

A Suggestion for Detecting Rotational Tunnelling of CD₃ - Groups by Multiple - Quantum Spectroscopy

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1 Introduction

Recently the NMR study of deuterated methyl groups and ammonium ions has become of interest [1], [2]. The comparison of tunnel splittings from protonated compounds and their deuterated analogs provides additional information about the rotational potential and thus the structure of the methyl site in the molecule [1], [3].

The quadrupole interaction of the deuterons enables the observation of a broader range of tunnel splittings by lineshape analysis than the dipole-dipole coupling in the protonated methyl group. At the same time the tunnel frequency of a deuterated compound is reduced relative to that of the protonated form. Both effects contribute, enlarging the number of compounds whose tunnel frequencies are accessible by single and multiple-quantum NMR spectroscopy.

Multiple-quantum spectroscopy has been used in many applications [4] - [6], one being high resolution NMR in solids. The observation of weaker interactions normally dominated by the quadrupole coupling in deuterated systems is possible by double-quantum NMR spectroscopy, since certain transitions are insensitive to the quadrupole interaction [7], [8].

Detecting rotational tunnelling of CD₃ - groups with multiple-quantum spectroscopy is a novel method of determining tunnel splittings directly from the NMR spectra. Even in powder spectra sharp peaks appear at the tunnel frequency. This method is based on

properties of the quadrupole interaction and it should be equally sensitive to all tunnel frequencies. However, the experimental efficiency of exciting and detecting even order multiple-quantum transitions with large frequencies limits the range of detectable tunnel frequencies to small magnitudes. This technique is therefore a good tool for observing rotational tunnelling of highly hindered methyl groups or examining systems for which the degeneracy of E states has been lifted due to coupled rotations of methyl groups [9] or molecular friction [10].

2 Rotational Tunnelling of Deuterated Methyl Groups

Methyl groups experience a steric hindrance from atoms of the same or neighboring molecules. At low temperatures the energy of the methyl group is not sufficient to allow the nuclei to hop over the potential maxima. However, wavefunction overlap of nuclei in neighboring potential minima leads to time independent rotational tunnelling. This manifests itself as a splitting of the rotational energy levels into A , E^a and E^b states, labeled according to the irreducible representations of the C_3 point group.

The magnitude of the energy gap between the groundstate (A) and the higher states (E^a , E^b) is given by the tunnel frequency ν_T (see also [11]). The degeneracy of the E states may be lifted by molecular fric-

tion [10]. Coupled rotations of two methyl groups result in a more complex energy level scheme with three large splittings and a small one within the combined E states [9], [12].

According to the Pauli principle the total wavefunction of the ground state must be totally symmetric under operations of the C_3 group. It is assumed that the methyl group is in its electronic and vibrational groundstate. Then the space and spin wavefunctions ϕ_R and ϕ_S connected to the nuclei of the methyl group must have correlated symmetries. Only the following combinations are allowed: $\phi_R^A \phi_S^A, \phi_R^{E^a} \phi_S^{E^b}, \phi_R^{E^b} \phi_S^{E^a}$ [13], [14].

Another way to describe the wavefunctions of the methyl group is to use direct products of space and spin wavefunctions for each deuteron of the methyl group. Since the individual nuclei of the methyl group are indistinguishable, the wavefunctions $\{uvw\}$ give the connections of the spin functions u, v and w to the space functions of the nuclei in the potential minima 1, 2 and 3 symbolized by the given order in the notation (for details see [1]). Spin functions are labeled $|\alpha\rangle, |0\rangle$ and $|\beta\rangle$, with magnetic quantum numbers $I_z = 1, 0$ and -1 respectively.

