

The pressure dependence of methyl tunnelling in acetylacetone

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 7375

(<http://iopscience.iop.org/0953-8984/5/40/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 01:56

Please note that [terms and conditions apply](#).

The pressure dependence of methyl tunnelling in acetylacetone

M R Johnson[†], A Aibout^{‡§}, A J Horsewill^{†||} and J Williams^{†¶}

[†] Department of Physics, University of Nottingham, Nottingham NG7 2RD, UK

[‡] Institut Laue–Langevin, BP-156X, 38042 Grenoble CEDEX, France

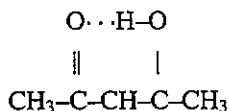
Received 18 May 1993, in final form 22 July 1993

Abstract. Pressure dependence measurements are reported on methyl tunnelling in acetylacetone and an isotopic derivative in which the hydrogen bond in the ENOL ring is deuterated. The effect of deuteration is to increase the intra-molecular component of the potential which hinders the reorientation of neighbouring methyl groups. Application of pressure, however, results in a decrease in the inter-molecular component of the hindering potential in both samples and the methyl group tunnelling frequency increases with compression. Above 3 kbar the principal tunnel peak no longer shifts with change in pressure but intensity is transferred progressively to new peaks. This structure is typical of coupled methyl groups and two models, coupled pairs and infinite coupled chains, are considered.

1. Introduction

The motional spectrum of methyl groups in the solid state at low temperature is dominated by quantum tunnelling at a frequency which is determined by a potential barrier which hinders reorientation about the threefold axis. The barrier has contributions of intra- and inter-molecular origin and reflects the molecular and electronic structure of the molecule and its environment. The frequency of tunnelling has an approximately exponential dependence upon the barrier height and so provides a particularly sensitive probe of the inter-molecular and intra-molecular forces in the molecular crystal. The application of external hydrostatic pressure to the sample [1–4] provides a convenient experimental technique for modifying the potential barrier and thereby probing the nature of the molecular forces through changes in the methyl tunnelling frequency. Such experiments have been adopted to investigate the inter-molecular forces in crystals. These can be successfully modelled in terms of pairwise inter-atomic potentials and the effect of increasing pressure can be to increase or decrease the hindering potential. We report on a series of inelastic neutron scattering (INS) investigations designed to study the pressure dependence of methyl tunnelling in acetylacetone.

Acetylacetone (2,4-pentanedione) is of particular interest since the stable tautomer is the ENOL structure [5],



[§] Present address: Département de Physique, Centre Universitaire de Mostaganem, Mostaganem 2700, Algeria.

^{||} Author for correspondence.

[¶] Present address: Science, Thomas House, George IV Street, Cambridge CB2 1HH, UK.

in which an intra-molecular hydrogen bond completes a six-membered ring structure at the centre of the molecule. Thus the possibility arises of pressure-induced changes in either the statics or dynamics of the hydrogen bond causing changes in the tunnelling frequencies of the neighbouring methyl groups. In order to probe such a coupling an isotopic modification to the molecule (acetylacetone-d₂) has been investigated in which the hydrogen bond has been deuterated. Despite the lack of crystal structure information on acetylacetone, which would reveal the relative positions and separations of neighbouring methyl groups, it is noted at the outset that with two methyl groups on the molecule, with the effect of pressure being to compress the crystal thereby reducing inter-molecular distances, inter-methyl group coupling may also become apparent at higher pressures.

2. Experimental techniques

The experiments were conducted on the backscattering spectrometer IN13 on the high-flux reactor of the Institut Laue-Langevin, Grenoble. This spectrometer has, in its optimum configuration, a resolution (FWHM) of 8 μeV and the details of its construction and operation have been discussed elsewhere [6]. The sample of acetylacetone, which is a liquid at room temperature, was obtained from the Aldrich Chemical Company. Some of the experiments were conducted using the partially deuterated derivative $\text{CH}_3\text{-CO-CD}(\text{COD})\text{-CH}_3$ (acetylacetone-d₂) which was produced by refluxing a mixture of acetylacetone and deuterium oxide for approximately 10 hours. The deuterated component was removed by distillation. Deuteration to a level of approximately 99% was achieved by repeating the procedure. The samples were mounted in cylindrical aluminium cells and occupied a 1 mm annulus between two concentric cylinders of average diameter 13 mm. All neutron scattering spectra were recorded for a sample temperature of 5 K. An array of detectors simultaneously recorded the spectra at 27 scattering angles between 24° and 135° but in order to maximize the counting statistics the spectra recorded by detectors at all angles were summed together. The spectra were normalized with a vanadium run and the scattering from the pressure cell and sample cell were eliminated by subtracting an empty can run. The spectral parameters were obtained by fitting each spectrum to Lorentzian lineshape functions convoluted with the measured instrumental resolution function. The cryogenic pressure system developed by the ILL has been described elsewhere [7]. It employs helium as the working fluid and pressures in the range 0–5 kbar could be achieved at temperatures down to 5 K. At elevated pressures helium freezes at temperatures above 20 K so care was exercised when cooling the pressure cell to 5 K to ensure that a uniform pressure was established across the sample.

