

Multiple quantum NMR study of correlation of two methyl groups

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(Received 2 June 1980; accepted 30 June 1980)

Molecules which have rotating groups may show coupled motions. As an example, two adjacent methyl groups may exhibit some degree of correlated motion as two wheels in gear.¹ The spectra obtained by traditional single quantum NMR in oriented molecules may sometimes be complicated and difficult to analyze. However, the techniques of multiple quantum (MQ) NMR spectroscopy can yield analyzable spectra²⁻⁶ and have been used to study conformation⁷ and correlated relaxation.⁸⁻¹¹ In this Communication, we would like to report the first preliminary and illustrative results on the study of correlation of two methyl groups by multiple quantum (MQ) NMR. We show that the high n -quantum spectra distinguish simply between the cases of uncorrelated motion (independent rotation) and correlated motion (geared rotation). As an example we present results on the system to partially oriented 2,3-dimethylmaleic anhydride oriented in a liquid crystal solvent.

The extent of the correlated motion of two neighboring rotating methyl groups is determined by the potential barrier of the coupling and the temperature of observation. The lifetime τ_c which characterizes the duration of the correlation may be classified into three categories: (I) completely uncorrelated motion ($\tau_c^{-1} \gg 10$ KHz), (II) completely correlated motion ($\tau_c^{-1} \ll 0.1$ KHz) and (III) intermediate case. The time scale defined here refers to the magnitude of the dipolar splittings. In the case of extremely short correlation time, the two methyl groups can be thought of as moving independently. There are therefore two different average dipole-dipole coupling constants, one intramethyl coupling constant and one intermethyl coupling constant as shown in Fig. 1(a). In the case of completely motion, there is one additional intermethyl coupling constant as shown in Fig. 1(b). For N spins it can be shown that the $N-2$ quantum spectrum is sensitive to two-body correlations and has a number of triplets equal to the number of different dipole couplings (i. e., the number of different pairs of spins). Thus in this case, there should be a distinction in the four-quantum spectrum between these two cases. It is found¹² by group theory that there are five transitions for the case (I) and seven transitions for the case (II) in the four-quantum manifold and there are two five-quantum and one six-quantum transitions for both cases. The number of four-quantum transitions (five expected for uncorrelated and seven for correlated motion) provides a ready test on the limits for two methyl groups.

As a specific example, samples of 2,3-dimethylmaleic anhydride (30% in mole) dissolved in *p*-octylphenyl 2-chloro-4-(*p*-heptybenzoxyloxy) benzoate were observed in a magnetic field of 42.5 kG at 50.0°C. The multiple quantum spectra were obtained by TPPI-ECHO

method.^{5,13} An ensemble average process was done on the multiple quantum spectra by taking averages of each spectrum of various preparation periods ranging from 1.0 msec to 7.0 msec. The experimental multiple quantum spectra of four, five, and six-quantum regions and the calculated stick spectra based on a model of completely uncorrelated motion are shown in Fig. 2 as a comparison. It is concluded that the two methyl groups of 2,3-dimethylmaleic anhydride rotate quite independently within the time scale defined by the inverse dipolar splittings. To observe a substantial change in the multiple quantum (MQ) NMR spectra due to the correlated motion, the correlation time τ_c should be longer than a few milliseconds. Some molecules with rotating groups of larger potential barrier may show a high degree of correlated motion at low temperature. Such multiple-quantum experiments on various molecules over a range of temperatures have been performed and will be reported in our full paper.

We would like to acknowledge the help of Mr. S. Sinton in computer simulation and Mr. S. Wolfe in sample syntheses.

This work has been supported by the Division of Materials Sciences, Office of Basic Energy Sciences, U. S.

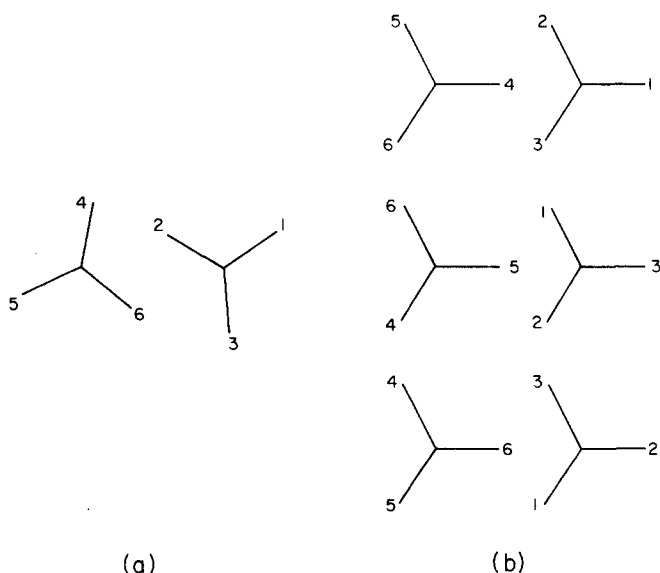


FIG. 1. (a) The geometry of two adjacent methyl groups. In the case of uncorrelated motion the two methyl groups move quite independently. On the average, the couplings between protons belonging to different methyl groups are equal. (b) With correlated motion, the averaged coupling between protons 1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