Symmetry-adapted wavefunctions with the required symmetries for space and spin parts are given by

$$\begin{aligned} A(uvw) &= \frac{1}{\sqrt{3}} ([uvw] + [vwu] + [wuv]) \\ E^a(uvw) &= \frac{1}{\sqrt{3}} ([uvw] + \varepsilon[vwu] + \varepsilon^*[wuv]) \\ E^b(uvw) &= \frac{1}{\sqrt{3}} ([uvw] + \varepsilon^*[vwu] + \varepsilon[wuv]) \\ \varepsilon &= \exp\left(i\frac{2\pi}{3}\right), \end{aligned} \quad (1)$$

where u, v and w can each be $\alpha, 0$ or β .

Since tunnelling results from the overlap of spatial wavefunctions of the nuclei in neighboring potential minima, the tunnelling Hamiltonian H_T can be defined by overlap parameters:

$$\begin{aligned} \langle \phi_R \phi_S | H_T | (E * \phi_R) \phi_S \rangle &= C \\ \langle \phi_R \phi_S | H_T | (C_3 * \phi_R) \phi_S \rangle &= -\Delta \\ \langle \phi_R \phi_S | H_T | (C_3^2 * \phi_R) \phi_S \rangle &= -\Delta. \end{aligned} \quad (2)$$

As required by symmetry the eigenfunctions transform as A and linear combinations of E^a and E^b states, with eigenvalues -2Δ and Δ respectively, giving an overall tunnel frequency of $\omega_T = 3\Delta$.

In the Zeeman rotating frame the total Hamiltonian H of the system during free evolution periods is given by:

$$H = H_T + H_Q + H_D. \quad (3)$$

where fast rotating (nonsecular) terms are neglected.

The quadrupole Hamiltonians $H_Q^{(i)}$ of the three deuterons of the methyl group contribute to the quadrupole Hamiltonian H_Q (we take $\eta = 0$):

$$\begin{aligned} H_Q &= \sum_{i=1}^3 H_Q^{(i)} \\ &= \sum_{i=1}^3 \frac{e^2 q Q}{8\hbar} (3 \cos^2 \Theta^{(i)} - 1) (3I_z^{2(i)} - I^{2(i)}) \\ &= \sum_{i=1}^3 \frac{1}{3} \omega_Q^{(i)} (3I_z^{2(i)} - I^{2(i)}). \end{aligned} \quad (4)$$

The electric field gradients along the C-D bonds of the three nuclei have different angles $\Theta^{(i)}$ relative to the magnetic field. Therefore the spatial part of the quadrupole Hamiltonian differs for the three nuclei of the methyl group.

The secular dipole-dipole Hamiltonian H_D has a similar form and is explicitly included in the numerical calculations. It is neglected in the analytical arguments, because it is about 500 times smaller than the quadrupole interaction.

The tunnelling Hamiltonian H_T has rotational symmetry, while the quadrupole interaction is a single particle interaction of one deuteron with its associated electric field gradient. It is this difference of the two interactions which makes it possible to obtain information about tunnelling from single- and multiple-quantum spectra.

3 Lineshape Analysis of Single-Quantum Spectra

If the tunnel frequency is of the order of the quadrupole frequency, i.e., $\nu_T < 2$ MHz, numerical calculations show that characteristic features in the single-quantum spectra allow the determination of the tunnel frequency (Fig.1).

The quadrupole interaction mixes A and E states of the same Zeeman level. This results in each line of the central doublet of the spectrum splitting into three lines. The magnitude of these splittings are a measure of the tunnel frequency. This can be described by perturbation theory.

With this method the tunnelling frequency of $[\text{Cu}(\text{CD}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$ can be determined to be 610 ± 60 kHz (Fig.2). The isotope factor ν_T^H/ν_T^D of the tunnel frequencies of the protonated versus the deuterated compound of $[\text{Cu}(\text{CD}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$ is calculated as approximately 100 [1].

