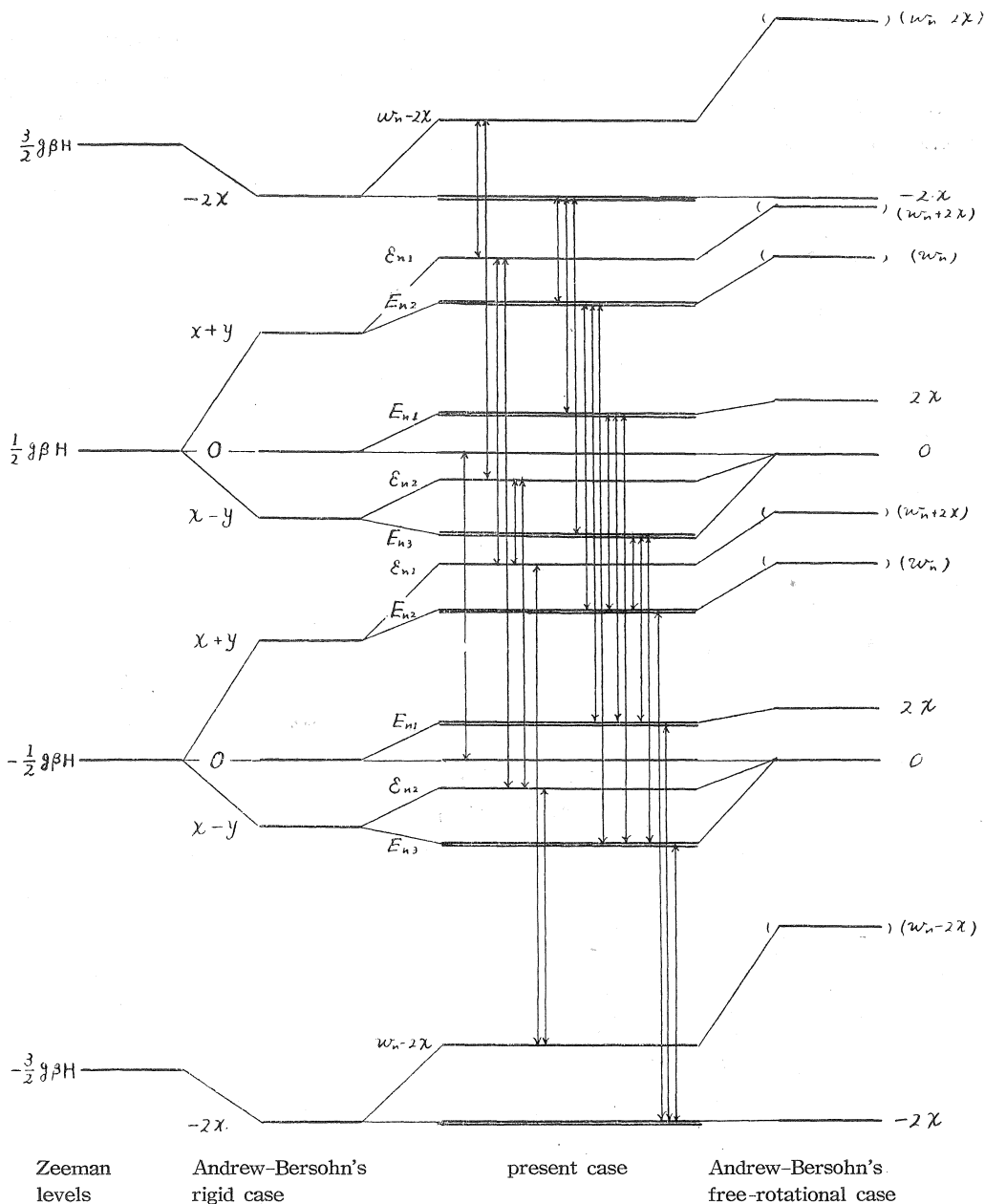


Fig I. The term splitting diagram of Zeeman levels

Taking into consideration that these terms do not change the order as w_n or d_n varies continuously, we obtain

$$E_{n1} \rightarrow w_n, \quad E_{n2} \rightarrow 2x, \quad E_{n3} \rightarrow 0.$$

We put together these results into the term-splitting diagram, Fig. I, in which selection rules of Sec. 6 are entered together.

