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## Effect of isotopic dilution in the methyl tunnelling spectra of molecular crystals

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**Abstract.** The rotational tunnel and torsion frequencies of crystalline nitromethane and toluene have been investigated using inelastic neutron scattering. The effects on these frequencies of complete deuteration, selective deuteration (in the case of toluene) and dilute mixing of the protonated species in a deuterated sample are reported. Small shifts in the tunnel frequencies of the protonated species dissolved in the deuterated matrix can be partially understood on the basis of lattice contraction upon deuteration. More surprising is the magnitude of the increase in the intrinsic energy width of both the tunnel and the torsional energy levels upon dilution.

### 1. Introduction

The properties of the methyl groups (or other molecular species) which experience large-amplitude motions can be substantially affected by their environment. The changes in these properties upon modification of the environment could be expected to provide information on the mechanism of these interactions. Because rotating methyl groups (being one dimensional) are thought to provide a simple model type for such studies, great interest (both experimental and theoretical) has been devoted to them. Among the experimental techniques used have been NMR, neutron scattering and optical spectroscopy. In several instances, the amount of information available is such that the single-particle potential required to describe the tunnel and torsional levels is well characterised ([1–5] and references therein).

At low temperatures (about 4 K), quantum mechanical effects dominate the rotational dynamics of the methyl groups. These effects are exhibited by the splitting of the rotational energy levels due to tunnelling between the equilibrium orientations of the methyl group. The magnitude of the splitting is very sensitive to the shape of the potential hindering the rotational motion. Measurements of the splitting of the ground state, which are most accurately achieved with neutron scattering, have provided important information on the potential. In most cases, a single-particle description—uncoupled methyl groups—seems to be adequate to account for the measurements. However, the effects of strongly coupled methyl groups have been observed. These

effects are most dramatic in those systems in which the methyl groups are very close together owing to their location on the same molecule. When the coupling is comparable with the single-particle hindering potential, collective effects manifest themselves as additional splitting of the energy levels. These effects have been measured recently for lithium acetate ([7, 8] and references therein). More subtle effects on the rotational properties can be expected in those systems in which the coupling is smaller [6]. Such effects have been investigated theoretically [9].

The two molecules studied here—nitromethane and toluene—are characteristic of the latter system in which the potential to the methyl group rotation (with barrier height around  $25B$ , where  $B = \hbar^2/2I$ ) is substantially larger than the coupling term. Their tunnelling spectra do exhibit a finite linewidth at 3 K which could be related to coupling effects [10]. Isotopic dilution measurements, in which small amounts of the protonated species of the molecule are placed in an environment of deuterated neighbours, should provide information on the coupling mechanism. The effect on the coupling due to a mass change can be studied without disturbing the molecular or crystal structure.

## 2. Experiments

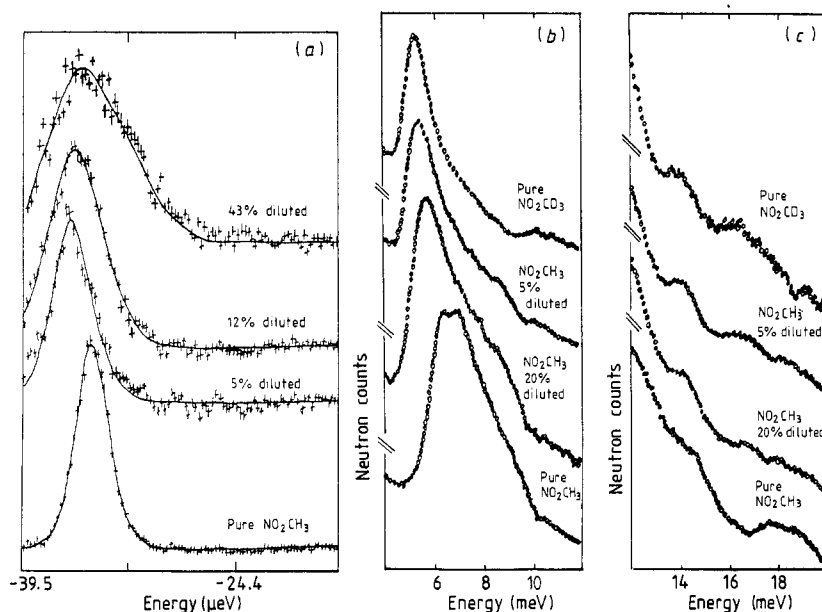
All the compounds were commercially available with an isotopic purity higher than 99%. The inelastic neutron scattering (INS) experiments were carried out at the high-flux reactor of the Institut Laue–Langevin in Grenoble with the back-scattering spectrometer IN10 for cold neutrons with an energy resolution of  $1.4 \mu\text{eV}$  (FWHM) and an energy range from  $-14$  to  $-40 \mu\text{eV}$  and at the National Bureau of Standards research reactor with the spectrometer BT4 with a resolution of  $0.53 \text{ meV}$  and an energy range from  $4$  to  $20 \text{ meV}$ .

