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LETTER TO THE EDITOR

The pressure dependence of methyl tunnelling in MDBP from field-cycling NMR spectroscopy

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Abstract. We report the first measurement of the pressure dependence of methyl tunnelling by NMR techniques. 4-methyl-2,6-ditertiary-butyl-phenol has been studied using a field-cycling technique to explore the anomalous proton magnetisation in magnetic field regions where the electron Larmor frequency of free radicals matches the methyl tunnelling frequency. The pressure dependence has been analysed to extract information about the inter-atomic potentials that contribute to the hindering potential barrier.

Molecular tunnelling of methyl groups has been of considerable interest in recent years as an example of the transition from quantum to classical dynamical behaviour. It has been shown that the behaviour depends solely on the temperature and the height of the hindering potential barrier (Clough *et al* 1982). The traditional method of changing the potential barrier has been to vary the molecular environment by changing the sample. A much cleaner method is to vary the pressure applied to a given sample. To date this has only been employed for studies by inelastic neutron scattering (INS) (Clough *et al* 1979, Cavagnat *et al* 1985, Heidemann *et al* 1987). However, the frequency window and resolution available for INS are limited. Magnetic resonance techniques are considerably more versatile in both respects, offering a series of windows covering seven orders of magnitude in the tunnelling frequency. Tunnelling experiments probe the first derivative of the inter-atomic potentials in molecular solids and thus permit a determination of the parameters describing the potentials, which are often difficult to measure otherwise.

We report the first pressure dependence measurements of methyl tunnelling by NMR. In particular we have used the field-cycling technique to study irradiated 4-methyl-2,6-ditertiary-butyl-phenol (MDBP). This technique is described in the literature (van Hecke and Janssens 1978, Clough *et al* 1984). Anomalies are observed in the proton magnetisation at magnetic fields where the MDBP methyl tunnel frequency matches the electron spin Larmor frequency of paramagnetic impurities (free radicals) induced by γ -irradiation. MDBP has been extensively studied at atmospheric pressure by ESR and ENDOR (Clough and Poldy 1969), and by field cycling (Clough and Mulady 1973) and neutron scattering (Clough and Heidemann 1979) and so represents a well characterised system in which to conduct the new experiments. Previous field-cycling experiments have indicated the existence of two tunnel resonances. One is associated with the methyl group on molecules damaged by irradiation. We have studied the other narrower tunnel resonance of undamaged molecules.

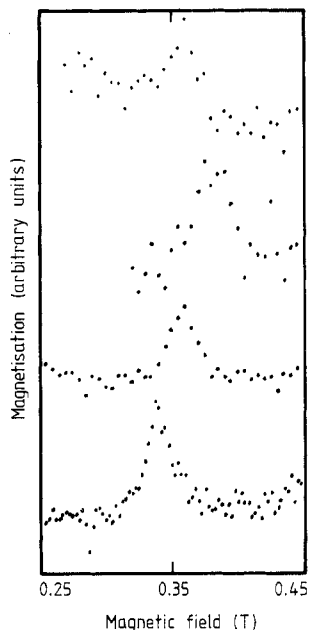


Figure 1. Methyl tunnel resonance spectra (4 K) recorded at, from bottom upwards, atmospheric pressure, 0.8 kbar, 1.6 kbar and 2.4 kbar.

The pressure bomb is built of stainless steel with 'O'-ring seals and is capable of achieving 2.5 kbar. It is based on the bomb described by Lambkin *et al* (1988) with the inner cylinder omitted to give a 10 mm inner bore. The capillary feed and external intensifier were used unchanged. RF feedthroughs were made from 'Thermocoax' cable brazed into the piston and then impregnated with epoxy resin at high pressure (100 bar). Two working fluids were used, perfluorohexane and a very low-viscosity fluorinated oil (Krytox GPL100). The fluids contained no hydrogen. The sample and NMR coil were immersed in the oil which also filled the lower end of the pressure capillary. The perfluorohexane filled the majority of the pressure capillary. The oil has a pour point (effective freezing temperature) of about 230 K, considerably higher than the perfluorohexane freezing temperature. However, it becomes an ever more viscous fluid as the temperature is lowered—rather than freezing suddenly. Such behaviour on solidifying assists in the establishment of hydrostatic pressure. The pressure was established and maintained at room temperature. The pressure bomb was then cooled slowly from the base in liquid-nitrogen vapour over typically 30 min until the oil was solid. Throughout the cooling the pressure was maintained through the perfluorohexane which remained liquid. We estimate that this procedure gave pressures, which were measured with a known pressure applied to the perfluorohexane, accurate to 10%. The experiments were performed at 4 K.

Figure 1 shows representative field-cycling tunnelling spectra measured at different pressures. Figure 2 shows the measured tunnel splitting at the seven pressures measured up to 2.4 kbar together with the barrier height calculated in the usual way by matrix diagonalisation (Clough *et al* 1982). As the pressure is increased a clear change is observed in the tunnel frequency which first increases with increasing pressure before decreasing again above approximately 1.6 kbar.

