Harmonic Oscillator Model for the Analysis of NMR Spectra of Di-substituted Benzenes

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Since the experiments of the high-resolution spectrum of the proton magnetic resonance in organic compounds showed very fruitful results, many efforts have been made to continue the measurements and to analyze the spectra of many compounds[1]. During these measurements, one encountered spectra so complicated that they can not be analyzed by the simple inspection of the chemical formula of the samples. These complicated spectra arise in the systems where the differences of the chemical shift values, $\Delta\sigma_{ij}$, and the spin-spin coupling constants, J_{ij}, are comparable to each other, where i and j refer to the resonating nuclei, and they can be analyzed by quantum-mechanical procedures. Two methods have so far been proposed for the analysis of these complicated spectra; one was shown by Banerjee, Das, and Saha[2] in the treatments of the two- and three-proton systems and the other, which is more general than the former, was shown by McConnell, McLean and Reilley[3].

This paper concerns the analyses of such

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1) See, for example, Pople, Schneider and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill Book Co. Inc., New York (1959).

2) N. K. Banerjee, T. P. Das and A. K. Saha, *Proc. Roy. Soc.* (*London*), A, 226, 490 (1954).

3) H. M. McConnell, A. D. McLean and C. A. Reilley, *J. Chem. Phys.*, 23, 1152 (1955).

complicated spectra, using di-substituted benzenes of the type X-  -Y as an example. The method to be shown here is based on the classical treatment of the nuclear magnetic resonance (NMR) phenomena, and is assumed to be helpful for chemists who are not familiar with the quantum-mechanical procedures to obtain the necessary understanding of the analysis of the NMR spectrum.

Analysis of NMR Spectrum by a Harmonic Oscillator Model

First, the nuclear magnetic resonance of a molecule which has only one hydrogen atom is considered. As there is no interest in the time-dependent phenomena, the equation of the classical or macroscopic vector $\vec{M}$ placed in a static magnetic field $\vec{H}_0$ may be written as

$$d\vec{M}/dt = \gamma\vec{M}\times\vec{H}_0 \qquad (1)$$

where, γ is the gyromagnetic ratio of proton. Eq. 1 is the formula given by Bloch[4]. The intensity of the signal due to the nuclear magnetic resonance can be measured by the x-component $\vec{M}(z//H_0)$ when $\vec{M}$ is forced to flip down onto the x-y plane by the interaction of the nucleus with the oscillating magnetic field $\vec{H}_1(t)$ which rotates in the x-y plane with the angular frequency ω_0. Thus, the resonance angular frequency is defined as that of $\vec{H}_1$ which flips $\vec{M}$ most effectively, called as the angular frequency of the Larmor precessional motion of $\vec{M}$ in the field of $\vec{H}_0$. Hence, we can calculate the resonant frequency and the relative intensity of the spectrum, even if we omit the effect of $\vec{H}_1$, and the contribution of $\vec{H}_1$ is taken into account in the considerations of the amplitude of the precession.

From (1), it is easily seen that M_x behaves as a simple harmonic oscillator which obeys Eq. 2 at resonance:

$$d^2M_x/dt^2+\omega_0^2M_x=0 \qquad (2)$$

On the other hand, the equation of the motion of a simple harmonic oscillator may be written as

$$m(d^2X/dt^2)+fX=0 \qquad (3)$$

where m and f are the mass and the force constant of the oscillator. Eq. 3 will become equal to Fig. 2 by making the following interpretation:

$$X=M_x,$$
$$f=\gamma H_0=\omega_0 \text{ and} \qquad (4)$$
$$m=1/\omega \ (=1/\omega_0 \text{ at resonance})$$

4) F. Bloch, *Phys. Rev.*, **70**, 460 (1946).

These relations can be extended to any many-spin system by slight modification of the definition of the force constants. For example, the straightforward extension to a two-spin system composed of two protons, A and B, may be made by additional replacement of the force constant, f, by the spin-spin coupling constant J as

$$f_{AB}=\pm J_{AB}/2 \qquad (4a)$$

A positive sign is used when $\vec{M}_A$ and $\vec{M}_B$ are parallel, and the negative sign antiparallel. The situation of this model of the interacting oscillators is illustrated in Fig. 1. The interaction energies of these oscillators refer the off-diagonal terms of secular equations, where the sign of eac term his taken to be positive as well as that of J. Justification of this choice of the sign will be given later.