6. Selection Rules and Line Shape.

Selection rules in the experiment of nuclear magnetic resonance must be obtained by calculating the matrix element of S_x with respect to new wave functions corresponding to the calculated energy levels. The matrix element of S_x with respect to Andrew-Bersohn's spin wave functions are

$$S_x = \begin{array}{c|ccc|c} & \frac{\sqrt{3}}{2} & & & \dots I^0 \\ & \frac{\sqrt{3}}{2} & & 1 & \dots I^a \\ \hline & & & -\frac{1}{2} & \dots I^b \\ & & -\frac{1}{2} & & \dots I^c \\ \hline & & -\frac{1}{2} & & \dots \bar{I}^c \\ & & & & \dots \bar{I}^b \\ \hline & 1 & & & \dots \bar{I}^a \\ & & & \frac{\sqrt{3}}{2} & \dots \bar{I}^0 \\ & & & \frac{\sqrt{3}}{2} & \dots \bar{I}^0 \end{array}$$

From Eqs. (22), (23), (25), and (28), the set of new wave functions are :

$$\begin{aligned} \phi^{oa} &= \psi^a I^o, & \phi_1^{\text{III}} &= k_{n11} \psi_1^{\text{III}} + k_{n12} \psi_2^{\text{III}} + k_{n13} \psi_3^{\text{III}}, \\ \phi^{ob} &= \psi^b I^o, & \phi_2^{\text{III}} &= k_{n21} \psi_1^{\text{III}} + k_{n22} \psi_2^{\text{III}} + k_{n23} \psi_3^{\text{III}}, \\ \phi^{oc} &= \psi^c I^o, & \phi_3^{\text{III}} &= k_{n31} \psi_1^{\text{III}} + k_{n32} \psi_2^{\text{III}} + k_{n33} \psi_3^{\text{III}}, \\ \phi^{\text{I}} &= \psi^{\text{I}}, & \phi_1^{\text{III}'} &= k_{n11} \psi_1^{\text{III}'} + k_{n12} \psi_2^{\text{III}'} + k_{n13} \psi_3^{\text{III}'}, \\ \phi_1^{\text{II}} &= c_{n11} \psi_1^{\text{II}} + c_{n12} \psi_2^{\text{II}}, & \phi_2^{\text{III}'} &= k_{n21} \psi_1^{\text{III}'} + k_{n22} \psi_2^{\text{III}'} + k_{n23} \psi_3^{\text{III}'}, \\ \phi_2^{\text{II}} &= c_{n21} \psi_1^{\text{II}} + c_{n22} \psi_2^{\text{II}}, & \phi_3^{\text{III}'} &= k_{n31} \psi_1^{\text{III}'} + k_{n32} \psi_2^{\text{III}'} + k_{n33} \psi_3^{\text{III}'}; \end{aligned} \tag{31a}$$

and

$$\begin{aligned} \bar{\phi}_1^{\text{III}} &= k_{n11} \bar{\psi}_1^{\text{III}} + k_{n12} \bar{\psi}_2^{\text{III}} + k_{n13} \bar{\psi}_3^{\text{III}}, & \bar{\phi}_1^{\text{II}} &= c_{n11} \bar{\psi}_1^{\text{II}} + c_{n12} \bar{\psi}_2^{\text{II}}, \\ \bar{\phi}_2^{\text{III}} &= k_{n21} \bar{\psi}_1^{\text{III}} + k_{n22} \bar{\psi}_2^{\text{III}} + k_{n23} \bar{\psi}_3^{\text{III}}, & \bar{\phi}_2^{\text{II}} &= c_{n21} \bar{\psi}_1^{\text{II}} + c_{n22} \bar{\psi}_2^{\text{II}}, \\ \bar{\phi}_3^{\text{III}} &= k_{n31} \bar{\psi}_1^{\text{III}} + k_{n32} \bar{\psi}_2^{\text{III}} + k_{n33} \bar{\psi}_3^{\text{III}}, & \bar{\phi}^{\text{I}} &= \bar{\psi}^{\text{I}}, \\ \bar{\phi}_1^{\text{III}'} &= k_{n11} \bar{\psi}_1^{\text{III}'} + k_{n12} \bar{\psi}_2^{\text{III}'} + k_{n13} \bar{\psi}_3^{\text{III}'}, & \bar{\phi}^{oc} &= \psi^c \bar{I}^o, \\ \bar{\phi}_2^{\text{III}'} &= k_{n21} \bar{\psi}_1^{\text{III}'} + k_{n22} \bar{\psi}_2^{\text{III}'} + k_{n23} \bar{\psi}_3^{\text{III}'}, & \bar{\phi}^{ob} &= \psi^b \bar{I}^o, \\ \bar{\phi}_3^{\text{III}'} &= k_{n31} \bar{\psi}_1^{\text{III}'} + k_{n32} \bar{\psi}_2^{\text{III}'} + k_{n33} \bar{\psi}_3^{\text{III}'}, & \bar{\phi}^{oa} &= \psi^a \bar{I}^o. \end{aligned} \tag{31b}$$

in which I^o , I^a , I^b , and I^c contained in the wave functions of Eq. (31a) are replaced by \bar{I}^o , \bar{I}^a , \bar{I}^b , and \bar{I}^c respectively. Then, Eq. (30) transforms to

