MULTIPLE-QUANTUM NMR STUDY ON CORRELATION OF TWO METHYL GROUPS

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Abstract

A multiple-quantum NMR study on the correlation of two methyl groups in the same molecular framework is presented. Because of increasing spectral simplicity in the multiple-quantum transitions of higher order, observation of 4-quantum spectrum serves as a simple test for any possible correlated motion between two methyl groups. Study of the effect of correlation on multiple-quantum spectrum of some molecules with two adjacent methyl groups is reported.

I. Introduction

Rotating groups in the same molecular framework may be sterically hindered by each other and such a coupled motion can be studied by NMR. As an example, two adjacent methyl groups may exhibit some degree of correlated motion as two wheels in gear[1−3]. In general, the spectra of oriented molecules obtained by traditional single-quantum NMR are complicated and may be sometimes difficult to analyze. However, the techniques of multiple-quantum (MQ) NMR spectroscopy can greatly simplify spectral analysis, and have been used to study conformation [4,5] and correlated relaxation[6−9].

We shall demonstrate the application of MQ NMR techniques to the study on the correlation of two adjacent methyl groups. Although the 2-body correlation also shows in regular single-quantum spectrum, the spectral complexity makes spectral assignment difficult. We shall show that 4-quantum spectrum is sensitive to the 2-body correlation[2] and thus can be used to distinguish the cases of uncorrelated motion from those of correlated motion.

II. Theory

Let us consider a system of two methyl groups as shown in Fig. 1. For the uncorrelated case, these two groups move independently of each other and their relative orientations are random. As a consequence of rapid reorientation, the time-average magnetic dipole-dipole couplings between protons belonging to different groups are equal. Nevertheless, this is not true

if these two methyl groups move in a correlated way as two wheels in gear. As shown in Fig. 1(b), the methyl group on the left rotates clockwise, however, while that on the right rotates counter-clockwise. Although each group rotates very fast about its 3-fold axis, the relative orientation is in good order. In this paper, we shall examine two extreme cases, i.e. the complete correlation and the complete non-correlation.

According to the top configuration of Fig. 1(b), there are four distinct intermethyl dipolar coupling constants:

$$a = D_{24} = D_{34},$$
$$b = D_{14} = D_{25} = D_{36},$$
$$c = D_{35} = D_{26},$$
$$d = D_{16} = D_{15}.$$

The time-averaged dipolar coupling constants are averaged over the three possible configurations as in Fig. 1(b) and they are given by

$$w = \langle D_{24} \rangle = \langle D_{34} \rangle = \langle D_{25} \rangle = \langle D_{36} \rangle = \langle D_{16} \rangle$$
$$= \langle D_{15} \rangle = (a + b + d)/3,$$
$$v = \langle D_{14} \rangle = \langle D_{26} \rangle = \langle D_{35} \rangle = (b + 2c)/3,$$
$$u = \langle D_{12} \rangle = \langle D_{13} \rangle = \langle D_{23} \rangle = \langle D_{45} \rangle$$
$$= \langle D_{46} \rangle = \langle D_{56} \rangle.$$

For the correlated motion, there are two different intermethyl dipolar coupling constants (w and v), and one intramethyl dipolar coupling constant (u). If the motion between two methyl groups is not correlated, one needs to average the dipolar couplings over additional six different configurations. It can be shown that all of the intermethyl dipolar couplings are equal to

$$x = (v + 2w)/3 = (2a + 3b + 2c + 2d)/3,$$

and there are only two distinct coupling constants (x and u). The difference in the number of intermethyl dipolar coupling constants has a striking effect on the symmetry of the Hamiltonian and the NMR spectrum. The symmetry group for two methyl groups in correlated motion is isomorphic to the symmetry group of cyclopropane molecule[10]. In the molecule of cyclopropane shown in Fig. 2, the dipolar couplings D_{14}, D_{35} and D_{26} are all equal, and they are different from the vales of D_{24} (D_{34}, D_{25}, D_{36}, D_{16} or D_{15}). Since there is an one-to-one correspondence between the dipolar couplings for cyclopropane molecule and the system of two correlated methyl groups, one may use the symmetry group D_{3h} of cyclopropane for the latter system.

