Methyl tunnelling spectroscopy in acetophenone

Methyl tunnelling spectroscopy in acetophenone

A M Alsanoosi, A J Horsewill and S Clough

Department of Physics, University of Nottingham, Nottingham NG7 2RD, UK

Abstract. Nuclear magnetic resonance (NMR) investigations of methyl tunnelling in aceto-phenone in the solid state are reported. Measurements of the proton spin–lattice relaxation time and of the methyl tunnelling frequency ($\nu_t = 1.435$ MHz) from dipole–dipole-driven low-field NMR demonstrate that the methyl group in acetophenone has an anomalously high potential barrier. A comparison with similar measurements on trans-4- phenyl-3-buten-2-one, along with a theoretical calculation of the respective barrier contributions, leads us to conclude that the origin of the barrier lies predominantly in the interaction between hydrogen atoms on the methyl and phenyl groups. The tunnelling sideband measurements reported extend the window of low-field NMR into the megahertz region and illustrate the existence of a NMR sideband intensity enhancement when the system is close to the level crossing between Zeeman states of the E and A manifolds, respectively.

1. Introduction

With the advent of experimental techniques which enable NMR spectroscopy to be performed at low field a new window in the frequency domain has been opened which enables the measurement of methyl tunnel frequencies in the range from 30 kHz to 1 MHz. We report upon an investigation of methyl tunnelling in acetophenone using the technique of dipole–dipole-driven nuclear magnetic resonance [1] in which the upper range of the frequency window has been extended to 1.5 MHz. The fact that NMR tunnelling sidebands of this frequency can be observed with measurable intensity has led to the discovery of an intensity enhancement which arises when the tunnelling sidebands, reflected through zero field, are in the vicinity of the parent NMR line. This condition coincides with a level crossing between tunnelling and Zeeman subsystems. Acetophenone has also proved to be of interest in respect of the anomalously high potential barrier to reorientation of its methyl group.

The magnitude and shape of methyl potential barriers reflect in detail the molecular and electronic structure of their environment. In recent years a variety of experimental techniques have been devised to enable accurate measurements of the magnitudes of the hindering barriers to be made. These involve direct measuements of the tunnelling frequency ν_t relating to the quantum mechanical motion of the CH_3 group at low temperatures. The tunnelling frequency is an approximately exponential function of barrier height V_3 and so provides a sensitive parameter by which to study potential barriers accurately.

The barriers to reorientation of CH_3 are typically in the range 100–2000 K (0.8–20 kJ mol^{-1}) and the corresponding tunnelling frequencies encompass a range of some seven

orders of magnitude. The latter may be measured by a variety of nuclear magnetic resonance and inelastic neutron scattering (INS) measurements in the solid state. In recent years, many methyl-group-containing materials have been studied, principally in pursuance of a complete understanding of the quantum mechanical and classical dynamics of the molecular rotor and the transition between the two regimes. As a result of these studies a sizeable quantity of data has now been formulated which enables patterns to be established between the known molecular and crystal structure and the measured barrier heights.

Particularly striking patterns have been observed in materials which contain carbonyl groups and materials in which the methyl group occupies a position on an alkyl chain. In the latter the methyl group is bonded directly to a sp^3 carbon atom, the barrier is large ($V_3 \simeq 1800$ K) and is predominantly steric and intra-molecular in origin [2]. When a methyl group occupies a position in the proximity of a carbonyl group, then non-bonding interactions between the two groups results in a comparatively low potential barrier ($V_3 \simeq 500$ K) which is predominantly inter-molecular in origin [3].

According to these well established patterns a study of acetophenone was undertaken in the expectation that the methyl group in this material would experience a low barrier. As will become apparent from the results to be presented in this paper, the measured barrier height and dynamical parameters conflict with this prediction. The origin of this discrepancy has been deduced by calculations of the barrier height based upon the crystal structure and by comparison with experiments on trans-4-phenyl-3-buten-2-one (TPB).