n-Quantum Spectra

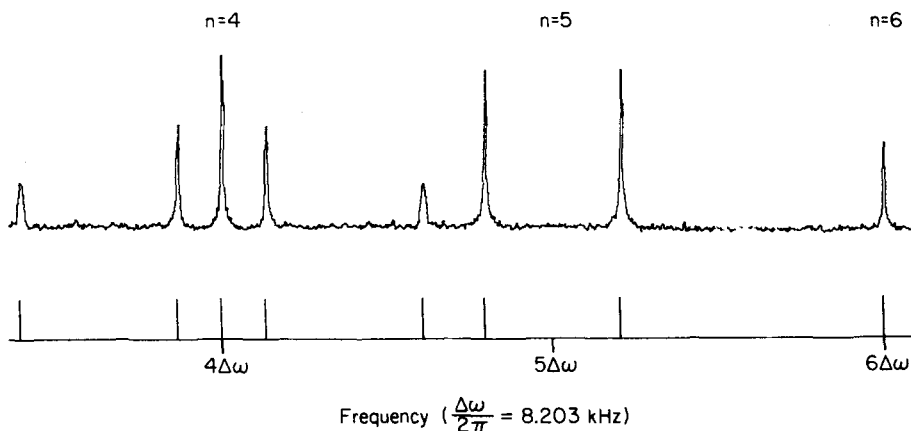
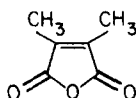


FIG. 2. (a) Spectrum of four, five, and six-quantum transitions. Five four-quantum transitions were observed. (b) Calculated stick spectrum assuming uncorrelated motion with intramethyl coupling constant equal to 2.00 KHz and intermethyl couplings constant equal to -0.59 KHz.

Department of Energy under Contract No. W7405-ENG-48.

¹E. E. Gurnell and P. Diehl, *Mol. Phys.* **24**, 489 (1972).

²W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.* **64**, 2229 (1976).

³S. Vega, T. W. Shattuck, and A. Pines, *Phys. Lett.* **37**, 43 (1976); S. Vega and A. Pines, *J. Chem. Phys.* **66**, 5626 (1977).

⁴A. Pines, D. Wemmer, J. Tang, and S. Sinton, *Bull. Am. Phys. Soc.* **23**, 21 (1978).

⁵G. Drobny, A. Pines, S. Sinton, D. Weitekamp, and D. Wem-

mer, *Faraday Symp. Chem. Soc.* **13**, 49 (1979).

⁶W. S. Warren, S. Sinton, D. P. Weitekamp, and A. Pines, *Phys. Rev. Lett.* **43**, 1791 (1979).

⁷S. Hsi, H. Zimmerman, and Z. Luz, *J. Chem. Phys.* **69**, 4126 (1978).

⁸M. E. Stoll, A. J. Vega, and R. W. Vaughan, *J. Chem. Phys.* **67**, 2029 (1977).

⁹A. Wokaun and R. R. Ernst, *Mol. Phys.* **36**, 317 (1978).

¹⁰R. Poupko, R. L. Vold, and R. R. Vold, *J. Magn. Reson.* **34**, 67 (1979).

¹¹J. Tang and A. Pines, *J. Chem. Phys.* **72**, 3290 (1980).

¹²J. Tang, Y-S. Yen, and A. Pines (to be published).

¹³G. Bodenhausen, R. L. Vold, and R. R. Vold, *J. Magn. Res.* **37**, 93 (1980).

Recoupling the angular momentum decoupling approximations^{a)}

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(Received 3 June 1980; accepted 1 July 1980)

The coupled states approximation¹⁻³ generally yields excellent results for a variety of scattering problems. However, there are a number of cases in which it is known to fail.⁴⁻⁷ We have developed a convenient and inexpensive method which significantly improves the coupled states results.

The close coupling equations, which are the exact equations for describing inelastic molecular collisions, may be written in the body-fixed frame of reference as²

$$\left(\frac{d^2}{dR^2} - \frac{\Lambda^0(J, j, n)}{R^2} + k_j^2 \right) \psi_{j,n}(R) - \sum_{j'} V_{jj'}^n(R) \psi_{j',n}(R) = \frac{\Lambda^+(J, j, n)}{R^2} \psi_{j, n+1}(R) + \frac{\Lambda^-(J, j, n)}{R^2} \psi_{j, n-1}(R). \quad (1)$$

Here n is the projection of \mathbf{j} onto the body-fixed z axis and $\Lambda^i(J, j, n)$ and $V_{jj'}^n(R)$ are the body-fixed matrix elements of the l^2 operator and the interaction potential, respectively.

The coupled states approximation consists⁸ of neglecting the right hand side of Eq. (1). This decouples the equations over the index n and drastically reduces the dimensionality of the coupled system. The effect of the neglected terms can be included to first order by a technique closely related to the distorted wave approximation. We have derived a matrix Green operator G in terms of the coupled states solutions φ determined by Eq. (1) with the right hand side set equal to zero. This Green operator has also been derived independently by