NMR FIELD CYCLING OF TUNNELLING MOLECULAR GROUPS AT HIGH PRESSURE.

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Introduction

The reorientation of small molecular groups by quantum tunnelling at low temperature and by thermally activated hopping at high temperature has recently excited much interest because of the lack of a formal model to describe the transition from quantum to classical behaviour and the realisation that the structure of gauge theory is a natural one with which to describe the interactions of dynamical systems with their environment [1].

Pressure offers one of the best means of varying the height of the potential barrier to reorientation. We have performed the first high pressure NMR measurements of molecular group tunnelling. The high pressure apparatus is described elsewhere [2].

Results

The methyl group on undamaged molecules of γ irradiated 4 methyl 2,6 ditertiarybutyl-phenol,MDBP, has a tunnelling frequency of 9.5 GHz [3]. This measurement is made by NMR field cycling in an experiment where the electron Zeeman splitting of the free radical is tuned to the tunnel splitting. We have studied this splitting up to 2.4 kbar. Below 1.6 kbar the tunnelling frequency increases with increasing pressure whilst above 1.6 kbar it decreases Only a decrease in tunnel frequency is expected in a naive analysis in which the effect of pressure is seen to increase the potential barrier to reorientation. Such a model neglects attractive components to the pairwise interaction between atoms. Assuming a Lennard Jones type potential between the methyl group and its nearest neighbour atoms on the next molecule we have been able to deduce power exponents of 13.9 and 7.3 for the repulsive and attractive components of the potential respectively [2]. Such a measurement would be difficult by other techniques.

Dimethyl sulfide is an interesting material in that it exhibits strong coupling between two identical methyl groups. This leads to two observed tunnel splittings, one of 750 kHz associated with single group rotation and one of 85 kHz associated with coupling [4]. We have recorded several spectra from this material at different pressures up to 2.6 kbar using low field cycling NMR in which low frequency irradiation is used to excite Larmor and tunnelling transitions. In most cases the 85 kHz splitting is observed to increase slightly with pressure. Within the experimental accuracy no change could be seen in the 750 kHz splitting. However in one series of scans recorded at 1.3 kbar a large and dramatic shift of the two splittings to 900 and 240 kHz respectively was observed. This is being investigated further.

We have studied the tunnelling of the ammonium group in ammonium persulfate. This is a three dimensional rotor and in the quantum regime can undertake reorientation about four three-fold axes simultaneously. Motion about three of these axes is stongly hindered. However reorientation about the remaining axis is relatively weakly hindered and gives rise to a tunnel splitting of 260 MHz at atmospheric pressure. The pressure dependence of the tunnelling frequency about this axis has been studied using a field cycling level crossing technique in which the proton Larmor frequency is tuned to the tunnelling frequency. Its value increases to 290 MHz at 2.4 kbar. Recently Clough, Mohammed and Horsewill (private communication) have reported an anomalous temperature dependence of the tunnelling spectrum in this material. Preliminary analysis demonstrates that the trajectory undertaken by the rotor about one axis is determined by the dynamics about another.

We have fulfilled our initial aim of demonstrating at high pressure the practicality of all types of field cycling experiments used in tunnelling. The aim now of this ongoing series of experiments is to develop tests of the new ideas relating to the application of gauge theory in condensed matter physics. In this respect three dimensional rotors such as ammonium groups and groups strongly coupled to a simple environment such as a second group are particularly important. The new variable of pressure provides a means of making prescribed changes to the environment and trajectories and of studying the effect of these changes on the dynamics.

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4 Clough S, Horsewill AJ, McDonald PJ and Zelaya FO 1985 Phys. Rev. Lett. 55 17