By use of the characteristic table for the D_{3h}-group[11], one can decompose the eigenstates of the m-quantum manifold into several irreducible representations. The result is given as follows:

$$m = 3: \; A_1',$$
$$m = 2: \; A_1' + A_2'' + 2E' + 2E'',$$
$$m = 1: \; 3A_1' + A_1'' + A_2'' + 3(2E') + 3(2E''),$$
$$m = 0: \; 3A_1' + A_1'' + A_2' + 3A_2'' + 3(2E') + 3(2E''),$$

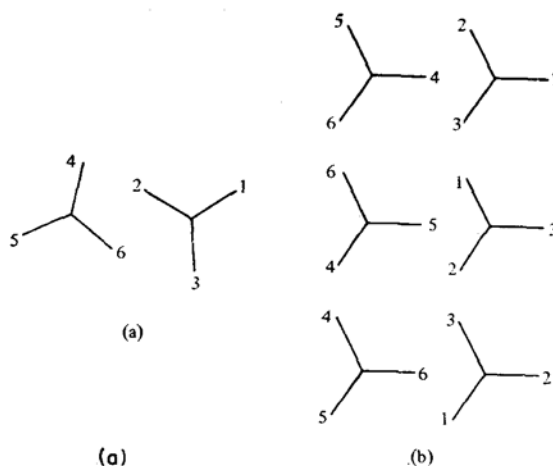where the states $2E'$ and $2E''$ are doubly degenerate. The energy level diagram is shown in Fig.

Fig. 1. (a) The geometry of two adjacent methyl groups. In the case of uncorrelated motion the two methyl groups move independently. On the average, the couplings between protons belonging to different methyl groups are equal. (b) With gearing motion, the averaged coupling between protons 1 and 4 is not equal to the coupling between 1 and 5. Thus, there are two intermethyl couplings and one intramethyl coupling.
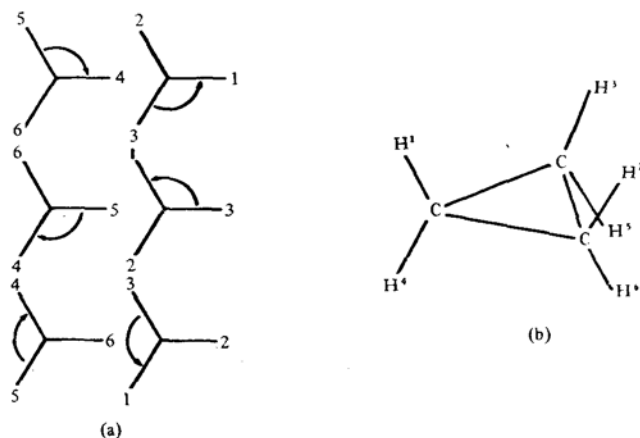

Fig. 2. (a) Methyl groups in the correlated motion. (b) The symmetry group for two correlated methyl groups is isomorphic to the symmetry group of cyclopropane. The average coupling constants $\langle D_{14} \rangle$ and $\langle D_{15} \rangle$ are different.

3. The states with negative m have the same decomposition as their mirror state with positive m. It can be shown from the above classification of irreducible representations of eigenstates that there are one 6-Q transition, $A_1'(m = -3) \rightarrow A_1'(m = 3)$, and two 5-Q transitions, $A_1'(m = -3) \rightarrow A_1'(m = 2)$, $A_1'(m = -2) \rightarrow A_1'(m = 3)$. Any pair of mirror states has the same dipolar energy shift. As a consequence, the transitions between these mirror states have no net dipolar shift and their transition lines are located at the center of corresponding m-Q domain. The 4-Q transitions of $A_1'(-2) \rightarrow A_1'(2)$, $A_2''(-2) \rightarrow A_2''(2)$, $2E'(-2) \rightarrow 2E'(2)$ and $2E''(-2) \rightarrow 2E''(2)$ are mirror-state transitions. They are all located at the center of 4-Q domain. Yet, there are three pairs of transitions $A_1'(-1) \rightarrow A_1'(3)$,