All measurements reported here have been conducted using the techniques of NMR spectroscopy in the solid state. The reorientation rate has been measured as a function of temperature using conventional measurements of the proton spin–lattice relaxation time T_1. The dynamics in the quantum mechanical regime have been studied by dipole–dipole-driven low-field NMR spectroscopy (acetophenone) and by field cycling level-crossing NMR spectroscopy (TPB).

2. Experimental details

Measurements of the proton spin–lattice relaxation time were conducted at 25 and 21 MHz using a pulsed NMR spectrometer. The magnetisation was saturated using a comb of 90° pulses and the recovered magnetisation measured after an interval of time τ by a single 90° pulse. The temperature of the sample was maintained using a helium cryostat incorporated into a superconducting magnet system. The temperature control and stability were within 0.2 K. The sample of acetophenone, which is liquid at room temperature, was sealed under vacuum in a glass ampoule, a freeze–pump–thaw sequence having been employed to eliminate atmospheric oxygen.

Dipole–dipole-driven NMR measurements were conducted at 4.2 K using a 26 MHz pulsed NMR spectrometer. A rapid field-switching superconducting magnet system was employed to facilitate the field-cycling routine as follows.

(i) Magnetisation was destroyed by a comb of 90° pulses at the NMR field (0.61 T).

(ii) The magnetic field was set to 0.61 T for 2 min to enable growth of known magnetisation.

(iii) The magnetic field was switched rapidly (less than 2 s) to low field B_r.

(iv) The sample was irradiated with radiation of frequency ν_{RF} for period of 10–30 s.

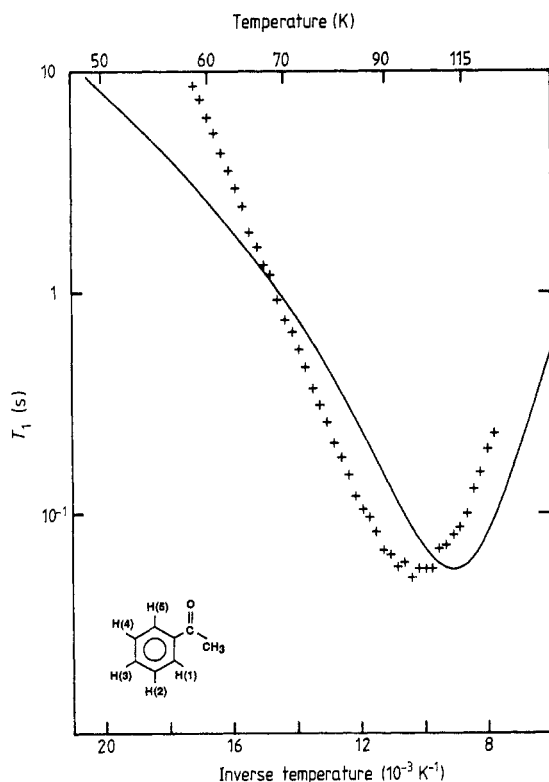(v) The magnetic field was switched rapidly to the NMR field.

Figure 1. Temperature dependence of T_1 in acetophenone (25 MHz): +, experimental data; ——, calculated $T_1(1/T)$ dependence using the model in [8] and the measured barrier height.

(vi) The magnetisation was measured by a 90° pulse.

The above procedure was repeated many times, decrementing B_r at each cycle, until the low-field NMR spectrum at constant frequency ν_{RF} had been swept.

The level-crossing NMR experiment TPB used a similar field-cycling sequence; in such an experiment, however, a search is made for anomalous spin–lattice relaxation at certain special field values where ν_t is equal to γB or $2\gamma B$. Here γ is the magnetogyric ratio of the proton. Consequently the field-cycling sequence omitted step (ii), the relaxation field B_r was of order 1 T and no RF irradiation was performed at step (iv). Details of the procedure have been reported in [4]. All experimental procedures reported here were controlled by a LSI-11 microcomputer system.

3. Results

The temperature dependence of the spin–lattice relaxation time T_1 recorded at 25 MHz in acetophenone is presented in figure 1. A single minimum is observed at a temperature θ_{min} of 97 K. According to the well established correlation [5] between θ_{min} and the tunnel frequency, we estimate ν_t to be of the order of a few megahertz and, on the

assumption of a threefold barrier, the corresponding barrier height is estimated to be 1180 K.