3. Results

NMR measurements of the spin-lattice relaxation time, T_1 , in acetylacetone at ambient pressure [8] exhibit two distinct minima suggesting the existence of two chemically distinguishable methyl groups with different threefold hindering potentials. The tunnel splittings corresponding to these two methyl groups have been measured directly at ambient pressure by INS and they are $42.1 \pm 0.2 \mu\text{eV}$ and $4.3 \pm 0.1 \mu\text{eV}$ respectively [9]. Acetylacetone-d₂ has a similar spin-lattice relaxation curve to acetylacetone [10], the difference being that the minima are shifted to higher temperature, indicating that deuteration

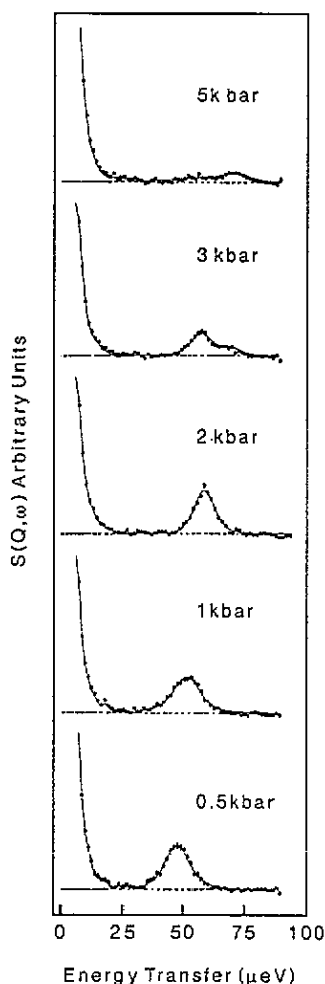


Figure 1. The pressure dependence of some of the methyl tunnelling spectra of acetylacetone- h_2 measured on IN13 in the low-energy transfer region. The temperature is 5 K.

of the hydrogen bond has the effect of increasing the barrier to reorientation of the methyl groups.

The first results to be presented in this paper are the pressure-dependent measurements of the protonated sample. These have been measured twice, on the first occasion in the energy range up to $90 \mu\text{eV}$ and on the second occasion up to the higher energy of $150 \mu\text{eV}$. Some of the neutron scattering spectra are presented in figure 1. The corresponding tunnelling splittings are plotted as a function of pressure in figure 2(a) and the line intensities are plotted in figure 2(b). The $42.1 \mu\text{eV}$ tunnel peak is clearly observed at ambient pressure. As the pressure is increased this peak maintains approximately constant intensity but moves to higher frequency reaching approximately $55 \mu\text{eV}$ at a pressure of 2.5 kbar. As the pressure is increased further up to 5.0 kbar it remains at approximately constant frequency, but decays in intensity. This pressure dependence of the principal tunnel peak is accompanied by the emergence of a satellite above 2.5 kbar at a fixed frequency of about $70 \mu\text{eV}$. Its intensity however grows monotonically with pressure until at 5.0 kbar it is bigger than the

original peak. The combined intensity of this pair of peaks decays with increase in pressure suggesting that the inelastic intensity must be transferred to a peak beyond the experimental frequency range. Accordingly this peak was found in the second set of measurements (see figure 3) with a frequency of $122 \mu\text{eV}$ and low intensity at 3.5 kbar. It moved to $113 \mu\text{eV}$ at 5.0 kbar and, like the $70 \mu\text{eV}$ tunnelling satellite, gained in intensity with increasing pressure. These data are incorporated in Figures 2(a) and 2(b). The integrated intensity of all three tunnelling peaks is also plotted in figure 2(b) and this quantity is independent of pressure within experimental accuracy. The $4.3 \mu\text{eV}$ tunnelling peak was not observed in these measurements as it lies within the elastic peak and resolution of the IN13 spectrometer. The possibility that the high-energy peak arose from multiple scattering has been considered but ruled out. Identical scans to those in figure 3 using the identical sample were made at 1.5 kbar and 2.5 kbar and no high-energy peak appears in these data.

