

Note on the NMR Spectra of Molecules with Periodic Internal Motions

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Abstract:

In the case of very large frequency of periodic motion, the spectrum of a molecule is identical with the spectrum of a fixed system described by the average Hamiltonian; theoretical proof of this well-known fact is presented and the necessary conditions are defined.

Note on the N.M.R. spectra of molecules with periodic internal motion

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In the case of very large frequency of periodic motion, the spectrum of a molecule is identical with the spectrum of a fixed system described by the average Hamiltonian; theoretical proof of this well-known fact is presented and the conditions necessary are defined.

The theory of N.M.R. spectra of molecules (systems) with exchanging nuclei has been studied by Gutowsky and Holm [1] and later, in a much more general form, by Alexander [2], who presented a complete solution of the shape of the spectrum (including relaxation effects) for the special case where the exchange can be described by the operator P ($P^2=1$), transforming the Hamiltonian H_1 into H_2 by a discontinuous process with a certain probability within unit time. This includes especially all cases of exchange of equivalent nuclei. In the limit of very rapid exchange there results a line spectrum given by the average Hamiltonian, $\frac{1}{2}(H_1+H_2)$.

Extensive experimental material [3] not only supports this result, but indicates that in the limiting case of rapid internal motion a line spectrum described by an effective Hamiltonian H_{eff} is also obtained for molecules the motion of which cannot be described by the operator P , or in cases where a continuous motion has to be considered (see [4], pp. 381–384). The Hamiltonian H_{eff} is usually assumed to be equal to the average Hamiltonian of the system; theoretically this case has not been treated so far. The present communication is concerned with the theory of N.M.R. spectra of molecules undergoing periodic internal motion, the period of the motion being much smaller than the spin–spin relaxation time T_2 .

Under this condition, spin–spin relaxation may be neglected and the Hamiltonian can be written in the form:

$$H = - \left\{ \sum_i \omega_i(t) \cdot I_{zi} + \sum_{kj} J_{jk}(t) \mathbf{I}_j \cdot \mathbf{I}_k \right\}, \quad (1)$$

where the chemical shifts $\omega_i(t)$ and coupling constants $J_{jk}(t)$ are periodic functions of time, and their frequency ν fulfils the condition:

$$1/\nu \ll T_2. \quad (2)$$

The Hamiltonian H can be expanded into a Fourier series:

$$\left. \begin{aligned} H &= H_0 + H_t, \quad H_0 = (1/T) \int_0^T H \cdot dt, \\ H_t &= H_1 \cos \nu t + H_2 \sin \nu t + H_3 \cos 2\nu t + H_4 \sin 2\nu t + \dots \end{aligned} \right\} \quad (3)$$

The spin eigenfunctions must obey the Schrödinger equation:

$$H\phi = i \frac{\partial \phi}{\partial t}. \quad (4)$$

A system with a time dependent Hamiltonian is not conservative and leads to a continuous spectrum. However, as stated above, systems with sufficiently high frequencies of internal motion yield line spectra, as in the strictly conservative case of fixed structures (i.e. the linewidth is given by spin-spin relaxation).

Conservative systems fulfil two conditions:

(a) Their eigenfunctions may be written in the form $\phi = f(t) \cdot \varphi(s)$. With the spin coordinates s and time coordinate t separated, the discrete orthonormal set of functions $\varphi(s)$ defines the set of discrete, mutually non-interacting, states of the system with a constant total spin and a constant z component of total spin.

(b) The energy of the system $\langle \phi | H \phi \rangle$ is independent of time.

Systems obeying only the first condition will in the following be designated as pseudo-conservative; let us now define the properties of a Hamiltonian necessary for fulfilling this condition.

Let us assume that:

$$\phi = f(t) \cdot \varphi(s). \quad (5)$$

From equations (4) and (3):

$$f(t) = f_0 \cdot \exp \left[-i \left(\frac{H_0 \varphi}{\varphi} t + \sum_{n=1}^{\infty} \left(\frac{\sin nvt}{nv} \cdot \frac{H_{2n-1} \varphi}{\varphi} + \frac{1 - \cos nvt}{nv} \cdot \frac{H_{2n} \varphi}{\varphi} \right) \right) \right]. \quad (6)$$

For $f(t)$ to be independent of the spin coordinates, the following relations must be valid:

$$H_k \varphi = \epsilon_k \varphi, \quad \epsilon_k = \text{const.}, \quad k = 0, 1, 2, 3, \dots \quad (7)$$

The functions φ must therefore be simultaneously eigenfunctions of all operators H_k , and this generally means that any pair of these operators must commute, i.e.