The predicted tunnel frequency is too small to be measured by neutron scattering techniques and level-crossing NMR spectroscopy. It is also at first sight outside the range normally considered appropriate for dipole–dipole-driven NMR spectroscopy. This is because the sidebands associated with the tunnelling transitions are well separated (about 3 MHz) from the main NMR line and as a result normally have a very low transition probability. It is possible, however, to envisage experimental parameters for the low-field NMR experiment in which these tunnelling sidebands appear with observable intensity. This occurs when the low-field irradiation frequency ν_{RF} is in the vicinity of $\nu_t/2$. In such a case the low-field tunnelling sideband is reflected through zero field to a field position in the proximity of its parent NMR line. As a result the transition probability is enhanced and the sideband appears with observable intensity.

The low-field NMR spectra of acetophenone are presented in figure 2. These were recorded using several low-field irradiation frequencies. The $\Delta m = \pm 1$ transition is denoted by the letter A, and the $\Delta m = \pm 2$ transition by the letter B. The corresponding tunnelling sidebands are indicated by lower-case letters a and b. The tunnelling frequency is measured to be 1.435 ± 0.005 MHz and figure 3 presents the calculated magnetic field dependence of the various NMR transition frequencies. A horizontal line on this diagram corresponds to a field-swept spectrum at constant ν_{RF} of the type recorded experimentally, and the open circles and crosses denote the magnetic fields at which transitions are observed. In the low-field spectra in figure 2 a frequency-independent transition (labelled C) occurs at a magnetic field of 84 G. If translated into frequency units using the magnetogyric ratio of the proton, this transition occurs at $\nu_t/4$ precisely. This has not been assigned conclusively but appears to originate from the fact that four simultaneous proton spin flips are driven by a single quantum $h\nu_t$.

The temperature dependence of T_1 in TPB recorded at 21 MHz is presented in figure 4. A single minimum is observed at a temperature θ_{min} of 51 K. On application of the correlation [5] the predicted tunnelling frequency is in the range accessible to level-crossing spectroscopy. Accordingly, figure 5 presents the field-cycling spectrum of this material. An anomaly in the field dependence of the partially recovered proton magnetisation, corresponding to the level crossing which occurs when $\nu_t = 2\gamma B$, appears at a field of 2.095 T. Hence we deduce the tunnel frequency of the methyl group in TPB to be 178.4 ± 0.3 MHz.

4. Discussion

4.1. Tunnelling sideband intensities

Experimentally, it is observed that the intensities of the tunnelling sidebands in the low-field spectrum of acetophenone become enhanced as ν_{RF} approaches $\nu_t/2$. Under these conditions a level crossing occurs between Zeeman states within the E and A multiplets and is identical with that observed under the condition $\nu_t = 2\gamma B$ in level-crossing NMR spectroscopy. An attempt has been made to model the behaviour of the sideband intensities theoretically.

The spin Hamiltonian for a methyl group consisting of an equilateral triangle of protons is given by