## 3. Results and discussion

### 3.1. Nitromethane

In previous studies, the methyl rotation in solid nitromethane has been described with a single-particle formalism ([11] and references therein). The measured energy levels are well accounted for by this potential. The tunnel spectrum at low temperature exhibits only one peak at  $35.1 \mu\text{eV}$ . This potential is probably the most thoroughly characterised of any condensed molecular system exhibiting hindered rotational motions. As yet unresolved is the observation that all the energy levels, both tunnel peak and torsional levels, have an intrinsic energy width (about  $2.6 \mu\text{eV}$  (FWHM) for the  $35.1 \mu\text{eV}$  tunnel peak). The crystal structure shows that each methyl group is surrounded by four other methyl groups separated by  $d\text{C}-\text{C} \approx 4 \text{ \AA}$  and with an H–H minimum distance of  $2.7 \text{ \AA}$  [11]. Thus, the observed width could indicate that some coupling effects are present in this compound.

A linear decrease in the tunnel frequency has been observed when dissolving  $\text{CH}_3\text{I}$  in  $\text{CD}_3\text{I}$  [12]. This observation is explained by an increase in the rotational potential with deuteration due to a change in the equilibrium orientation. It is also well known that the fully hydrogenated species have a greater volume by about 0.5% than the fully deuterated species [13, 14]. Indeed, such a volume contraction would be equivalent to a pressure increase of  $0.5 \text{ kbar}$  [15] and, as shown in the previous studies [3], could involve a similar effect on the tunnel peak frequency. In the present case, when dissolving

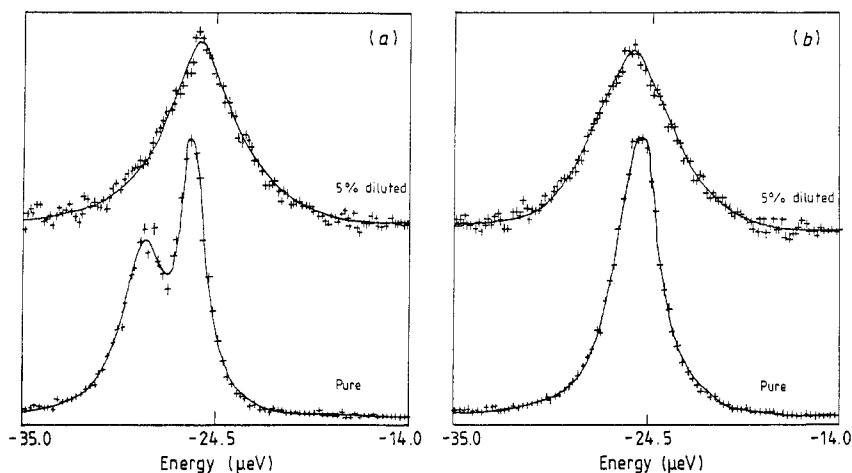


**Figure 1.** INS spectra of crystallised nitromethane ( $\text{NO}_2\text{CH}_3$ ) pure and dissolved in  $\text{NO}_2\text{CD}_3$  at 4 K: (a) tunnelling spectra (IN10;  $Q = 4 \text{ \AA}^{-1}$ ); (b), (c) torsional spectra. ( $x\%$  concentration  $\text{NO}_2\text{CH}_3$  in  $(100-x)\% \text{NO}_2\text{CD}_3$ .)