Even if the tunnel splitting is much larger than the quadrupole frequency, tunnelling can be distinguished from fast rotation. The quadrupole interaction mixes

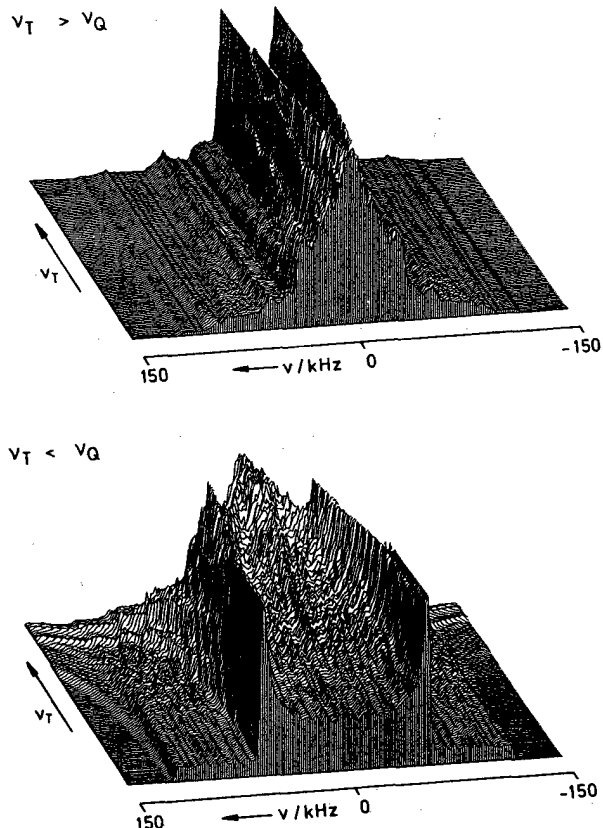


Figure 1: Representation of computed powder patterns for rotational tunnelling of CD_3 - groups with tunnelling frequencies larger (top) and smaller (bottom) than the quadrupole frequency $\nu_Q = e^2qQ/h$ (ν_T on a logarithmic scale).

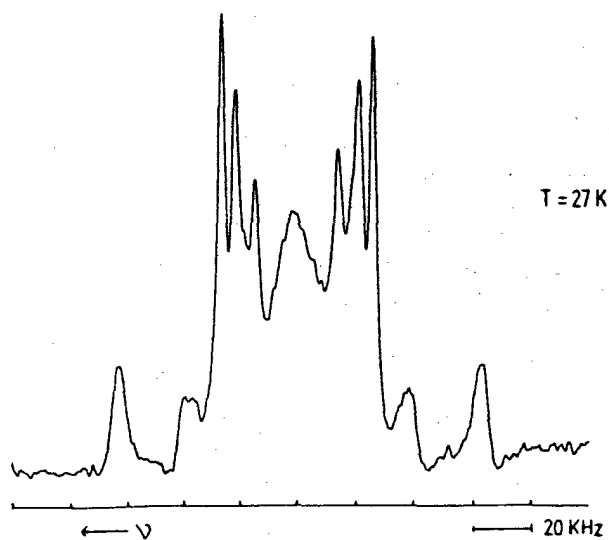


Figure 2: ^2H NMR spectra of $[\text{Cu}(\text{CD}_3\text{CO}_2)_2] \cdot \text{H}_2\text{O}$ measured at 27 K using a Bruker CXP 300 FT spectrometer at 46.07 MHz.

the E^a and E^b states, which are degenerate irrespective of the size of the tunnel frequency. This leads to the splitting μ in the energy level scheme (Fig.3). From transitions within these states the outer and middle peaks result.

For $\nu_t < \nu_Q = \frac{e^2qQ}{h} \approx 200$ kHz the determination of the tunnel splitting from single quantum spectra is difficult, since the spectra show a broad line with small peaks (Fig.1 bottom). It is this region where the use of multiple-quantum spectroscopy is sensitive and necessary.