$$[H_i, H_j] = 0, \quad i, j = 0, 1, 2, 3, \dots \quad (8)$$

Energy will then be expressed as:

$$E = E_0 + \epsilon_1 \cos vt + \epsilon_2 \sin vt + \epsilon_3 \cos 2vt + \epsilon_4 \sin 2vt + \dots \quad (9)$$

In order to determine the real shape of the spectrum of a pseudo-conservative system, transition probabilities have to be determined in the presence of a perturbation of the form:

$$h_x = h_1 \cos \omega t, \quad h_y = -h_1 \sin \omega t. \quad (10)$$

After a conventional transformation of the preceding relations into rotating coordinates we obtain:

$$\left. \begin{aligned} \phi(t) &= \exp(iI_z \omega t) \phi_r(t), \\ H_r &= H_0 + H_t + \beta, \quad \beta = \sum_j \gamma_j h_1 I_{xj}, \end{aligned} \right\} \quad (11)$$

where γ_j = gyromagnetic ratio. Equation (4) now yields (in operator form):

$$\left. \begin{aligned} \phi_r(t) &= \exp[i(\gamma + \beta)t], \\ \gamma &= H_0 t + \int_0^t H_t dt + \omega \sum_i I_{zi}. \end{aligned} \right\} \quad (12)$$

The probability of a transition from state† m into state m' is then given by the relation:

$$P_{mm'}(t) = |\langle \varphi_{m'} | \phi_m \rangle|^2 = |\langle \varphi_{m'} | \exp(iI_z \omega t) \cdot \exp[i(\gamma + \beta t)] \varphi_m \rangle|^2 \\ = |\{\exp[i(\gamma + \beta t)]\}_{m'm}|^2.$$

The functions φ_m are eigenfunctions of γ , so that:

$$\{\exp[i(\gamma + \beta t)]\}_{m'm} = \exp(i\gamma_m) \delta_{m'm} + \frac{\exp(i\gamma_{m'}) - \exp(i\gamma_m)}{\gamma_{m'} - \gamma_m} \cdot \beta_{mm'} \cdot t \\ + \text{terms of higher order in } \beta_{mm'}.$$

Consequently

$$P_{mm'}(t) = 2|\beta_{mm'}|^2 \cdot t^2 \cdot \frac{1 - \cos(\gamma_{m'} - \gamma_m)}{(\gamma_{m'} - \gamma_m)^2}$$

and on account of relation (12) and the selection rule $\beta_{mm'} = 0$ for $m' \neq m \pm 1$:

$$\left. \begin{aligned} P_{mm'}(t) &= 2|\beta_{mm'}|^2 \cdot \frac{1 - \cos[(\omega - \omega_0)t + \mathcal{H}_t/\nu]}{(\omega - \omega_0 + \mathcal{H}_t/\nu)^2}, \\ \omega_0 &= E_{0m} - E_{0m'}, \\ \mathcal{H}_t &= \sum_{n=1}^{\infty} \frac{1}{n} \{(\epsilon_{2n-1}^{m'} - \epsilon_{2n-1}^m) \sin n\nu t + (\epsilon_{2n}^{m'} - \epsilon_{2n}^m) \cdot (1 - \cos n\nu t)\}. \end{aligned} \right\} \quad (13)$$

Spin-spin relaxation will be manifested, in the simplest case, by an additional member in the denominator of relation (13), equal to $(1/T_2)^2$ (see [4], p. 37). If the perturbation is present for a sufficiently long time (slow passage conditions), the member $\mathcal{H}_t/\nu t$ in the denominator can be neglected in comparison with $(1/T_2)^2$ regardless of the value of the frequency ω . The signal sweep time T_{exp} must of course fulfil the condition:

$$T_{\text{exp}} \gg \frac{T_2}{\nu} \cdot \max_t |\mathcal{H}_t|. \quad (14)$$

As long as this condition is fulfilled, resonance frequencies and half-band widths will be identical with the corresponding values of the system with the Hamiltonian H_0 . As the average value of the expression $\cos[(\omega - \omega_0)t + \mathcal{H}_t/\nu]$ is equal to zero for almost all ω (i.e. but for an enumerable set of points), as for $\cos(\omega - \omega_0)t$, relation (14) leads simultaneously to equal transition intensities for the Hamiltonians H and H_0 . Violation of relation (14) will lead to a change of the halfband width and intensity of transitions, whereas the frequencies will remain unchanged as long as condition (2) remains valid.

