Methyl group tunnelling and dynamic nuclear polarization

M. Paley[1]
[1]Academic Radiology, University of Sheffield, Sheffield, Yorkshire, United Kingdom

INTRODUCTION

Dynamic Nuclear Polarization (DNP) is of increasing interest in MR imaging and spectroscopy because of the enormous increase in sensitivity (up to factors ~10^5) compared to thermal polarization at room temperature. Introduction of the low temperature, microwave pumped free radical dissolution technique has revolutionised the ability to investigate spectroscopy in vitro and in vivo (1). However, there are other possible routes to achieve high nuclear polarization at low temperatures, which do not use applied microwave radiation. The methyl group is a fascinating example of a one dimensional quantum rotor in a three-fold hindering barrier which, because of its low moment of inertia, is capable of tunnelling at enormous rates (up to 10's of GHz) even at cryogenic temperatures, thus giving rise to dramatic spin-lattice relaxation and polarization effects. The Haupt effect, related to dipolar order in rapidly cooled free rotor tunnelling methyl groups, has recently been suggested as a cause of anomalous polarization in DNP experiments (2).

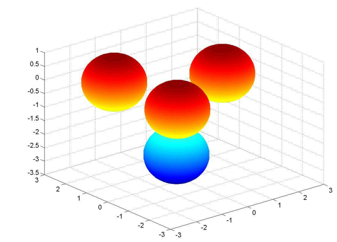
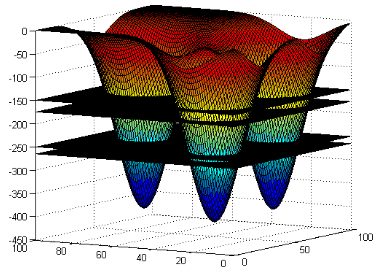


Figure 1 Stylized (not to scale) 3D model of a CH3 group. Rotation occurs around an axis through the carbon atom and the centre of the methyl triangle.
Figure 2 Three-fold potential barrier with ground and first excited state eigenvalues for methyl group protons at low temperatures.

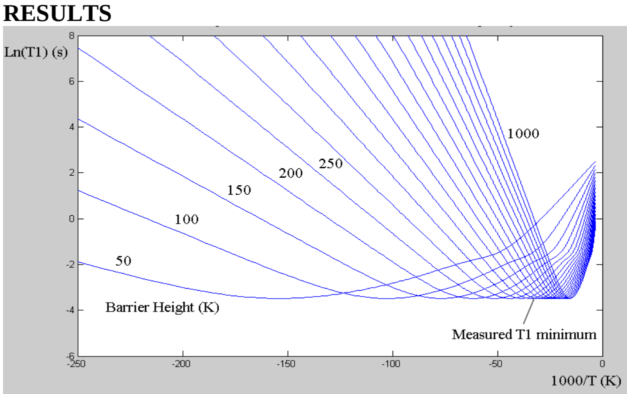


In a wide range of methyl containing materials, Clough et al. found a strong correlation between the temperature of the T_1 minimum versus inverse temperature and the tunnel frequency of the methyl rotor using NMR and neutron scattering techniques and developed a theoretical model to predict T_1 versus temperature based solely on the methyl barrier height (3). This correlation allows methyl tunnel frequencies to be accurately estimated using a simple T_1 versus temperature experiment. Once the tunnel frequency is known then B_0 field switched Tunnel Magnetic Resonance (TMR) energy level crossings can be established to generate nuclear polarization with or without the presence of a free radical species, depending on tunnel frequency and switched magnetic field strength. Previously unpublished results of a TMR DNP experiment in Zinc Acetate containing free radicals measured at 4.2K are presented here as an example of DNP without microwave irradiation.

METHODS

T_1 versus temperature was measured using saturation recovery for a polycrystalline sample of Zinc Acetate at 21MHz using a Helium gas flow cryostat. Temperature was varied by adjusting the gas flow rate and through use of a resistive PID controlled heater. The TMR observation was also performed at 21MHz in γ-irradiated $ZnAc_2D_2O$at 4.2K by saturation at 21MHz / 0.5T, evolution in a variable switched B_0 field for 60s followed by signal measurement back at 21MHz / 0.5T.

RESULTS



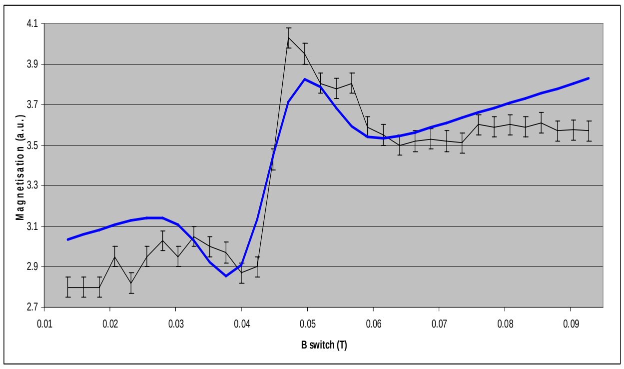


Figure 1 shows calculated $\ln(T_1)$ versus inverse temperature for tunnelling methyl groups as a function of hindering barrier height increasing from 50K to 1000K in steps of 50K for temperatures in the range 4K to 300K calculated using the methyl group thermometer model (3). The position of the T_1 minimum in Zinc Acetate was found at 28K which corresponds to a barrier height of 420K and a tunnel frequency of 1.2 GHz. This was confirmed by inelastic neutron scattering where a methyl tunnelling peak was measured at 4.9μeV for $ZnAc_2H_2O$ and 5.3 μeV for $ZnAc_2D_2O$. Figure 2 shows the tunnel magnetic resonance in γ-irradiated $ZnAc_2D_2O$ showing the dynamic polarization produced at 4.2K when the field was switched to a value where the electron spin resonance frequency of γ–generated free radicals matched the methyl group tunnel frequency but without microwave irradiation. The solid line is a fit to $(B-Bt)*\exp(-(B-Bt)^2) + m*B + c$ where Bt is the field at which the level crossing occurs, B is the switched field and m=0.08 and c=2.9 are constants (4). The measured tunnel frequency was thus 1.29GHz.

DISCUSSION

The tunnelling methyl group is a well characterised quantum system and can generate polarization either through electronic-nuclear transitions for low rotational barrier materials using low field magnetic fields or purely nuclear transitions in the absence of free electrons for high rotational barrier materials (lower tunnel frequencies) and higher switched magnetic fields. Use of quantum tunnelling methyl groups to generate polarization in combination with the dissolution method offers many future possibilities for in vitro and in vivo experiments with increased sensitivity. 1.Ardenkjaer-Larsen et al. PNAS, 2003,100:10158. 2. Saunders M et al. DNP Conference, Nottingham, 2007 3. Clough S. et al., J Phys C, 1981, 14; L525 . 4. Clough S et al. J. Phys. C. 1982; 15: 3803-3808