4 Multiple-Quantum Spectroscopy

In order to describe the evolution of the spin system, the density matrix formalism has to be used [6]

$$\begin{aligned} \rho(t_0 + \Delta t) &= \exp(-iH\Delta t)\rho(t_0)\exp(iH\Delta t) \\ &= \sum_{r,s} (\langle M_r | \rho(t_0) | M_s \rangle \times \\ &\quad \exp(-i(\omega_r - \omega_s)\Delta t) | M_r \rangle \langle M_s |). \end{aligned} \quad (5)$$

$\rho(t_0)$ is the density matrix at time t_0 . M_r and M_s are the eigenstates of the time independent Hamiltonian H with eigenfrequencies ω_r and ω_s .

Peaks at the tunnel frequency in the spectra can appear if the eigenfrequencies of some states M_r and M_s differ by the tunnel frequency

$$\omega_r - \omega_s = \omega_T, \quad (6)$$

while the density matrix element for those states does not vanish

$$\langle M_r | \rho(t_0) | M_s \rangle \neq 0. \quad (7)$$

4.1 Frequency Condition

For systems with large tunnel splittings compared to the quadrupole splitting in high fields the energy levels are dominated by the Zeeman interaction and the tunnel splitting (Fig.3). For this case the energy level diagram can be determined analytically. The A and E states are further shifted and split by the quadrupole interaction. In both the A and E systems some states are shifted by the same amount λ (compare Eqn. 9). Coherences between those A and E states evolve with the tunnel frequency. In all cases these are even order multiple quantum coherences.

The eigenstates whose energy levels are shifted by λ are those for which all nuclei of the methyl group have spin wavefunctions with magnetic quantum numbers ± 1 . Since the quadrupole interaction is quadratic in

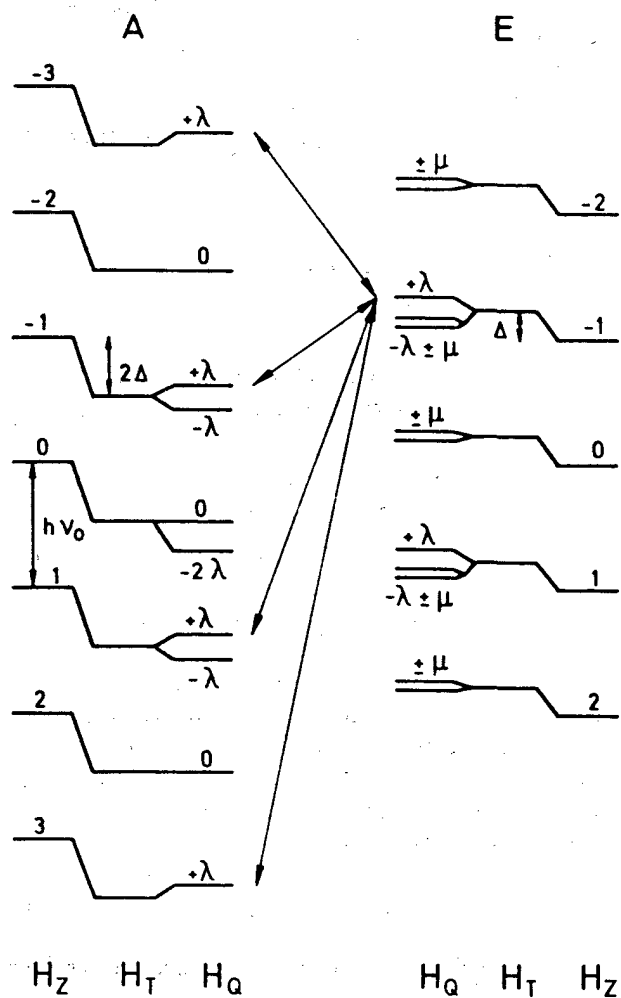


Figure 3: The energy level scheme for rotational tunnelling of CD_3 - groups in a high magnetic field ($\nu_0 \gg \nu_T \gg \nu_Q$). Only the rotational ground state is shown. λ and μ are orientation dependent splittings and shifts due to the quadrupole interaction [1].