$G_2 =$		$\frac{3}{2} c_{11}, \frac{3}{2} c_{21}$	$\frac{3}{2} k_{11}, \frac{3}{2} k_{21}, \frac{3}{2} k_{31}$	$\frac{3}{2} k_{11}, \frac{3}{2} k_{21}, \frac{3}{2} k_{31}$	$\frac{3}{2} k_{11}^2 - \frac{1}{2}, \frac{3}{2} k_{11}k_{21}, \frac{3}{2} k_{11}k_{31}$	$\frac{3}{2} k_{11}k_{21}, \frac{3}{2} k_{21}^2 - \frac{1}{2}, \frac{3}{2} k_{21}k_{31}$	$\frac{3}{2} k_{11}k_{31}, \frac{3}{2} k_{21}k_{31}, \frac{3}{2} k_{31}^2 - \frac{1}{2}$	$\frac{3}{2} k_{11}^2 - \frac{1}{2}, \frac{3}{2} k_{11}k_{21}, \frac{3}{2} k_{11}k_{31}$	$\frac{3}{2} k_{11}k_{21}, \frac{3}{2} k_{21}^2 - \frac{1}{2}, \frac{3}{2} k_{21}k_{31}$	$\frac{3}{2} k_{11}k_{31}, \frac{3}{2} k_{21}k_{31}, \frac{3}{2} k_{31}^2 - \frac{1}{2}$	$\frac{3}{2} k_{11}^2 - \frac{1}{2}, \frac{3}{2} k_{11}k_{21}, \frac{3}{2} k_{11}k_{31}$	$\frac{3}{2} k_{11}k_{21}, \frac{3}{2} k_{21}^2 - \frac{1}{2}, \frac{3}{2} k_{21}k_{31}$	$\frac{3}{2} k_{11}k_{31}, \frac{3}{2} k_{21}k_{31}, \frac{3}{2} k_{31}^2 - \frac{1}{2}$	$\frac{3}{2} c_{11}^2 - \frac{1}{2}, \frac{3}{2} c_{11}c_{21}$	$\frac{3}{2} c_{11}c_{21}, \frac{3}{2} c_{21}^2 - \frac{1}{2}$	$\frac{3}{2} k_{11}, \frac{3}{2} k_{21}, \frac{3}{2} k_{31}$	$\frac{3}{2} k_{11}, \frac{3}{2} k_{21}, \frac{3}{2} k_{31}$	$\frac{3}{2} c_{11}, \frac{3}{2} c_{21}$	$w_x - 2x$	M_3
																			$2x$	$\frac{3}{2}$
																			$2x$	
																			0	$\frac{1}{2}$
$\frac{3}{2} c_{11}$																			ϵ_{n1}	
$\frac{3}{2} c_{21}$																			ϵ_{n2}	
	$\frac{3}{2} k_{11}$																			E_{n1}
	$\frac{3}{2} k_{21}$																			E_{n2}
	$\frac{3}{2} k_{31}$																			E_{n3}
			$\frac{3}{2} k_{11}$																	E_{n1}
			$\frac{3}{2} k_{21}$																	E_{n2}
			$\frac{3}{2} k_{31}$																	E_{n3}
																				E_{n1}
																				E_{n2}
																				E_{n3}
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																				E_{n2}
																				E_{n3}
																				E_{n1}
																				E_{n2}
																				E_{n3}
																				ϵ_{n1}
																				ϵ_{n2}
																				0
																				$2x$
																				$2x$
																				$\frac{3}{2}$

(32)

Now selection rules are summarized that

$$\Delta M_s = \pm 1 \quad (\text{and forbidden between the terms of different multiplicity}).$$

These absorption lines which are allowed by these selection rules gives a central line accompanied by a set of fine structure composed of nine pairs of lines

$$\begin{aligned} \mathbf{h} &= \pm(1/2\mu)(w_n - 2x - \varepsilon_{n1}), \quad \mathbf{h} = \pm(1/2\mu)(w_n - 2x - \varepsilon_{n2}), \quad \mathbf{h} = \pm(1/2\mu)(\varepsilon_{n1} - \varepsilon_{n2}), \\ \mathbf{h} &= \pm(1/2\mu)(-2x - E_{n1}), \quad \mathbf{h} = \pm(1/2\mu)(-2x - E_{n2}), \quad \mathbf{h} = \pm(1/2\mu)(-2x - E_{n3}), \\ \mathbf{h} &= \pm(1/2\mu)(E_{n1} - E_{n2}), \quad \mathbf{h} = \pm(1/2\mu)(E_{n2} - E_{n3}), \quad \mathbf{h} = \pm(1/2\mu)(E_{n3} - E_{n1}). \end{aligned}$$

where if \mathbf{H} denotes the resonance field of given nucleus, and $\mathbf{H}_0 = (h/2\mu) f_0$ denotes the applied magnetic field, the resonance shift \mathbf{h} is defined by $\mathbf{h} = \mathbf{H}_0 - \mathbf{H}$.