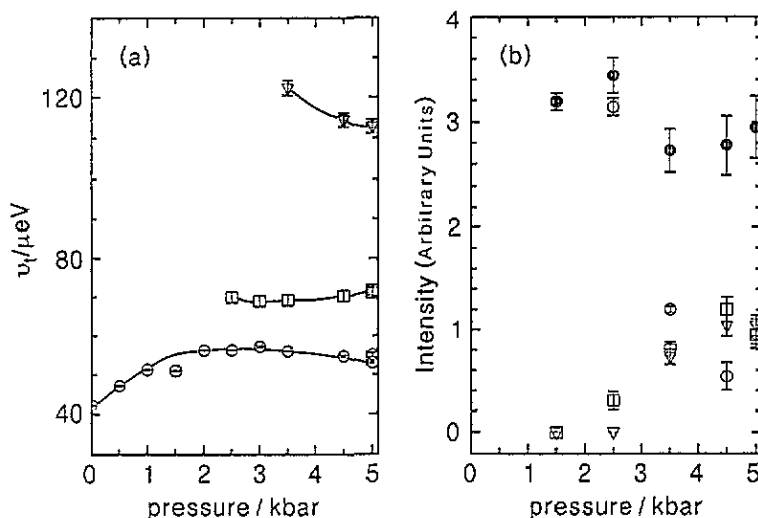


Figure 2. The pressure dependence of (a) the methyl tunnelling splittings and (b) the intensities of the methyl tunnelling peaks in acetylaceton-h2. The principal tunnelling peak (O), the satellite to the principal tunnelling peak (□), the high energy transfer peaks (▽) and the combined intensities of these three peaks (●). The solid lines in 2(a) are guides to the eye.

The INS spectra recorded on the deuterated sample, acetylaceton-d2, are presented in figure 4 and the pressure dependence of the tunnel splittings and line intensities are plotted in figure 5. At ambient pressure the tunnel peak appears at $34.0 \pm 0.2 \mu\text{eV}$ thereby confirming the conclusion from the NMR T_1 data that the corresponding methyl group experiences a higher barrier as a result of the hydrogen bond deuteration. No satellite is apparent at low pressures. As the pressure is increased the principal tunnel peak moves to higher frequency reaching $50 \mu\text{eV}$ at 3.0 kbar. Thereafter a small satellite on the tunnel peak emerges at $60 \mu\text{eV}$. The intensity of the principal peak decays slowly up to about 3 kbar whereafter the emergence of the satellite is accompanied by a decrease in the combined intensity of these two peaks. Compared with the protonated sample the satellite in the deuterated sample possesses lower intensity and never outgrows the principal tunnelling peak. A single scan was made up to higher energy transfers ($\approx 150 \mu\text{eV}$) at the highest pressure but no additional peaks were observed at high frequency.

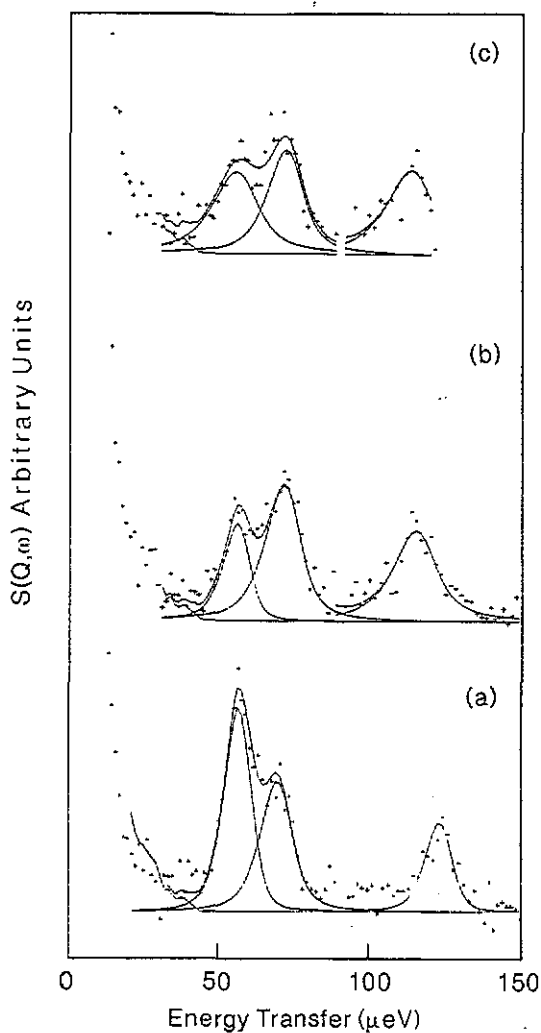


Figure 3. The pressure dependence of the methyl tunnelling spectra of acetylacetone- h_2 measured up to high-energy transfer on IN13. (a) 3.5 kbar, (b) 4.0 kbar and (c) 5.0 kbar. The temperature is 5 K.