$\text{NO}_2\text{CH}_3$  in  $\text{NO}_2\text{CD}_3$ , the  $\text{CH}_3$  tunnel peak shifts towards high energies almost exponentially as the dilution increases (figure 1). However, more surprising and not noted in [12] is the broadening of the tunnel line with isotopic dilution (figure 1). Broadening of the torsional levels also occurs here on dilution to such an extent, in fact, that no clearly resolved torsional peak corresponding to the  $\text{CH}_3$  torsion is observed in the diluted sample (figure 1). Instead, as can be seen in the figure, only additional scattering to that present in the deuterated sample exists in the energy region where the  $\text{CH}_3$  torsion is expected.

Some inhomogeneities in the diluted samples could explain this observed broadening. Small-angle neutron scattering (SANS) experiments were realised with a pure  $\text{NO}_2\text{CD}_3$  sample and a 10% diluted  $\text{NO}_2\text{CH}_3$  sample. Careful cooling of outgassed compounds was effected to obtain samples with as few grains as possible to avoid the surface contribution to SANS of these grains ( $\lambda = 5 \text{ \AA}$ ). However, there is no clear evidence of the presence of clusters of  $\text{NO}_2\text{CH}_3$  in  $\text{NO}_2\text{CD}_3$ ; both pure and diluted samples exhibit small-angle scattering corresponding to spherical clusters of around  $85 \text{ \AA}$  radius. Indeed, cracks, crystallinities, etc, which are impossible to avoid completely in the sample preparation, could mask any signal from  $\text{NO}_2\text{CH}_3$  clusters if they exist.

Another hypothesis could be considered which takes into account the dynamic coupling of the methyl group with its surroundings. The motion of the protons performing torsion is substantially larger than that of the deuterons ( $\langle u^2 \rangle_{\text{lib}} = 0.06 \text{ \AA}^2$  for  $\text{CH}_3$  and  $\langle u^2 \rangle_{\text{lib}} = 0.04 \text{ \AA}^2$  for  $\text{CD}_3$  [16]) and the torsional frequencies of each is also quite different [3, 13, 14]. Thus, it is possible that the dynamic coupling of the H atoms of the  $\text{CH}_3$  group with the surrounding D atoms in a diluted sample could be quite different from that with surrounding H atoms in pure  $\text{NO}_2\text{CH}_3$  sample. No dramatic change was found in the activation energy of the methyl rotation measured by quasi-elastic neutron



**Figure 2.** INS tunnelling spectra of  $\alpha$  crystallised toluene (a)  $\text{C}_6\text{H}_5\text{CH}_3$  and (b)  $\text{C}_6\text{D}_5\text{CH}_3$  pure and 5% concentration  $\text{C}_6\text{H}_5\text{CH}_3$  (a) or  $\text{C}_6\text{D}_5\text{CH}_3$  (b) in 95%  $\text{C}_6\text{D}_5\text{CD}_3$  at 4 K (IN10;  $Q = 4 \text{ \AA}^{-1}$ ).

scattering as would be expected for such a great change in the character of the torsional mode in diluted samples.

### 3.2. Toluene

A similar problem is found in  $\alpha$  crystallised toluene. As expected from the structural data, the tunnel spectrum of toluene  $\text{C}_6\text{H}_5\text{CH}_3$  exhibits two well resolved peaks at 28.5 and 26  $\mu\text{eV}$  at low temperature (figure 2), corresponding to the two different methyl rotors present in the  $\alpha$  crystallised structure [4]. A single-particle formalism has been used to describe the methyl rotation in this compound. A great deal of data, recently completed with a pressure experiment with  $\text{C}_6\text{D}_5\text{CD}_3$  [17], has led to characterisation of two potential energy functions for these two rotors, one being more hindered than the other [4].