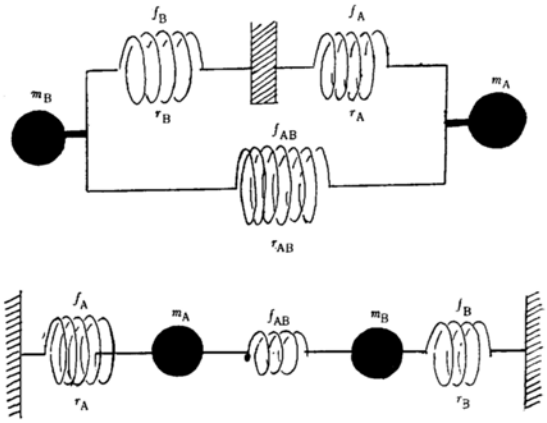

Fig. 1. Explanation of the oscillator model.
(a) $f_{AB}=J_{AB}/2$
(b) $f_{AB}=J_{AB}/2$

The potential energy of the system may be written as Eq. 5,

$$V=1/2\cdot[f_A(\Delta r_A)^2+f_{AB}(\Delta r_{AB})^2+f_B(\Delta r_B)^2] \qquad (5)$$

where r_A, r_B and r_{AB} are the elongations of the springs, A, B and C, whose force constants are f_A, f_B, and f_{AB}, respectively. The expression (5) may be rewritten by the Cartesian coordinate x as

$$\begin{aligned} V&=1/2\cdot[(f_A+f_{AB})x^2{}_A+2f_{AB}x_Ax_B \\ &\quad+(f_B+f_{AB})x^2{}_B] \\ &=1/2\cdot[(\omega_A+J_{AB}/2)M^2{}_{Ax}+J_{AB}M_{Ax}M_{Bx} \\ &\quad+(\omega_B+J_{AB}/2)M^2{}_{Bx}] \end{aligned} \qquad (6)$$

In Eq. 6 we used the relations, $\Delta r_A=x_A$, $\Delta r_B=-x_B$ and $\Delta r_{AB}=x_A+x_B$.

The kinetic energy of the system, T, is as shown by

$$T=m[\dot{x}^2_A+\dot{x}^2_B]/2 \tag{7}$$

$$=[\dot{M}^2_{Ax}+\dot{M}^2_{Bx}]/2\omega \tag{7a}$$

As the x-y components of the magnetic vectors, $\vec{M}_{Axy}$ and $\vec{M}_{Bxy}$ rotate about the z-axis, the x-components of these vectors may be written as

$$\left.\begin{aligned} M_{Ax}&=M_{Axy}\cos\omega t \\ M_{Bx}&=M_{Bxy}\cos\omega t \end{aligned}\right\} \tag{8}$$

Substituting Eq. 8 into Eqs. 6a and 7a, the motion of M_{Ax} and M_{Bx} are given by the classical equation of motion,

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{M}_{ix}}\right)+\frac{\partial V}{\partial M_{ix}}=0 \quad (i=A, B)$$

which leads a set of two homogeneous equations,

$$(\omega_A+J_{AB}/2-\omega)M_{Ax}+J_{AB}M_{Bx}/2=0 \tag{10}$$

$$J_{AB}M_{Ax}/2+(\omega_B+J_{AB}/2-\omega)M_{Bx}=0 \tag{10a}$$

These equations have a non-vanishing solution only when the determinant of the coefficients of M_{Ax} and M_{Bx} is zero, i.e.,

$$\begin{vmatrix} \omega_A+J_{AB}/2-\omega, & J_{AB}/2 \\ J_{AB}/2, & \omega_B+J_{AB}/2-\omega \end{vmatrix}=0 \tag{11}$$

and from the secular equation (11), we obtain the relation,

$$\omega_0=1/2\cdot[(\omega_A+\omega_B)+J_{AB}\pm(\sigma^2_{AB}+J^2_{AB})^{1/2}] \tag{12}$$

where $\sigma_{AB}=\delta_A-\delta_B$ is the chemical shift between the protons of A and B. Similar treatment of model 2b gives the resonant frequency,

$$\omega_0=1/2\cdot[(\omega_A+\omega_B)-J_{AB}\pm(\sigma^2_{AB}+J^2_{AB})^{1/2}] \tag{12a}$$