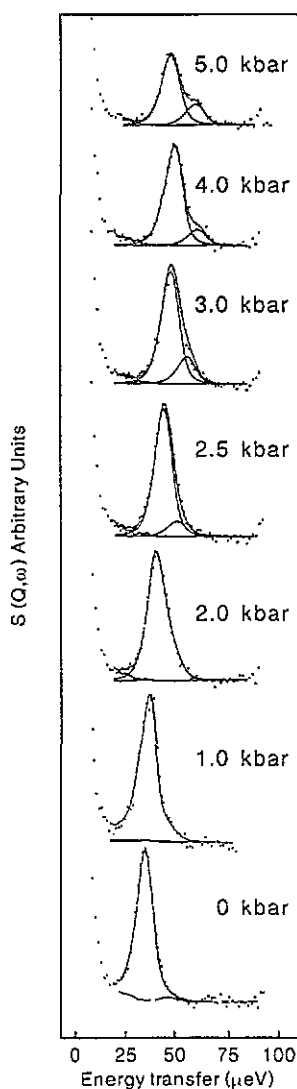


Figure 4. The pressure dependence of the methyl tunnelling spectra of acetylacetone- d_2 measured on IN13. The temperature is 5 K.

The pressure dependences of these isotopically related samples are broadly similar and can be described in terms of two stages which are smoothly connected. In the first stage, from atmospheric pressure up to about 3 kbar, the tunnel peak moves to higher frequency with approximately constant intensity. During the second stage, which extends up to the highest pressures, the tunnel peak remains at approximately the same frequency but decays in intensity while a satellite emerges on the high-frequency side of the tunnel peak and grows in intensity. The differences between the two samples arise from the second stage being further advanced in the protonated sample, where the intensity of the satellite outgrows that of the principal peak. The combined intensity of the principal and satellite peaks decays but in the protonated sample the lost intensity is transferred to the emerging high-frequency

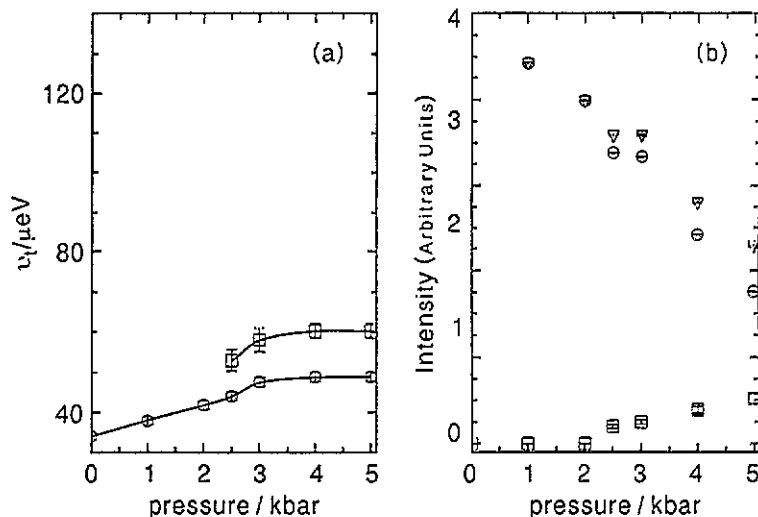


Figure 5. The pressure dependence of (a) the methyl tunnelling splittings and (b) the intensities of the methyl tunnelling peaks in acetylaceton-d₂. The principal tunnelling peak (○), the satellite to the principal tunnelling peak (□), and the combined intensities of these two peaks (▽). The solid lines in 5(a) are guides to the eye.

peak. In the deuterated sample a corresponding high-frequency peak was not observed. The elastic intensity for the deuterated sample was independent of pressure and that for the protonated sample was independent of pressure below 4 kbar, however the latter did show a small increase in elastic intensity above 4 kbar. In both isotopically related materials the line intensities and line positions evolved smoothly with increasing pressure. The crystal structure of this material is not known, neither is its pressure dependence, however the smooth evolution with pressure of the spectra means that there is no evidence of abrupt phase transitions. In the ensuing analysis the results from the protonated sample will be treated at length and the results from the deuterated sample will then be considered as a second example of the same phenomenon.

4. Analysis

The dynamics of methyl groups in crystals at low temperature can be analysed in terms of single methyl groups, pairs of coupled methyl groups [11, 12] and infinite chains of coupled methyl groups [13, 14]. Below we consider how each of these analyses applies to the methyl groups in acetylaceton.