$$H_s = H_Z + H_d + H_t$$

where H_Z is the Zeeman interaction of the proton spins with the applied magnetic field
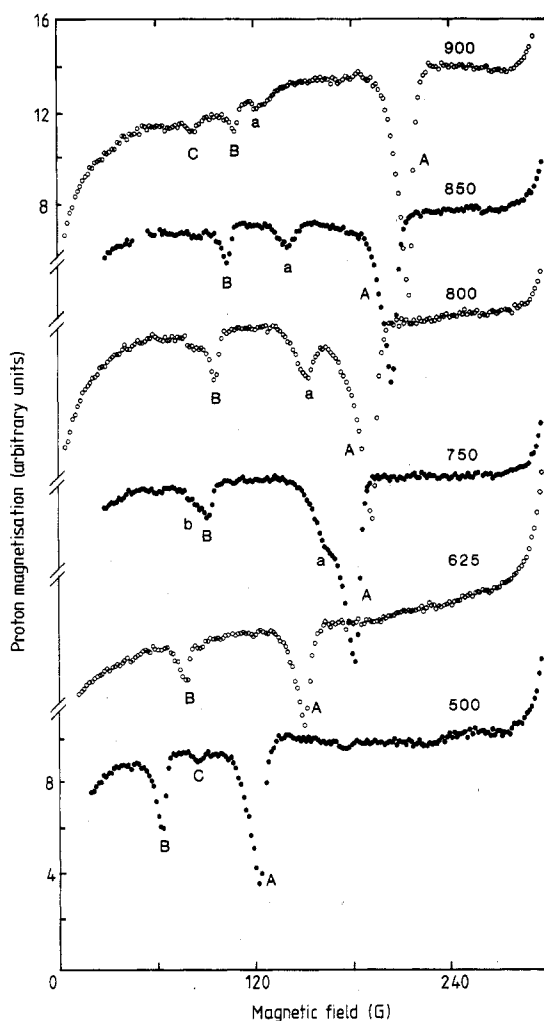
$$H_s = -\hbar \gamma B_z \sum_{j=1}^{3} I_{jz}.$$

Figure 2. The low-field NMR spectra (4 K) of acetophenone recorded at a variety of frequencies (given on curves in kHz). The tunnelling sidebands are labelled (a) and (b); see text for details. The NMR transitions $\Delta m = \pm 1$ and $\Delta m = \pm 2$ are labelled A and B, respectively.

H_t is an exchange term to represent the tunnelling motion. Using the approach in [6] the energy shifts associated with tunnelling has been incorporated with the use of an equivalent spin operator

$$H_t = -2J \sum_{j>k} I_j \cdot I_k.$$

H_d is the untruncated dipolar Hamiltonian representing the dipole–dipole interaction between the three proton spins. Following the notation in [7], this may be written as a
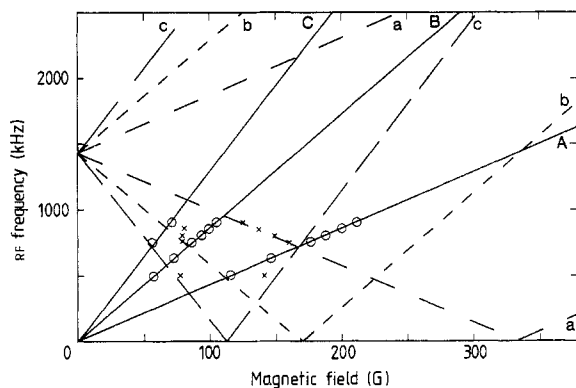
Figure 3. Calculated magnetic field dependence of the low-field NMR and tunnelling sideband frequencies: a horizontal line represents a field-swept spectra at constant ν_{RF}; $\bigcirc$, $\times$, experimental data.
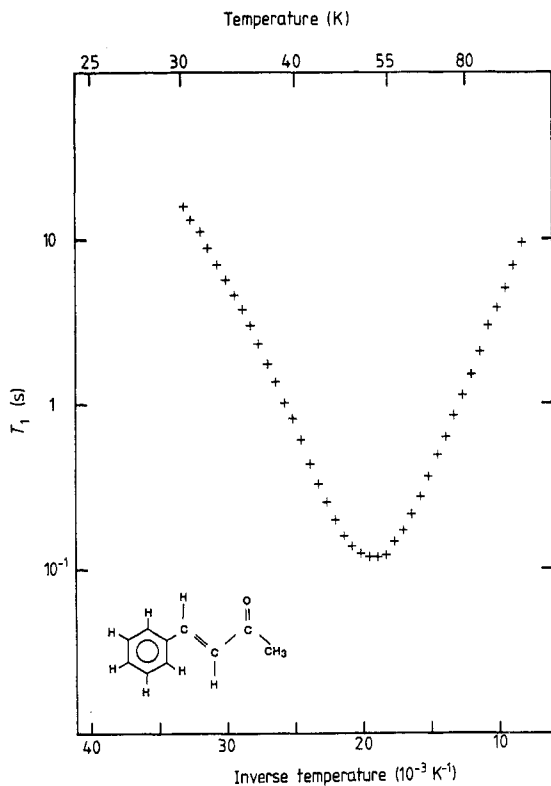