Upon deuterating the benzene ring only, the tunnel spectrum is strongly perturbed. The peaks are shifted towards lower energies and their splitting is greatly reduced ( $\nu_t = 24.7$  and 25.8  $\mu\text{eV}$  in  $\text{C}_6\text{D}_5\text{CH}_3$ ) (figure 2). A zero-point vibrational energy effect was previously proposed to explain these differences [4].

However, a more thorough analysis of these  $\text{CH}_3$  tunnel spectra reveals a great difference between the two peaks widths. Indeed, the peak at 26  $\mu\text{eV}$  (or 24.7  $\mu\text{eV}$ ) has a width of the same order of magnitude as the resolution whereas the peak at 28.5  $\mu\text{eV}$  (or 25.8  $\mu\text{eV}$ ), fitted with a Gaussian line, has an intrinsic width of about 3  $\mu\text{eV}$  (FWHM). The presence of two components with very different widths in the  $\text{C}_6\text{D}_5\text{CH}_3$  tunnelling spectra was confirmed by a temperature effect study [4]. Again, some coupling effects could occur for the less hindered methyl rotor.

When dissolving  $\text{C}_6\text{D}_5\text{CH}_3$  and  $\text{C}_6\text{H}_5\text{CH}_3$  in fully deuterated  $\text{C}_6\text{D}_5\text{CD}_3$ , the  $\text{CH}_3$  tunnel spectrum of the  $-d_5$  derivative is very slightly shifted towards high energies and much broadened (intrinsic width of about 5.4  $\mu\text{eV}$  (FWHM)), whereas that of the  $-d_0$  compound is strongly perturbed and becomes very similar to that of the diluted  $\text{C}_6\text{D}_5\text{CH}_3$  (figure 2). Thus, it appears that deuteration of the benzene ring and deuteration of

the neighbouring methyl groups affect the tunnel transitions of the CH<sub>3</sub> groups in  $\alpha$  crystallised toluene differently. A pure intra-molecular zero-point vibrational effect cannot entirely account for the observed changes in the tunnel spectrum when deuterating the benzene ring. A volume contraction due to deuteration would be only about 0.3% [13, 14] and would lead to a larger splitting of the tunnelling peaks as observed with a pressure increase [4], just the contrary to what is observed here.

On the other hand, the effect of the deuteration of the surrounding methyl groups on the tunnel peak frequency seems very weak but, as in nitromethane, leads to a marked broadening of the peaks. The same hypotheses could be used to explain this effect but, in addition, some difference between the H–H and H–D interactions, which is certainly related to the bond length (C–H is larger than C–D) and vibrational anharmonicity difference, could be assumed.

#### 4. Conclusion

Until now, the isotopic effect has only been used and interpreted as a simple mass effect in the analysis of the tunnelling spectra of the methyl group. In the past few years, more accurate measurements have revealed additional effects which occur in these materials on deuteration or isotopic dilution.

The tunnelling spectra changes observed on deuteration or isotopic dilution are not yet fully understood. The tunnelling frequency changes (from 4 to 16%) could be related either to a slight volume contraction associated with the CH and CD bond length difference or to a change in the equilibrium orientation of the molecules. On the other hand, the broadening of the torsional and tunnelling peaks on isotopic dilution could be due to either some disorder in the diluted sample or to different dynamical coupling of the CH<sub>3</sub> group when it is surrounded by other CH<sub>3</sub> groups or by CD<sub>3</sub> groups.

Thus, isotopic dilution does not lend itself to simple interpretation of the coupling mechanism. However, it illustrates well the high sensitivity of the CH<sub>3</sub> tunnelling to the molecular environment.

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