4.1. Isolated methyl groups; the single particle model

An isolated methyl group in a crystal lattice is described by the Hamiltonian

$$H_s(\theta) = -(\hbar^2/2I)(\partial/\partial\theta)^2 + (V/2)(1 - \cos 3\theta) \quad (1)$$

which represents a single particle in a periodic potential of magnitude V , which has approximately three-fold symmetry [15]. The solutions of $H_s(\theta)$ consist of a hierarchy of torsional levels and the degeneracy of each of these is lifted by tunnelling between

neighbouring wells. Thus each torsional level is composed of an A-symmetry singlet and an E-symmetry doublet separated by a tunnel splitting which is determined by V . Table 1 shows the hindering potentials that would give rise to the observed tunnelling splittings for methyl groups behaving as single particles from which it can be seen how V responds to the applied pressure. At ambient pressure the two minima observed in the temperature dependence of T_1 are in quantitative agreement [16] with the observed principal tunnelling splitting and the low-frequency tunnelling splitting. These are assigned to two distinguishable methyl groups in each system. The emergence of the satellite and high-frequency peaks at high pressure cannot be explained by the single-particle model because isolated methyl groups have a unique ground state tunnelling splitting. The relative intensities of the observed peaks also make it unlikely that they can be assigned to additional distinguishable methyl groups, unless these are present in very unusual relative abundance. We have considered the possibility that slow motion within the intra-molecular hydrogen bond could give rise to modulation of the barrier height to methyl reorientation. The effect of this could conceivably lead to a spectrum in which extra tunnelling peaks appear with non-integral intensities. However, it is noted that the isotopic effect on substitution of deuterium in the hydrogen bond is not large.

Table 1. The measured methyl tunnelling splittings and the corresponding hindering potentials, V , using the single-particle model.

		Ambient pressure	Intermediate pressure (≈ 3 kbar)	High Pressure (≈ 5 kbar)
Acetylacetone-h ₂	Low-frequency peak	$4.3 \pm 0.1 \mu\text{eV}$ $V = 441 \text{ K}$		
	Principal tunnelling peak	$42.1 \pm 0.2 \mu\text{eV}$ $V = 225 \text{ K}$	$56.0 \pm 0.3 \mu\text{eV}$ $V = 201 \text{ K}$	$55 \pm 1 \mu\text{eV}$ $V = 197 \text{ K}$
	Satellite		$69 \pm 3 \mu\text{eV}$ $V = 186 \text{ K}$	$72 \pm 3 \mu\text{eV}$ $V = 183 \text{ K}$
	High-frequency peak		$122 \pm 5 \mu\text{eV}$ $V = 140 \text{ K}$	$113 \pm 4 \mu\text{eV}$ $V = 149 \text{ K}$
Acetylacetone-d ₂	Principal tunnelling peak	$34.0 \pm 0.2 \mu\text{eV}$ $V = 244 \text{ K}$	$48 \pm 2 \mu\text{eV}$ $V = 214 \text{ K}$	$49 \pm 2 \mu\text{eV}$ $V = 212 \text{ K}$
	Satellite		$58 \pm 5 \mu\text{eV}$ $V = 199 \text{ K}$	$60 \pm 4 \mu\text{eV}$ $V = 197 \text{ K}$

4.2. Pairs of coupled methyl groups

The structure of the high-pressure spectra in both samples suggests that the methyl groups are not behaving independently but are coupled. A pair of coupled rotors is described by the Hamiltonian

$$H_c = H_s(\theta) + H_s(\phi) + (W/2)(1 - \cos 3(\theta - \phi)) \quad (2)$$

where W is the magnitude of the coupling potential. The nine rotational ground states have symmetry AA(1), AE(4), E^aE^b(2) and E^aE^a(2), the latter three symmetry species constituting a triplet of energy levels with average splitting ω_4 which is separated from the AA singlet by a frequency ω_1 . The multiplicities of these rotational levels, shown in brackets, change to

32, 16, 8 and 8 respectively when the spin states of the protons are taken into consideration. Thus a typical ground state spectrum of the four transitions that can be driven by a single neutron is a singlet and a triplet with intensities given by the multiplicities of the rotation-spin states. Contour plots of ω_1 and ω_4 in figure 6 illustrate the complex relationship between these frequencies and the potentials V and W . From these two figures it can be seen that the relevant region of parameter space is defined by $W(K) < 0$ in which the large coupling term frustrates the tunnelling causing a decrease in the tunnel frequency ω_1 and gives rise to a significant splitting in the triplet determined by a significant ω_4 .