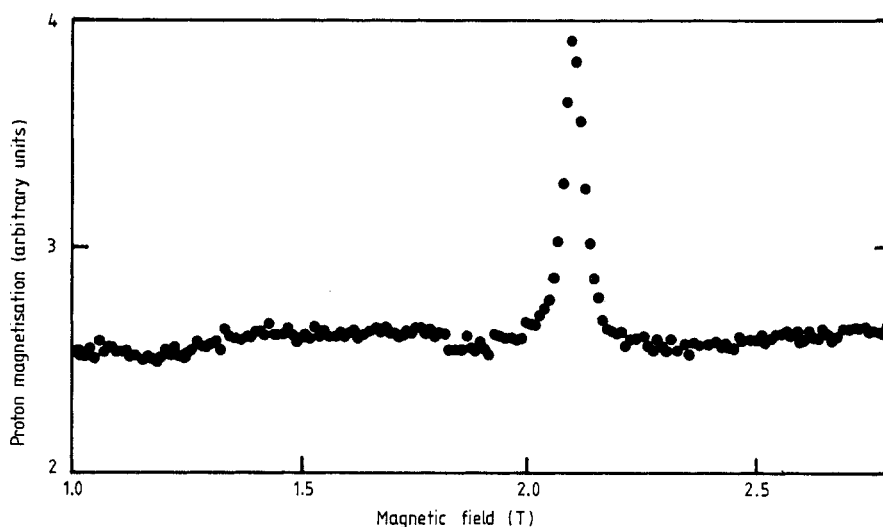**Figure 4.** Temperature dependence of T_1 in TPB (21 MHz).

Figure 5. Field-cycling level-crossing NMR spectrum of TPB recorded at 4 K.

scalar product of two second-rank tensors representing spin and spatial contributions, respectively:

$$H_{\mathrm{d}} = \sum_{j>k} \sum_{q=-2}^{+2} A_{jk}^{(q)} F_{jk}^{(q)} .$$

Using a procedure of diagonalisation of the spin-Hamiltonian matrix in the simple basis $|m_I^{(1)} m_I^{(2)} m_I^{(3)}\rangle$ (the numbers 1, 2, 3 label the protons), the relative transition probabilities of the tunnelling sidebands and of the $\Delta m = \pm 2$ peak have been calculated using time-dependent perturbation theory for a series of frequencies ν_{RF}. These were calculated by choosing a magnetic field value in H_Z such that the transition of interest was resonant with the applied RF frequency. The results are presented in figure 6, where the calculation has been performed upon a single methyl group oriented at a fixed arbitrary angle to the applied field.