I_z , it acts in the same way on both wavefunctions.

$$\begin{aligned} (3I_z^{2(i)} - I^{2(i)})|\alpha\rangle &= |\alpha\rangle \\ (3I_z^{2(i)} - I^{2(i)})|\beta\rangle &= |\beta\rangle \end{aligned} \quad (8)$$

Therefore the quadrupole interaction for those wavefunctions of the methyl group can be written as a multiple of the identity operator:

$$\begin{aligned} H_Q[uvw] &= \sum_{i=1}^3 \frac{1}{3} \omega_Q^{(i)} (3I_z^{2(i)} - I^{2(i)}) [uvw] \\ &= \frac{1}{3} (\omega_Q^{(1)} + \omega_Q^{(2)} + \omega_Q^{(3)}) [uvw] \end{aligned} \quad (9)$$

for

$$u, v, w = \alpha, \beta.$$

Since the tunnelling Hamiltonian affects only the space part and does not involve spin transitions the total Hamiltonian for this subsystem is given by

$$H = H_T + H_Q = H_T + \lambda I, \quad (10)$$

neglecting the dipole-dipole interaction.

The eigenstates and eigenfrequencies are then dominated by the tunnelling Hamiltonian

$$\begin{aligned} E^a, E^b &: +\Delta + \lambda \\ A &: -2\Delta + \lambda. \end{aligned} \quad (11)$$

The frequency differences are the tunnel frequency between the A and E states; they are zero within each symmetry state as well as between the E^a and E^b levels:

$$\begin{aligned} A - E &: 3\Delta = \omega_T \\ E - E &: 0. \end{aligned} \quad (12)$$

If the E states are no longer degenerate, the energy difference between the E^a and E^b states appears as well.

This holds independently of the size of the tunnel frequency, since it is a result derived from properties of the quadrupole interaction.

4.2 Matrix Element Condition

Coherences between the states given above can be observed at the tunnel frequency only if the transitions are not symmetry forbidden, i.e., if

$$\langle E(u'v'w') | \rho(t_0) | A(uvw) \rangle \neq 0. \quad (13)$$

$\rho(t_0)$ is the density matrix at the time t_0 containing even order multiple-quantum operators. It is created

by pulse sequences during the preparation period, e. g., by a simple two pulse sequence [8]. The generation of multiple-quantum coherences involves a quadratic Hamiltonian, in this case the quadrupole Hamiltonian.

As an example of an even order multiple-quantum Hamiltonian consider the double-quantum Hamiltonian :

$$H_{DQ} = D^{(1)} + D^{(2)} + D^{(3)} \quad (14)$$

where

$$D^{(i)} = C^{(i)} \left(I_x^{2(i)} - I_y^{2(i)} \right) \equiv C^{(i)} Q^{(i)} \quad (15)$$

or

$$D^{(i)} = C^{(i)} \left(I_x^{(i)} I_y^{(i)} + I_y^{(i)} I_x^{(i)} \right) \equiv C^{(i)} Q^{(i)}.$$

The space parts $C^{(i)}$ are different for the three deuterium nuclei of the methyl group, since they depend on the space parts of the quadrupole Hamiltonian, which are distinct because of the relative orientation of the C-D bonds to the magnetic field. The double-quantum Hamiltonian can create coherences between the different symmetry states, if it contains terms of symmetries other than A . It can be divided into symmetry adapted parts:

$$H_{DQ} = D^A + D^{E^a} + D^{E^b} \quad (16)$$

with

$$\begin{aligned} D^A &= \frac{1}{3} \left(C^{(1)} + C^{(2)} + C^{(3)} \right) \times \\ &\quad \left(Q^{(1)} + Q^{(2)} + Q^{(3)} \right) \\ D^{E^a} &= \frac{1}{3} \left(C^{(1)} + \varepsilon^* C^{(2)} + \varepsilon C^{(3)} \right) \times \\ &\quad \left(Q^{(1)} + \varepsilon Q^{(2)} + \varepsilon^* Q^{(3)} \right) \\ D^{E^b} &= \frac{1}{3} \left(C^{(1)} + \varepsilon C^{(2)} + \varepsilon^* C^{(3)} \right) \times \\ &\quad \left(Q^{(1)} + \varepsilon^* Q^{(2)} + \varepsilon Q^{(3)} \right) \end{aligned} \quad (17)$$

where ε is given in equation 1.