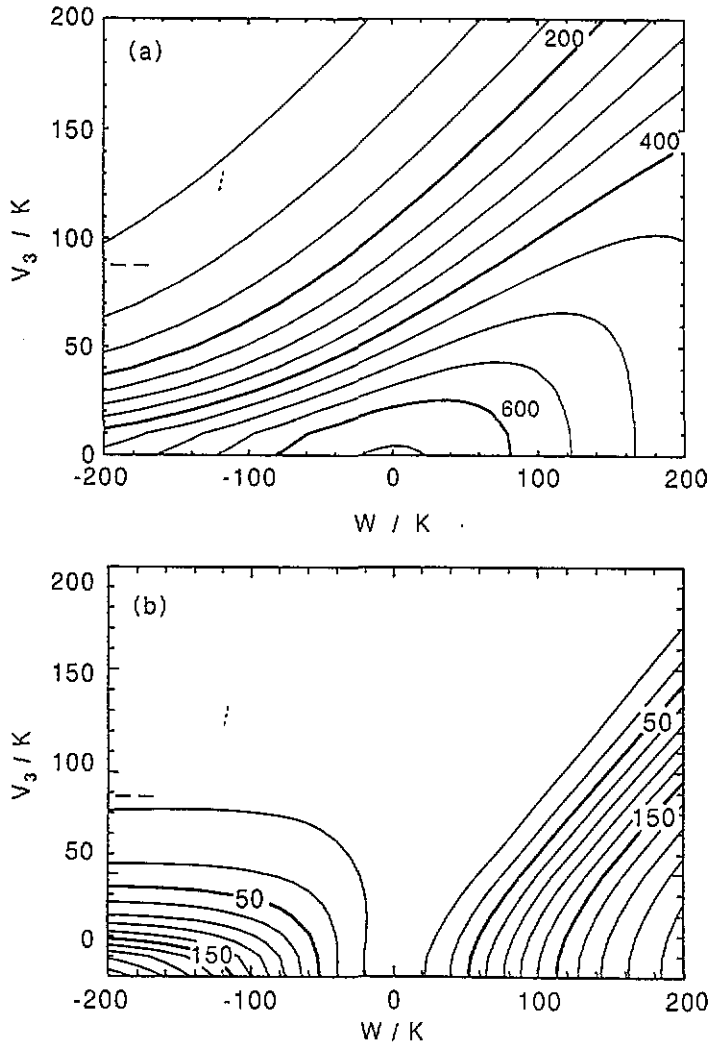


Figure 6. Contour plots for (a) the large ground state tunnel splitting ω_1 (μeV) and (b) the small ground state tunnel splitting ω_4 (μeV), for a pair of coupled methyl groups. The trajectories represented in figure 7 (— — —) and figure 8 (---) are shown.

Figure 7 shows a set of simulated spectra for fixed V (87 K) and variable W . The structure in the principal tunnelling feature arises from the triplet of ground state transitions

but only a peak and one satellite are apparent due to the intensities derived from the above-mentioned multiplicities and the Gaussian width corresponding to the resolution of the spectrometer. That the satellite occurs on the low-energy side of the principal peak and that the relative intensity of these two peaks is fixed negates this application of coupled pairs of rotors to acetylacetone.

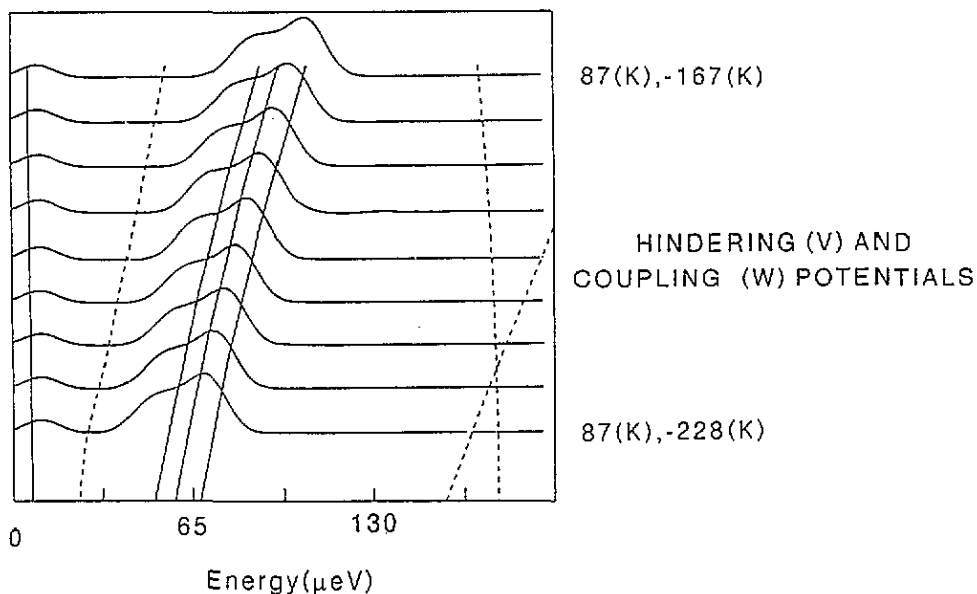


Figure 7. Simulated spectra for a pair of coupled methyl groups assuming Gaussian lineshapes. The solid lines show the variation of the ground state tunnel frequencies with change in coupling potential W . The dashed lines show the predicted positions of the tunnel frequencies in the first excited state.