$A_1'(-3) \to A_1'(1)$ which have non-zero dipolar shift. Consequently, there are, in total, seven distinct 4-Q transition lines with one in the middle of 4-Q domain and three on each side.
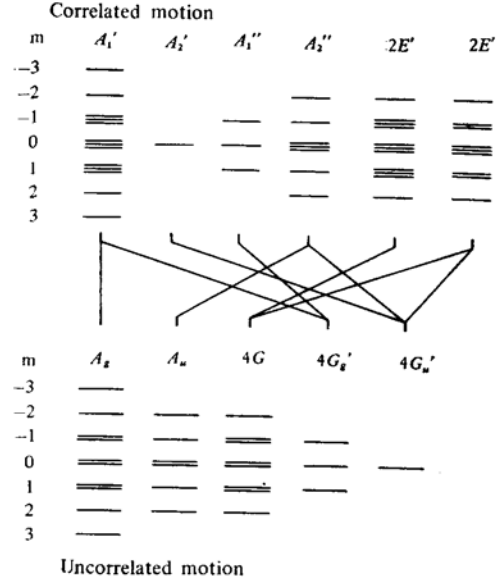

Fig. 3. Energy-level diagrams for two methyl groups in the correlated motion or uncorrelated motion. The number of multiple-quantum transitions can be found from the diagrams. There are one 6-Q, two 5-Q transitions for both cases, but five 4-Q transitions for the uncorrelated motion, and seven for the correlated motion.

The dipole-dipole interaction Hamiltonian of two methyl groups in correlated motion is given by

$$H = H_u + H_v + H_w$$
$$= u \sum_{i<j} U_{ij} + v \sum_{i<j} V_{ij} + w \sum_{i<j} W_{ij},$$

where H_u is the Hamiltonian for the intramethyl dipolar interaction, H_v and H_w are the intermethyl dipolar Hamiltonians. The bilinear operators U_{ij}, V_{ij} and W_{ij} are given in the same form as

$$U_{ij}, V_{ij}, W_{ij} = I_{iz}I_{jz} - (I_{i+}I_{j-} + I_{i-}I_{j+})/4. \quad \cdot$$

The subscripts i and j refer to different sets o methyl protons as

$$U_{ij}: (i,j) = (1,2),(1,3),(2,3),(4,5),(4,6),(5,6),$$
$$V_{ij}: (i,j) = (1,4),(2,6),(3,5),$$
$$W_{ij}: (i,j) = (2,4),(3,4),(1,5),(2,5),(1,6),(3,6).$$

It can be shown that eigenenergies of $A'_1(3)$ and $A'_1(2)$ are given by

$$H|A_1'(3)\rangle = 3(2u + v + 2w)/4|A_1'(3)\rangle$$

and

$$H\,|\,A'_1(2)\rangle = 0.$$

The eigenenergies for the triplet of A'_1 (1) can be found by matrix diagonization of

$$H = \begin{bmatrix} -\dfrac{v}{4} - \dfrac{w}{2} & -\dfrac{w}{\sqrt{2}} & -\dfrac{v}{2} - \dfrac{w}{2} \\[2.5ex] -\dfrac{w}{\sqrt{2}} & -\dfrac{u}{2} + \dfrac{3}{4}v - \dfrac{w}{2} & -\dfrac{u}{\sqrt{2}} \\[2.5ex] -\dfrac{v}{2} - \dfrac{w}{2} & -\dfrac{u}{\sqrt{2}} & -u - \dfrac{v}{4} + \dfrac{w}{2} \end{bmatrix}.$$

By use of the results from the above analysis, theoretical spectra of 4-, 5- and 6-Q trasitions can be generated for given values of u, v and w.

In the uncorrelated case, the symmetry is higher and the symmetry group is different from D_{3h} By using the symmetry group for each methyl group, D_3, one may obtain the resultant representation by making direct product of two D_3-groups as

$$(A_1 + 2E) \times (A_1 + 2E) = A_1 \times A_1 + 2A_1 \times E + 2E$$
$$\times A_1 + 4E \times E.$$

Since two methyl groups are identical, one should include the permutation symmetry and introduce the symmetric and antisymmetric forms for wavefunctions. The energy level diagram is shown in Fig. 3. It can be shown that there are five distinct 4-Q transitions instead of seven as in the correlated case. The eigenstates relevant to our analysis for 4-, 5- and 6-Q transitions are the symmetric wavefunctions of the $A_1 \times A_1$-type, i.e. A_g.