It is reasonable to assume that the energy absorbed by the system at resonance is proportional to the magnitude of the mean kinetic energy of the oscillator, i.e., to the square of the vector $\vec{M}_{xy}=\vec{M}_{Axy}+\vec{M}_{Bxy}$. Hence, the relative intensity of the spectrum at the frequency ω_0, $I(\omega_0)$, is calculated from Eq. 10 or 10a with the normalization condition of the magnetic vector, (13),

$$M_{Axy}(\omega_0)^2+M_{Bxy}(\omega_0)^2=1 \tag{13}$$

as

$$I(\omega_0)=[M_{Axy}(\omega_0)+M_{Bxy}(\omega_0)]^2 \tag{14}$$

$$=1-2\frac{(\omega_A-\omega_0)(\omega_B-\omega_0)}{(\omega_A-\omega_0)^2+(\omega_B-\omega_0)^2} \tag{15}$$

The calculated spectrum is shown in Fig. 2.

Although the present method of analysis is based on the classical treatment of an oscillator model, it is shown that the results of this analysis are in accordance with those to be obtained quantum-mechanically.

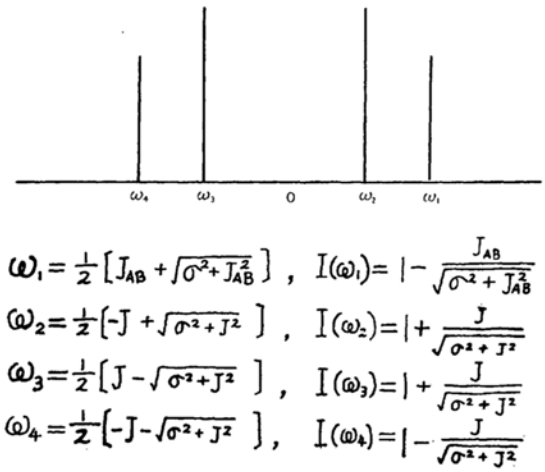

Fig. 2. Calculated spectrum.

The quantum-mechanical Hamiltonian of a two-spin system in a laboratory coordinate system may be expressed as

$$\mathcal{H}=-\gamma_A\vec{I}_A\cdot\vec{H}_A-\gamma_B\vec{I}_B\cdot\vec{H}_B+J_{AB}\vec{I}_A\cdot\vec{I}_B \tag{16}$$

The time-dependent Schroedinger equation is given by Eq. 17 in a rotating coordinate system which rotates with angular velocity, $\vec{\omega}$, as

$$i\hbar\dot{\Psi}_r=[-\gamma_A\vec{I}_A(\vec{H}_A+\omega/\gamma_A) -\gamma_B\vec{I}_B(\vec{H}_B+\omega/\gamma_B)+J\vec{I}_A\vec{I}_B]\Psi_r \tag{17}$$

The fields at I_A and I_B are effectively reduced to zero, provided that the angular velocities of the coordinates are given by

$$\vec{\omega}_A=-\gamma_A(\vec{H}_A-J_{AB}\vec{I}_B/\gamma_A) \tag{18}$$

and

$$\vec{\omega}_B=-\gamma_B(\vec{H}_B-J_{AB}\vec{I}_A/\gamma_B) \tag{18a}$$

If we return to the laboratory coordinate system, the effective fields at $\vec{I}_A$ and $\vec{I}_B$ are written as

$$\vec{H}_A-J_{AB}\vec{M}_B/2\gamma_A \tag{19}$$

and

$$\vec{H}_B-J_{AB}\vec{M}_A/2\gamma_B \tag{19a}$$

respectively.

By assuming the macroscopic equations which have the same form as Eq. 1, we obtain the equations,

$$d\vec{M}_A/dt=\gamma_A\vec{M}_A\times(\vec{H}_A-J_{AB}\vec{M}_B/2\gamma_A) \tag{20}$$

and

$$d\vec{M}_B/dt=\gamma_B\vec{M}_B\times(\vec{H}_B-J_{AB}\vec{M}_A/2\gamma_B) \tag{20a}$$

By taking the time-independence of the components of M_{Az} and M_{Bz} into consideration,

Eqs. 22 and 22a are substituted into Eqs. 21 and 21a, respectively.