The experimentally observed dramatic enhancement in the transition probability of the tunnelling sideband of $\Delta m = \pm 1$ is clearly reproduced in the calculations reported in figure 6. The calculated transition probability of the $\Delta m = \pm 2$ NMR peak (broken curve) is also presented in the figure for the purposes of comparison. The experimental integrated intensities of the $\Delta m = \pm 1$ sideband and $\Delta m = \pm 2$ NMR peak have been evaluated for $\nu_{\mathrm{RF}} \geqslant 800$ kHz. These data are incorporated in figure 6 where the experimental data have been scaled such that the experimental and theoretical values for the sideband intensity recorded at 800 kHz are in agreement. The qualitative agreement in this region is good. However, two observations are noteworthy. Firstly sidebands are not observed experimentally for $\nu_{\mathrm{RF}} < \nu_{\mathrm{t}}/2$. Similar observations are commonly made in low-field studies of this kind whereby the high-field $\Delta m = \pm 1$ sideband is often absent [1]. Secondly the observed intensity of these 'forbidden' transitions with respect to the $\Delta m = \pm 1$ NMR line are some 50 times larger than the calculated ratios of the respective transition probabilities. These observations emphasise the inadequacy of the time-dependent perturbation theory approach in this case. At such low values of applied
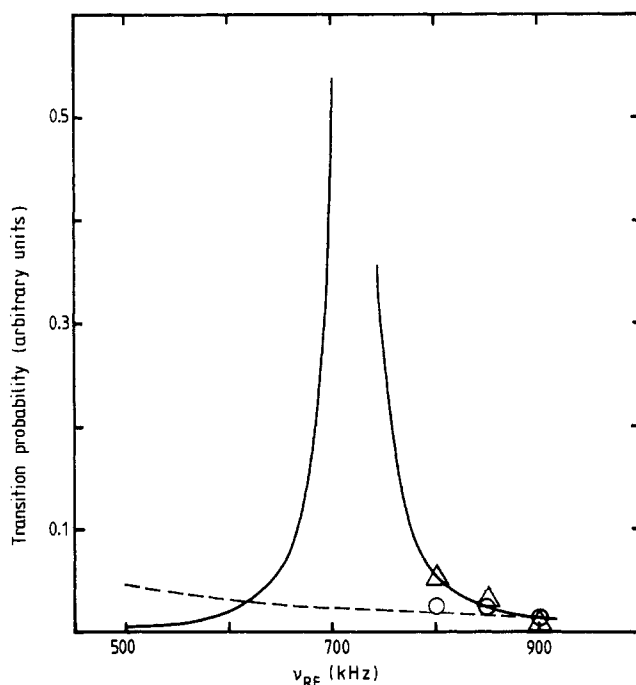
Figure 6. The calculated transition probabilities of the $\Delta m = \pm 1$ tunnelling sideband (——) and the $\Delta m = \pm 2$ NMR peak (– – –) as a function of applied RF frequency ν_{RF}. The scaled experimental values of the integrated intensities of the $\Delta m = \pm 1$ tunnelling sideband ($\triangle$) and the $\Delta m = \pm 2$ NMR peak ($\bigcirc$) are also shown.

magnetic field the RF field can no longer be considered a small perturbation and a full treatment should acknowledge the dipole–dipole-driven nature of the transitions as discussed in [1]. The effects of saturation have also been ignored in the theoretical treatment. Furthermore, as stated in an earlier paper [1], the lineshape may contain further information relating to the dynamics of the nuclei. Experimental and theoretical investigations are currently being pursued to investigate these phenomena in general.

4.2. The thermally activated reorientation rate τ^{-1}

If the measured value of the tunnelling frequency is employed and on the assumption of threefold symmetry for the barrier, the reorientation rate τ^{-1} has been calculated as a function of temperature according to the methyl thermometer model in [8]. For the purposes of comparison the results are plotted as a full curve on the T_1 data in figure 1 where the familiar expressions have been employed to relate τ^{-1} to T_1 [9]. The position of the minimum in T_1 is predicted at 108 K, at a slightly higher temperature than observed experimentally. The activation energy in the vicinity of the T_1 minimum is in good agreement; however, the non-Arrhenius behaviour at low temperatures is not observed in the experimental data presented.

4.3. The potential barrier to reorientation

On the assumption of threefold symmetry the height of the potential barrier to reorientation of the CH_3 group in acetophenone has been calculated from the measured

tunnelling frequency. Its magnitude is 1320 K. This value is to be compared with those observed in related materials in which the methyl group is adjacent to a carbonyl group, e.g. acetone [4] and the homologous series of ketones [3], in which the barrier height is typically observed to be in the range 400–700 K. The large discrepancy between the barrier height in acetophenone and its relatives requires explanation. There appear to be three possibilities for its origin: firstly the proximity of the phenyl ring, secondly the presence of unusually large inter-molecular contributions to the barrier or thirdly intra-molecular effects related to the conjugation through the molecule.

TPB is a close relative of acetophenone. The conjugation extends from the phenyl ring and along the carbon chain. The methyl group is, however, no longer in such close proximity to the phenyl ring. From the measured value of the tunnelling frequency the threefold barrier height in TPB is calculated to be 632 K and is of comparable magnitude with that of the ketones. Consequently the third possibility is eliminated.