The dipole-dipole interaction Hamiltonian of two uncorrelated methyl groups is given by

$$H = H_u + H_v.$$

This is a special situation of the previous case by making the coupling constants v and w equal. It can be shown in a similar way that

$$H\,|\,A_g(3)\rangle = 3(2u + 3v)/4\,|\,A_g(3)\rangle$$

and

$$H\,|\,A_g(2)\rangle = 0.$$

The eigenenergies for the doublet of $A_g(1)$ can be calculated by diagonization of a 2×2 matrix and are found to be

$$\lambda_\pm = -\frac{3}{4}u - \frac{1}{4}v \pm \frac{1}{2}\left(\frac{9}{4}u^2 + 7v^2 - 3uv\right)^{1/2}.$$

As a consequence, the dipolar-frequency shifts in the 6-, 5- and 4-Q spectra are given by

$$m = 6: \ 0,$$
$$m = 5: \ \pm 3(2u + 3v)/4,$$
$$m = 4: \ \pm\left(\frac{9}{4}u + \frac{5}{2}v \pm \frac{1}{2}\left(\frac{9}{4}u^2 + 7v^2 - 3uv\right)^{1/2}\right).$$

From exprimental 4-, 5- and 6-Q spectra and the above relation, one can determine the coupling

constants u and v.

III. Experiments and Conclusions

The extent of the correlated motion that two adjacent rotation methyl groups have is determined by the potential barrier of the interaction and by the temperature of observation. According to the duration of correlation τ_c, the degree of correlation can be classified into three main categories: (i) completely uncorrelated motion ($\tau_c^{-1} \gg 10$ kHz); (ii) completely correlated motion ($\tau_c^{-1} \gg 0.1$ kHz); (iii) the intermediate case. The time scale defined here refers to the magnitude of the dipolar splittings.

As discussed earlier, the number of 4-Q transitions (five expected for uncorrelated and seven for correlated motion) provides a ready test of the limits for the motion of two methyl groups. As an example, a sample of 2,3-dimethylmaleic anhydride (30% in mole), dissolved in a liquid crystal solvent of p-octylphenyl-2-chloro-4-(p-heptybenzoxyloxy)benzeoate, was studied by using MQ NMR techniques in a magnetic field of 42.5 kG at 50°C. The MQ spectra were obtained by the TPPI method[12]. An ensemble average was done by taking averages of each spectrum in various preparation periods ranging 1—7 ms. The experimental MQ spectra of 4-, 5- and 6-Q regions are shown in Fig. 4. Assuming that the intramethyl dipolar coupling constant u is equal to 2.00 kHz and that the intermethyl coupling constant v is equal to -0.59 kHz, the spectra are best fitted with the model of completely uncorrelated motion. The calculated stick spectrum using the above parameters is shown in Fig. 4, and is in agreement with the experimental spectrum.

Another type of molecule with two methyl groups in close positions was also studied. The experimental spectra of MQ transitions of 1,8-dimethyl naphthalene are shown in Figs. 5 and 6. The protons at the ring positions were substituted by deuterons. During the evolution period of the MQ-pulse sequence, an RF radiation was applied to decoupling the interaction between deuterons and methyl protons. One may notice that the MQ-spectra of higher order are simpler
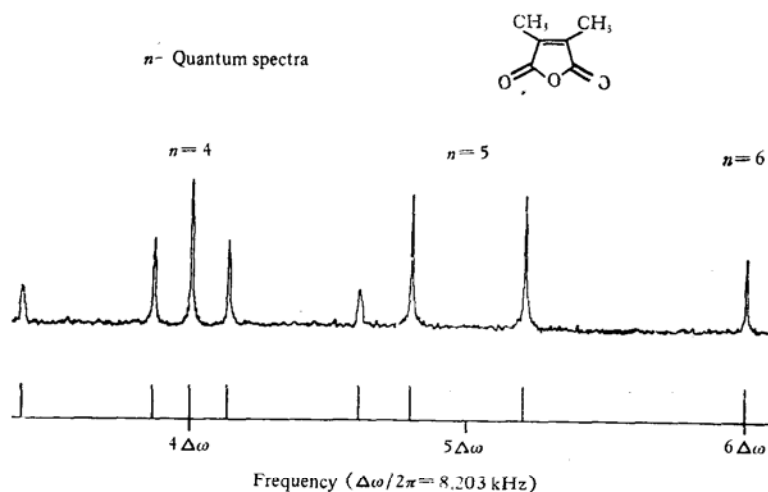