Since the $C^{(i)}$ differ for all three nuclei the first factors do not vanish. The spin parts can create the coherences between states of different symmetries:

$$\begin{aligned} \langle E^a(u'v'w') | D^{E^a} | A(uvw) \rangle &\neq 0 \\ \langle E^b(u'v'w') | D^{E^b} | A(uvw) \rangle &\neq 0. \end{aligned}$$

Because

$$\langle E^b | D^{E^a} | E^a \rangle \neq 0,$$

transitions within the E - system give rise to a sharp peak at zero frequency or, in case of lifted degeneracy of E^a and E^b states, at their frequency difference. Here also no dependence on the tunnelling frequency is involved.

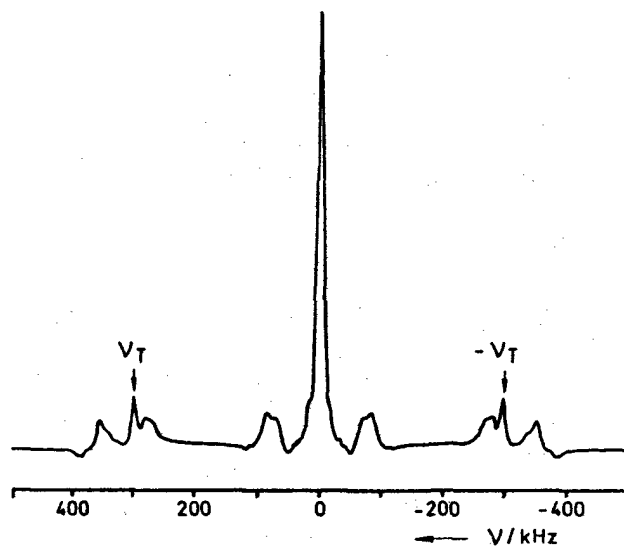


Figure 4: Simulated multiple-quantum spectrum of CD_3 - groups with tunnelling frequency $\nu_T = 300$ kHz for a powder (100 orientations) calculated for the three pulse sequence $90_x - 7\mu s - 90_x - t_1 - 90_x - 7\mu s$.

5 Numerical Calculations

Numerical calculations for some double-quantum spectra were performed. The spectrum (Fig.4) is calculated for a three pulse sequence to excite and detect multiple-quantum spectra applied to a deuterated methyl group with a tunnel frequency of 300 kHz. 100 single-crystal spectra per one sixth of the sphere are added to simulate a powder system.

The spectrum shows sharp peaks at the tunnel frequency and at zero frequency. These lines are independent of the orientation. Other orientation dependent coherences give broad lines in the spectra. Some are centered around the tunnel frequency peak, resulting from transitions between A and E states. Other lines are distributed around the zero peak. They originate from coherences within each of the symmetry states A , E^a and E^b and between E^a and E^b states. All lines outside of the peak at zero frequency are observable only in a system of coupled deuterons.

6 Conclusion

It is shown analytically and numerically that even order multiple-quantum spectroscopy applied to rotational tunnelling of deuterated methyl groups is a potentially useful method for the observation of tunnel splittings directly from the NMR spectra.

This method is based on the properties of the quadrupole interaction which acts upon spin states with magnetic quantum numbers ± 1 in the same way. It also makes use of the single particle character of the quadrupole interaction, allowing for nonzero transition

probabilities at the tunnel frequency.

The method is especially sensitive to small tunnel frequencies. It is therefore a good tool to observe systems with highly hindered rotations of methyl groups or systems where the degeneracy of the E system is lifted by molecular friction or by coupling to other rotors. We are currently performing experiments on such systems.

7 Acknowledgement

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