Inter-molecular contributions to the barrier in acetophenone have been calculated according to the theoretical model in [10]. The model assumes pairwise interactions between the hydrogen atoms of the methyl group and the atoms of neighbouring molecules. There are three terms contributing to the energy of interaction between two atoms, namely

(i) electrostatic energy V_{es},
(ii) dispersive energy and
(iii) short-range repulsive energy.

The latter two collectively represent the van der Waals interaction energy V_{VW}. In a similar manner to [11], these have been modelled as follows:

$$V_{es} = q_H q_X / 4\pi\varepsilon_0 \Gamma_{HX}$$

where q_H and q_X represent the net charges on the methyl hydrogen atom and atom X on a neighbouring molecule, respectively. Γ_{HX} is the inter-atomic distance.

The interaction term

$$V_{VW} = k_H k_X [-A/\gamma^6 + C \exp(-\alpha\gamma)]$$

represents a Kitaigorodskii potential [12] for the van der Waals contribution where $\gamma = \Gamma_{HX}/\Gamma_{HX}^0$ and $\Gamma_{HX}^0 = 2(R_H^W R_X^W)^{1/2}$. Here R_X^W is the van der Waals radius of atom X. k_X is a parameter of order unity and A, C and α are parameters which are independent of the chemical species ($A = 9.22$ meV Å^{-6}, $C = 2.03 \times 10^6$ meV and $\alpha = 12.35$; $k_H = 1$, $k_O = 1.36$ and $k_C = 1$). The inter-molecular contribution to the barrier has been calculated by performing a lattice sum over all pairwise interactions between the methyl hydrogen atoms and the atoms of adjacent molecules as a function of the CH$_3$ rotation angle φ. The inter-atomic distances were determined from the low-temperature crystal structure of acetophenone [13], the lattice sum extending over a cube of linear dimension five unit cells. The atomic charges in the electrostatic term q_X were obtained from the CNDO calculations in [14]. To facilitate the calculation, the methyl group of molecule zero in the central unit cell was modelled as a rigid equilateral triangle of hydrogen atoms of dimensions appropriate to a methyl group. It was this methyl group which was rotated. All other methyl groups were assumed stationary and the hydrogen atom positions used were those determined by x-ray diffraction. The truncation of the lattice to 125 unit cells led to no significant error.

Figure 7(*a*) presents the results of the calculation. The inter-molecular potential energy of the methyl group has been plotted as a function of rotation angle and the
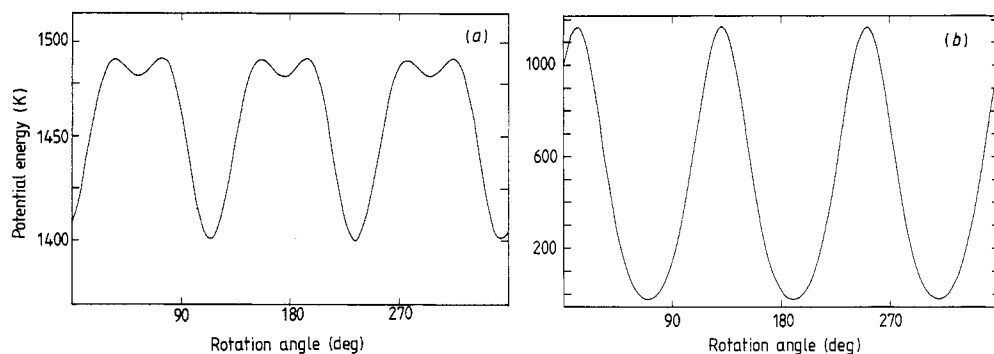
Figure 7. (*a*) The calculated inter-molecular contribution to the potential barrier in acetophenone. The potential energy of the methyl group is recorded as a function of rotation angle. See text for details. (*b*) The calculated potential energy representing the pairwise interaction between hydrogen atoms of the methyl group with hydrogen atom H(1) of the phenyl group.

figure represents a sum of the electrostatic and the van der Waals contributions. The electrostatic potential energy alone contributes approximately 25% of the inter-molecular barrier. The calculated potential barrier has approximately threefold symmetry with a magnitude of 90 K; so evidently it is not the origin of the unusually high barrier in acetophenone.