The set of simulated spectra in figure 8 are derived from a cut through the contour plots in which neither V nor W is constant. The principal tunnel peak is a superposition of the triplet of ground state tunnel transitions while the satellite and high-frequency peak are individual transitions ($E^a E^b - E^a E^a$ and $A E - E^a E^b$ respectively) within the first excited torsional level. The different Boltzmann factors for these two torsional levels, arising from the 6 meV energy difference, goes some way to accounting for the intensity variations of the three peaks. Evidently, however, the intensity of the satellite can never outgrow the principal peak if the relative populations of the torsional levels are determined by a 'temperature'. To complete this model of the pressure dependence the first stage can be simulated by a vertical cut through the contour plots ($W = -122$ K). Progress along the combined trajectory with increasing pressure is nonlinear, equal increments in pressure causing progressively smaller changes in the potential. Throughout the trajectory there is a peak a few μeV from the origin arising from the small splitting of the ground state triplet which corresponds to the 4.3 μeV peak observed in previous experiments. A similar two-legged trajectory has been derived for the deuterated sample which fits the observed data and predicts the existence of a low frequency peak at a few μeV and a high-frequency peak at about 120 μeV . That this was not observed experimentally could be due to the low intensity of peaks associated with first excited transitions.

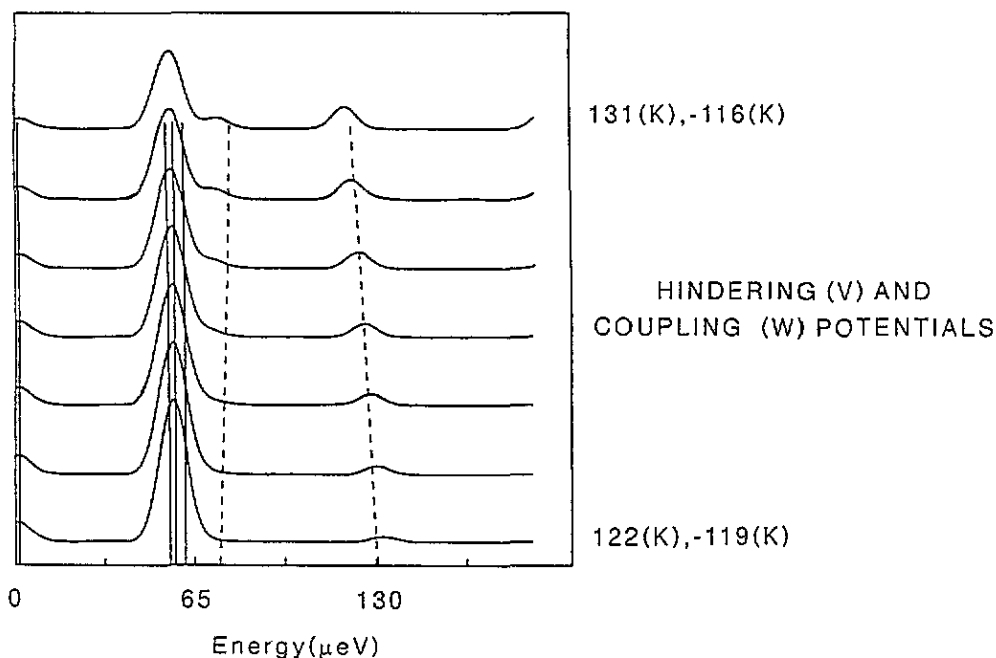


Figure 8. Simulated spectra for a pair of coupled methyl groups assuming Gaussian lineshapes. The format is the same as for figure 7. In this case both V and W vary to simulate the effect of pressure. This may be compared with the experimental data in figure 3 but it should be noted that the intensities assume populations of the excited torsional state which are not in thermal equilibrium with the lattice.

4.3. Infinite chains of coupled methyl groups

The Hamiltonian describing a one-dimensional chain of coupled methyl groups (labelled j) is

$$H_{sG} = \sum_j -\frac{\hbar^2}{2I} \left(\frac{\partial}{\partial \theta_j} \right)^2 + (V/2)(1 - \cos 3\theta_j) + (W/2)(1 - \cos 3(\theta_{j+1} - \theta_j)) \quad (3)$$

which is equivalent to that of the sine-Gordon potential when the coupling potential is reduced to a quadratic for small amplitude angular oscillations. In a classical coupled system of this kind, the excitations are partially localized solitons, antisolitons and breathers. When the energy of the breather exceeds twice the rest-mass of the soliton it can decay into a soliton-antisoliton pair. The quantum sine-Gordon theory also allows for delocalized in-phase and out-of-phase tunnelling excitations which are described respectively by the single-particle Hamiltonian (1) and the modified single-particle Hamiltonian below