The equations for the x-components of Eqs. 20 and 20a are

$$dM_{Ax}/dt=(\gamma_A-J_{AB}M_{Bz}/2)M_{Ay}+J_{AB}M_{By}M_{Az}/2 \quad (21)$$

and

$$dM_{Bx}/dt=(\gamma_B-J_{AB}M_{Az}/2)M_{By}+J_{AB}M_{Ay}M_{Bz}/2 \quad (21a)$$

where

$$\left.\begin{aligned}M_{Ax}&=M_{Axy}\cos\omega t\\ M_{Ay}&=-M_{Axy}\sin\omega t\end{aligned}\right\} \quad (22)$$

and

$$\left.\begin{aligned}M_{Bx}&=M_{Bxy}\cos\omega t\\ M_{By}&=-M_{Bxy}\sin\omega t\end{aligned}\right\} \quad (22a)$$

Experimental

Calculations and measurements of the NMR spectra were performed for the di-substituted benzenes of the type of X-  -Y: *p*-aminobenzoic acid was dissolved in a concentrated aqueous solution of potassium hydroxide, and *p*-toluidine, *p*-nitrophenol, and *p*-nitrobenzaldehyde were dissolved in carbon tetrachloride, methanol and acetone, respectively. These solutions were saturated at 28°C and sealed in the glass tubes with the diameter of 3.5~3.8 mm.

The apparatus of the NMR measurements is the one constructed in this laboratory having the same structure as the one reported by Gutowsky et al. before[5], and operated at the frequency of 27.030 Mc. The samples were spinned during the measurements. The separations of each component of the spectra were measured on the recorded charts using the records of ethanol as the standard reference: the J value of the coupling between the methyl and methylene groups in ethanol was taken as 6.90 cps.[5]

Discussion

In Fig. 3, the spectrum for the anisaldehyde is shown as an example of NMR measurements. The values of the chemical shift and the spin-spin couplings were calculated from Eqs. 12 and 12a as listed in Table I. The maximum error in the results of Table I is about 10%, which is assumed to be mainly due to the fluctuations in the chart speed of the recorder. Rigorously speaking, the compounds used here are not the two-spin system, but belong to four-spin system, and the values listed in Table I contain some error due to this approximation. But, this error is assumed to be quite small.

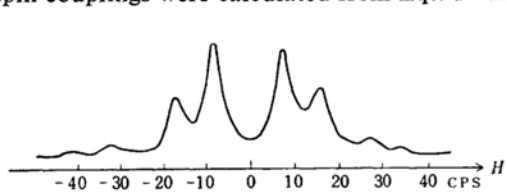

Fig. 3. The spectrum of anisaldehyde. Resonance frequency=27 Mc.

TABLE I. J AND σ VALUES OF THE RING PROTONS OF X-  -Y TYPE MOLECULES

RES. FREQ.=27 Mc.

X	Y	J cps.	σ cps.
-CHO	CH_3O-	8.62	24.2
-COOH	NH_2-	8.21	30.1
$-CH_3$	NH_2-	8.70	13.54
$-NO_2$	HO-	9.06	31.1
$-NO_2$	OHC-	9.24	6.6

It is seen in Table I that the σ's are dependent on the species of the substituents of X and Y, whereas J's are not dependent with a constant value of about 8.7($\pm$0.5) cps. If we can assume that an additive law holds with the chemical shifts of the ring protons, δ, of monosubstituted benzenes, the magnitudes of σ's could be related by the relation,

$$|\sigma|=|(\delta_X{}^o-\delta_Y{}^m)-(\delta_Y{}^o+\delta_X{}^m)| \quad (23)$$

where, for example, $\delta_X{}^o$ and $\delta_Y{}^m$ refer to the chemical shifs of *ortho*-proton of X and the meta-proton of Y, respectively.

We calculated the magnitudes of σ by using the values of δ's for the monosubstituted benzenes reported by Corio and Dailey[7], and compared the calculated results with those obtained experimentally. Agreements are not good between the σ's of calculation and of observation whereas the observed values of σ's showed good proportionality to $|\delta_x{}^o-\delta_y{}^o|$. This seems to suggest that the additivity does not hold with the δ's for the ring protons of di-substituted benzenes.

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5) H. S. Gutowsky, L. Meyer and R. E. McClure, *Rev. Sci. Inst.*, **24**, 644 (1953).
6) J. T. Arnold, *Phys. Rev.*, **102**, 136 (1956).
7) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).