The results of this calculation in conjunction with the experimental results on TPB lead us to conclude that it is the proximity of the phenyl ring to the methyl group which gives rise to the anomalous potential barrier in acetophenone. This interaction may be calculated by using a highly simplified model in which valence forces are ignored and the barrier is assumed to arise from pairwise interactions between the hydrogen atoms of the methyl group and the atoms of the phenyl ring in the same molecule. The distance of closest approach of a methyl hydrogen atom with the phenyl hydrogen atom H(1) is 1.85 Å and using the same model and parameters for V_{VW} presented earlier the barrier contribution has been calculated and drawn in figure 7(*b*). This contribution, V_{VW}(P–H), has threefold symmetry and arises predominantly from the methyl hydrogen–phenyl hydrogen atom H(1) interaction. The inclusion of the other atoms on the phenyl ring in the calculation makes no significant contribution. V_{VW}(P–H) is predominantly repulsive and has a magnitude of 1200 K; so even on the basis of this simplified model is confirmed as being the leading term giving rise to the potential barrier. It is to be noted that valence forces, particularly those between the methyl and carbonyl groups have been ignored. The agreement with experiment is surprisingly good.

5. Conclusions

The techniques of methyl tunnelling spectroscopy have been employed in the study of the molecule of acetophenone and its relative, TPB, in the solid state. Dipole–dipole-driven low-field NMR has been employed to measure the tunnelling frequency of the methyl group in acetophenone under the influence of the potential barrier. At 1.435 MHz the measured tunnelling frequency is the largest recorded by this technique and its observation illustrates the existence of a sideband enhancement which occurs when the

RF frequency is of the order of half the tunnelling frequency. The origin of the anomalously high potential barrier observed in acetophenone has been traced to the pairwise interaction between just two atoms, namely the hydrogen atoms of the phenyl ($H(1)$) and methyl groups, respectively. A full calculation of the inter-molecular potential energy of the methyl group shows that this contributes less than 10% to the total barrier.

Acknowledgments

References

[1] Clough S, Horsewill A J, McDonald P J and Zelaya F O 1985 *Phys. Rev. Lett.* **55** 1794
[2] Abed K and Clough S 1987 *Chem. Phys. Lett.* **142** 209
[3] Green R M and Horsewill A J 1986 *Mol. Phys.* **57** 887
   Horsewill A J, Green R M and Alsanoosi A M 1987 *Springer Proceedings in Physics* vol 17 (Berlin: Springer) p 28
[4] Clough S, Horsewill A J and McDonald P J 1984 *J. Phys. C: Solid State Phys.* **17** 1115
[5] Clough S, Heidemann A, Horsewill A J, Lewis J D and Paley M N J 1981 *J. Phys. C: Solid State Phys.* **14** L525
[6] Apaydin F and Clough S 1968 *J. Phys. C: Solid State Phys.* **1** 932
[7] Wolf D 1979 *Spin Temperature and Nuclear Spin Relaxation in Matter* (Oxford: Clarendon)
[8] Clough S, Heidemann A, Horsewill A J, Lewis J D and Paley M N J 1982 *J. Phys. C: Solid State Phys.* **15** 2495
[9] Kubo R and Tomita K 1954 *J. Phys. Soc. Japan* **9** 888
[10] Caillet J and Claverie P 1975 *Acta Crystallogr.* A **31** 448
[11] Cavagnat D and Pesquer M 1986 *J. Phys. Chem.* **90** 3289
[12] Kitaigorodskii A I, Mirskaya and Nauchitel V 1970 *Sov. Phys.–Crystallogr.* **14** 769
[13] Tanimoto Y, Kobayashi H, Nagakura S and Saito Y 1973 *Acta Crystallogr.* B **29** 1822
[14] Gacoin P and Leclercq J M 1973 *J. Chem. Phys.* **59** 4351