In the absence of attractive components to the pairwise interaction between atoms, it would be anticipated that the application of pressure would increase the barrier height

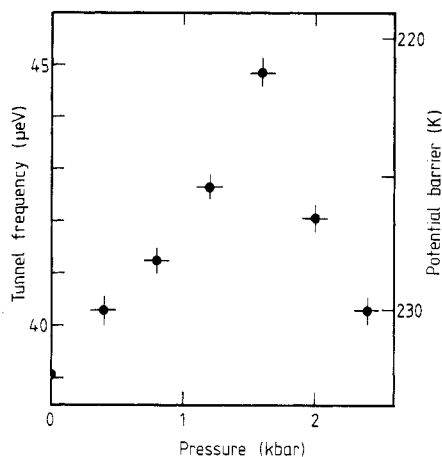


Figure 2. The measured pressure dependence of the methyl tunnel splitting in MDBP and the calculated threefold potential barrier height.

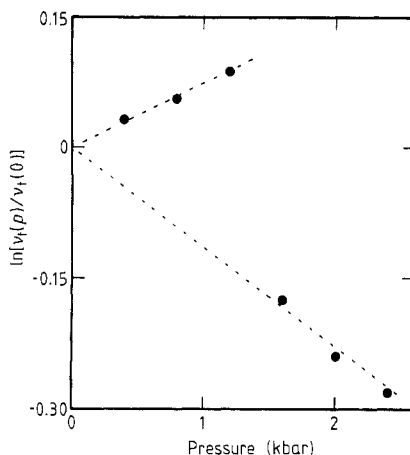


Figure 3. The logarithmic dependence of the reduced tunnel frequency ($\nu_t(p)/\nu_t(0)$) on pressure for the low- and high-pressure regimes. See the text for details.

and so reduce the tunnelling frequency. In our experiments, however, we observe a decrease in the barrier up to 1.6 kbar. This can only be explained by the presence of attractive components in the inter-atomic potentials and we extend the model developed by Clough *et al* (1979) to include these and also correct a minor error in their derivation. A common phenomenological expression for inter-atomic potentials between two atoms is

$$V(r) = K_{\text{rep}}r^{-n_{\text{rep}}} - K_{\text{attr}}r^{-n_{\text{attr}}}$$

where K_{rep} and K_{attr} are constants determining the magnitudes of the repulsive and attractive components respectively. For the case of a Lennard-Jones potential the power law exponents are given by $n_{\text{rep}} = 12$ and $n_{\text{attr}} = 6$ for the repulsive and attractive components respectively. We use this potential to describe that between the methyl group and its environment under the assumption that the barrier is dominated by the presence of a single neighbouring atom a distance r away (an analysis of the structure of MDBP does indeed show that an OH group on an adjacent molecule is nearby; see Maze-Baudet 1973) and use our tunnelling data to derive the power law exponents in the phenomenological expression. For low pressures ($p < 1.6$ kbar) the barrier is dominated by attractive components to the potential and for higher pressures ($p > 1.6$ kbar) it mainly reflects the repulsive components. We thus divide our data into two sets and analyse them separately.

In the two regimes the tunnelling frequency has been plotted on a logarithmic scale as a function of pressure (figure 3) and fitted to the expression

$$\nu_t(p) = \nu_t(0) \exp(-p/p_0). \quad (1)$$

$\nu_t(0)$ is the zero-pressure tunnelling frequency equal to 39.1 μeV (measured) for the low-pressure data and 53.5 μeV (by extrapolation) for the high-pressure data. p_0 is found to be -13.0 and 8.7 kbar for the low- and high-pressure data respectively. To a very

good approximation the tunnelling frequency displays an exponential dependence upon the barrier height, B . We have determined the relationship to be

$$\nu_t = 627 \exp(-0.0119B) \quad 10 < \nu_t < 100 \mu\text{eV} \quad (2)$$

where ν_t is in μeV and B in kelvin. Comparison of (1) and (2) suggests that there is a linear relationship between the barrier height and pressure:

$$B(p) = B(0)(1 + \alpha p).$$

Differentiating gives

$$\alpha = (1/B(0))(\partial B(p)/\partial r) \partial r/\partial p.$$

The barrier is proportional to the first derivative of the potential which is assumed to be of the form Kr^{-n} . Hence

$$\alpha = -(n + 1)r^{-1} \partial r/\partial p.$$

Introducing the bulk compressibility $\kappa = (-3/r) \partial r/\partial p$ we obtain

$$\alpha = [(n + 1)/3]\kappa.$$

The values of α for the attractive and repulsive regimes deduced from figure 3 and equation (2) are -0.0278 and 0.047 kbar^{-1} respectively. A typical value of κ for molecular solids is 0.01 kbar^{-1} (Rice and Jortner 1965) and this leads to values for the exponents in the potential of $n_{\text{rep}} = 13.9$ and $n_{\text{attr}} = 7.3$.

The agreement with power laws exemplified by models such as the Lennard–Jones 12–6 model is gratifying. Many of the assumptions in our model are not severe. It might be argued that intra-molecular contributions to the potential are relatively insensitive to pressure and thus distort the result. However, since the barrier reflects the gradient of the potential and is itself differentiated in the analysis, pressure-independent contributions are not included and do not invalidate the result, which therefore describes the inter-molecular potential.

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