$$H = H_s(\theta) + (W/2)(1 - \cos 6\theta). \quad (4)$$

Following the analysis of Fillaux *et al* [13, 14] for 4-methyl pyridine the principal peak has to be assigned to the out-of-phase tunnelling mode and the slightly higher frequency of the satellite then corresponds to the in-phase mode. Using values for the hindering and coupling potentials derived from this assignment the spectrum for the breather mode is calculated as shown in table 2. Soliton and antisoliton excitations have not been calculated

since their high rest mass renders them insignificant at the temperature of these experiments. From the table it can be seen that the breather frequency, corrected for small amplitude excitations (see [13, 14]), is of the right order of magnitude and moves towards the other peaks with increase in pressure. However as in the foregoing analyses the intensities are not in good agreement. The in-phase mode with the lowest zero-point energy is expected to have the greatest intensity and yet has to be assigned to the satellite while the breather has such a high rest mass energy that its intensity should be practically zero.

Table 2. Breather spectrum calculated from the assignment of tunnelling excitations to lower frequency peaks using the quantum sine-Gordon theory.

	Low pressure (3 kbar)	High pressure (5 kbar)
Principal peak (out-of-phase tunnelling)	56 μeV	55 μeV
Satellite (in-phase tunnelling)	69 μeV	72 μeV
Hindering potential V	201 K	197 K
Coupling Potential W	52.4 K	48.4 K
Breather rest mass	405 μeV	386 μeV
0-1 breather transition frequency	410 μeV	385 μeV
Corrected breather transition frequency	198 μeV	186 μeV
Observed breather frequency	122 μeV	113 μeV

5. Conclusion

The analysis of these results is not simple and the interpretation is subject to uncertainty both because of the inadequacy of the existing models to fully explain the observed spectra and also because of the absence of information on the crystal structure. The first observation is that, although the pressure dependence has been described as a two-stage process, the induced changes in frequency and intensity are progressive, there being no evidence of any abrupt phase changes. Secondly, the results for the two samples are broadly similar indicating that the effect of the deuteration of the hydrogen bond is to distort the local molecular environment of the methyl groups, changing the threefold hindering potential, and to increase the pressure at which the satellite emerges. It does not appear that the hydrogen bond motion is coupled to the methyl groups, otherwise suppressing this motion by deuteration would profoundly change the tunnelling spectrum of the methyl groups in the deuterated sample. Thirdly, the structure of the tunnelling peaks suggests coupled pairs of methyl groups, the principal peak arising from a ground state triplet of transition frequencies, while the satellite and highest-frequency peaks correspond to tunnelling transitions in the first excited torsional level, thereby explaining their common intensity-pressure dependence. A model of infinite chains of coupled methyl groups has also been considered but it gives poor agreement with the intensities of the peaks in the observed spectra.

Acknowledgments

MRJ is grateful to the SERC for the award of a postgraduate scholarship.

References

- [1] Clough S, Heidemann A, Paley M and Vettier C 1979 *J. Phys. C: Solid State Phys.* **12** L781
- [2] McDonald P J, Vijayaraghaven D, Debenham P M and Horsewill A J 1993 *Mol. Phys.* **78** 219
- [3] Cavagnat D, Magerl A, Vettier C, Anderson I S and Trevino S F 1985 *Phys. Rev. Lett.* **54** 193
- [4] Aibout A, Carlile C J and Horsewill A J 1992 *J. Phys.: Condens. Matter* **4** 8903
- [5] Andreassen A L and Bauer S H 1972 *J. Mol. Struct.* **12** 381
- [6] Blank H and Maier B (eds) 1988 *Guide to Neutron Research Facilities at the ILL* Copies available from the Scientific Secretary, ILL, Grenoble, France
- [7] Paureau I and Vettier C 1975 *Rev. Sci. Instrum.* **46** 1484
- [8] Horsewill A J, Alsanoosi A M and Carlile C J 1987 *J. Phys. C: Solid State Phys.* **20** L869
- [9] Aibout A 1990 *PhD Thesis 'Quantum Aspects of Molecular Motion Studied by NMR and INS'* University of Nottingham unpublished
- [10] Horsewill A J, Johnson M R and Tomsah I B I in preparation
- [11] Clough S, Heidemann A, Horsewill A J and Paley M N J 1984 *Z. Phys. B* **55** 1
- [12] Hausler W and Huller A 1985 *Z. Phys. B* **59** 177
- [13] Fillaux F and Carlile C 1990 *Phys. Rev. B* **42** 5990
- [14] Fillaux F, Carlile C and Kearley G J 1991 *Phys. Rev. B* **44** 12280
- [15] Clough S, Horsewill A J and Johnson M R 1993 *Phys. Rev. A* **47** 3420
- [16] Clough S, Heidemann A, Horsewill A J, Lewis J D and Paley M 1982 *J. Phys. C: Solid State Phys.* **15** 2495