$f(t)$ will be independent of the spin coordinates (see equation (6)) even in systems which are not pseudo-conservative in cases where the frequency ν increases above all limits and where the functions φ are eigenfunctions of H_0 . The pseudo-conservative system may therefore be regarded as a good approximation of a general system for large frequencies ν . In the preceding relations the values ϵ_k^m must be substituted by the expectation values $\langle \varphi_m | H_k \varphi_m \rangle$. This approxima-

† The state of the system is described by the value of the z component of the total spin.

tion is valid, according to expression (6), when:

$$\nu \gg \max_t \left| \sum_{n=1}^{\infty} \frac{1}{n} \{ \langle \varphi | H_{2n-1} \varphi \rangle \sin nvt + \langle \varphi | H_{2n} \varphi \rangle (1 - \cos nvt) \} \right|. \quad (15)$$

The spectrum of a general molecule with periodic motion will therefore be reduced to the spectrum of a fixed system with an average Hamiltonian H_0 when the following conditions are fulfilled:

(1) The period of internal motion is much smaller than the spin-spin relaxation time (condition 2).

(2) The signal sweep time is large enough to fulfil condition (14).

(3) In systems which are not pseudo-conservative, the frequency of internal motion of the molecule must be large enough to fulfil the inequality (15). When this condition is not fulfilled, the eigenfunctions of the system cannot be approximated by relation (5).

Example

In order to illustrate the requirements imposed upon the frequency of internal motion by the various conditions stated above, a simple AB system with the following parameters (rotating $-\text{CH}_2\text{R}$ group) will be analysed:

$$\begin{aligned} \omega_A &= \omega_{0A} + q \cdot \cos vt, & \delta &= \omega_{0A} - \omega_{0B} = 20 \text{ c.p.s.}, \\ \omega_B &= \omega_{0B} + q \cdot \cos (vt + 2\pi/3), & q &= 20 \text{ c.p.s.}, \\ J_{AB} &= 15 \text{ c.p.s.} = \text{const.}, & T_2 &= 4 \text{ sec.} \end{aligned}$$

Let the signal sweep time be 0.5 sec (for a half-band width of 0.5 c.p.s.), i.e. practically the upper limit of T_{exp} . According to condition (2) we obtain $\nu \gg 0.25$ c.p.s. For the Hamiltonian of this system:

$$\begin{aligned} H_0 &= -(\omega_{0A} I_{zA} + \omega_{0B} I_{zB} + J_{AB} \mathbf{I}_A \cdot \mathbf{I}_B), \\ H_1 &= q(I_{zB}/2 - I_{zA}), \\ H_2 &= -\frac{\sqrt{3}}{2} q I_{zB}. \end{aligned}$$

H_1 and H_2 do not commute with H_0 , so that the system is not pseudo-conservative and the conditions (14) and (15) have to be fulfilled.

Number of state	Eigenfunctions φ	$\nu \gg$
1	$\alpha\alpha$	18.7
2	$\frac{3}{10} (\alpha\beta + \frac{1}{3}\beta\alpha)$	20.7
3	$\frac{3}{10} (\frac{1}{3}\alpha\beta - \beta\alpha)$	20.7
4	$\beta\beta$	18.7

Table 1. Eigenfunctions and the corresponding values of the right-hand side of inequality (15) in c.p.s.

The eigenfunctions of Hamiltonian H_0 and the corresponding values of the right side of the inequality (15) are given in table 1; from the table it can be seen that the system will be approximated by eigenfunctions of the form (5), as long as $\nu \gg 20$ c.p.s. The requirements of condition (15) are therefore about two orders

Transition	Frequency in c.p.s. relative to band centre	Relative intensity	$\max_t \mathcal{H}_t $
1-2	-5	1.6	33
3-4	-20	0.4	33
1-3	+20	0.4	19
2-4	+5	1.6	19

Table 2. Parameters of allowed transitions of the system investigated.

of magnitude more stringent than those of condition (2). In table 2, the transition energies and intensities are given for the Hamiltonian H_0 , as well as the corresponding values of $\max_t |\mathcal{H}_t|$. As $T_2/T_{\text{exp}} = 8$, condition (14) yields approximately $\nu \gg 250$ c.p.s., and this requirement is again about one order of magnitude more stringent compared with condition (15). A decrease of the frequency ν will therefore first be manifested by an increase of the half-band width (in the range $\nu \sim 200$ – 2000 c.p.s.) and only later by frequency changes.

REFERENCES

- [1] GUTOWSKY, H. S., and HOLM, C. H., 1956, *J. chem. Phys.*, **25**, 1228.
- [2] ALEXANDER, S., 1962, *J. chem. Phys.*, **37**, 967, 974.
- [3] LOEWENSTEIN, A., and CONNOR, T. M., 1963, *Ber. Bunsen Ges.* **67**, 280.
- [4] POPLE, J. A., 1959, *High-resolution Nuclear Magnetic Resonance* (New York).