The transition probability p of each component line is given by the square of corresponding component of matrix (32). These probabilities are functions of $\cos \phi$ as it is seen from Eqs. (18), (21), (24), (26), (27), and (29). And also from these equations \mathbf{h} must be a function of $\cos \phi$. In powdered samples, orientations of small crystals composing the powder are distributed uniformly in the whole solid angles, and so powdered crystal line shape $F(\mathbf{h})$ is given by

$$F(\mathbf{h}) = p(\cos \phi) \frac{d(\cos \phi)}{d\mathbf{h}} \quad (33)$$

i) For the central line,

$$\begin{aligned} p &= \left(\frac{1}{2}\right)^2 + \left(\frac{3}{2}c_{n11}^2 - \frac{1}{2}\right)^2 + \left(\frac{3}{2}c_{n21}^2 - \frac{1}{2}\right)^2 + 2\left[\left(\frac{3}{2}k_{n11}^2 - \frac{1}{2}\right)^2 + \left(\frac{3}{2}k_{n21}^2 - \frac{1}{2}\right)^2\right. \\ &\quad \left.+ \left(\frac{3}{2}k_{n31}^2 - \frac{1}{2}\right)^2\right]; \end{aligned}$$

ii) For pairs $\mathbf{h} = \pm(w_n - 2x - \varepsilon_{n1})/2\mu$ and $\mathbf{h} = \pm(w_n - 2x - \varepsilon_{n2})/2\mu$,

$$p = \frac{3}{4}c_{n11}^2 \quad \text{and} \quad p = \frac{3}{4}c_{n22}^2 \quad \text{respectively.}$$

iii) For the pair $\mathbf{h} = \pm(\varepsilon_{n1} - \varepsilon_{n2})/2\mu$,

$$p = \frac{9}{4}c_{n11}^2 c_{n21}^2;$$

iv) For pairs $\mathbf{h} = \pm(-2x - E_{n1})/2\mu$, $\mathbf{h} = \pm(-2x - E_{n2})/2\mu$, and $\mathbf{h} = \pm(-2x - E_{n3})/2\mu$,

$$p = \frac{3}{2}k_{n11}^2, \quad p = \frac{3}{2}k_{n21}^2 \quad \text{and} \quad p = \frac{3}{2}k_{n31}^2 \quad \text{respectively};$$

v) For pairs $\mathbf{h} = \pm(E_{n1} - E_{n2})/2\mu$, $\mathbf{h} = \pm(E_{n2} - E_{n3})/2\mu$, and $\mathbf{h} = \pm(E_{n3} - E_{n1})/2\mu$

$$p = \frac{9}{2}k_{n11}^2 k_{n21}^2, \quad p = \frac{9}{2}k_{n21}^2 k_{n31}^2 \quad \text{and} \quad p = \frac{9}{2}k_{n31}^2 k_{n11}^2 \quad \text{respectively.}$$

Putting these p 's into Eq. (33), and eliminating $\cos \phi$, F is expressed as a function of \mathbf{h} , and it results in the nuclear resonance line shape of isolated rotating triangular spins corresponding to an individual vibrational level specified by n .

To take account of influence of neighbouring spins, according to Pake¹¹ and Andrew-Bershon⁹, if we assume that each line of shift \mathbf{h} has an Gaussian shape, Eq. (34)

$$S(\mathbf{h}^* - \mathbf{h}) = \exp[-(\mathbf{h}^* - \mathbf{h})^2/2\beta^2], \quad (34)$$

the new line shape $f(\mathbf{h}^*)$ is given by Eq. (35)

$$f(\mathbf{h}^*) = \int_{-\infty}^{\infty} S(\mathbf{h}^* - \mathbf{h}) \cdot F(\mathbf{h}) \cdot d\mathbf{h}. \quad (35)$$

The actual line shape is the summation of the contribution from the each vibrational levels which has population expressed as Boltzman-factor. If we write the line-shape of an individual vibrational level specified by n , $f_n(\mathbf{h}^*)$, the actual line-shape is given as follows :

$$f(\mathbf{h}^*) = \sum_n e^{-\frac{W_n}{kT}} f_n(\mathbf{h}^*) \quad (36)$$

Therefore, it may be said that the temperature dependence of the line shape of proton magnetic spectrum of CH_3 group in the line width transition region is given by Eq. (36).

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