Fig. 4. (a) Spectra of 4-, 5- and 6-Q transitions in dimethyl maleic anhydride. Five of the 4-Q transitions were observed. (b) Calculated stick spectrum when assuming that in the uncorrelated motion the intramethyl coupling constant is equal to 2.00 kHz and intermethyl coupling constant equal to -0.59 kHz.

than the usual 1-Q spectrum. The calculated stick spectrum assuming uncorrelated motion is also in agreement with the experimental spectrum.
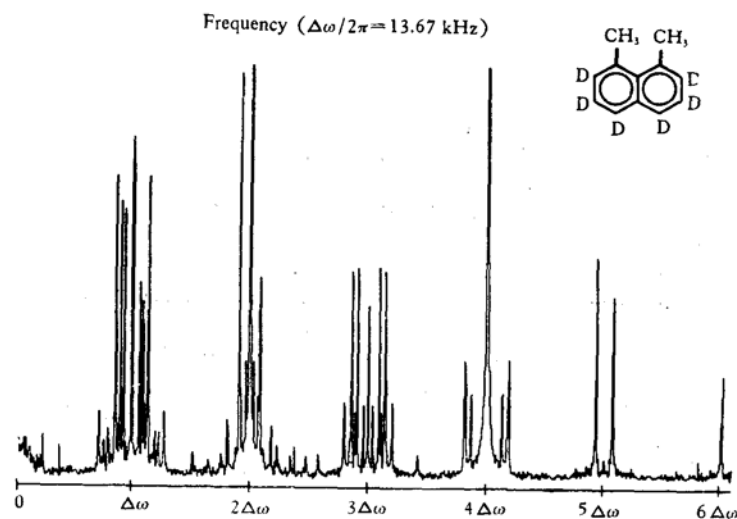

Fig. 5. Multiple-quantum spectra of 1,8-dimethyl naphthalene with ring protons deuterated. MQ-spectra of higher order are simpler than the regular single-quantum spectrum.
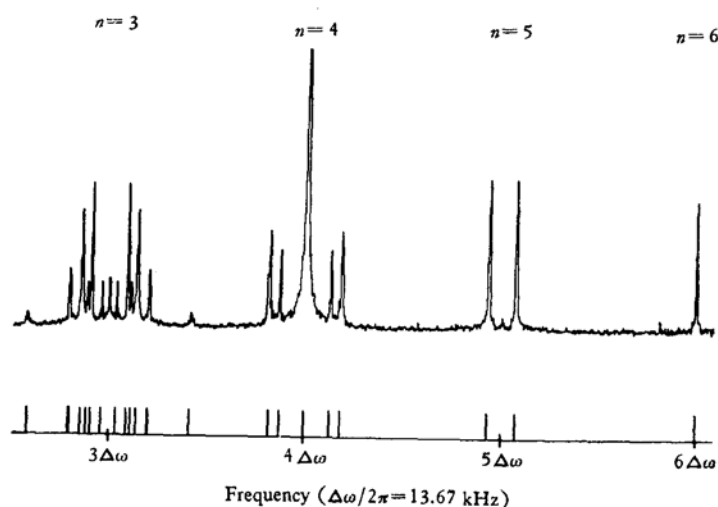

Fig. 6. The top figure shows the experimental spectra of 3-, 4-, 5- and 6-Q transitions of 1,8-dimethyl naphthalene. The lower stick spectra are obtained by assuming the methyl groups to be in uncorrelated motion.

In conclusion, we have demonstrated that the MQ-spectra of higher order are simpler than the regular single-quantum spectrum. As a consequence, spectral analysis and study of correlation of motional groups are greatly simplified. Within the time scale defined by the inverse of dipolar splittings, the two methyl groups of both types of molecules rotate quite independently. To be able to observe effects of correlation on NMR spectra, the correlation time of motion is required to be longer than a few milliseconds. Molecules with rotating groups of larger poten-

tial barrier may show a higher degree of correlation motion and correlated motion may be observed at low temperatures.

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