THE POLARISATION OF ^{14}N AND ^{15}N NUCLEI IN POLARISED PROTON TARGETS USING IRRADIATED AMMONIA

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The steady state and transient behaviour of the nitrogen polarisation in dynamically polarised irradiated ammonia has been experimentally investigated. It is concluded from the results obtained with both ^{14}N and ^{15}N that these nuclei are in spin temperature equilibrium with the protons under the conditions normally existing in polarised targets and hence the nitrogen polarisation may be calculated from the measured proton polarisation.

1. Introduction

For many years the standard target materials used in dynamically polarised proton targets were chemically doped monohydric or dihydric alcohols. This situation has recently changed because of the development of irradiated ammonia which has a better performance both in terms of polarisable proton content and resistance to beam induced radiation damage. However, the use of this material does introduce one possible new problem because the associated nuclei are ^{14}N which have spin 1 and are therefore polarisable, rather than ^{12}C and ^{16}O which both have spin zero. In scattering experiments where it is not possible to distinguish free proton from bound nucleon scattering it is necessary to have a knowledge of the nitrogen polarisation, as the effective polarisation seen by the experiment will be different from the measured proton polarisation. An investigation has therefore been made of the ^{14}N polarisation in irradiated ammonia under experimental conditions similar to those existing in operational polarised targets. Studies have also been made under the same conditions on ammonia manufactured with 100% enriched ^{15}N.

2. The spin temperature model

The spin temperature model [1] has been used very successfully to describe the behaviour of the nuclear spin systems during dynamic polarisation in a number of solid materials, including alcohols. When two or more nuclear species are present, it predicts that the spin systems will be coupled when an alternating mag-

netic field, having a frequency close to the spin resonance frequency of the electron centres used in the polarisation process, is applied. The Zeeman energy reservoirs of the nuclear spin systems are then thermally linked via their interaction with the electronic non-Zeeman reservoirs. If this interaction is strong enough, the nuclear spin systems can be considered to be in thermal equilibrium, that is they have equal spin temperatures. In these circumstances the polarisation of each species can be precisely related using Brillouin functions [1]. The equal spin temperature hypothesis has been confirmed in monohydric alcohols [2,3] and in dihydric alcohols [4] for protons, deuterons and ^{13}C nuclei. However, measurements made in ammonia containing both deuterons and protons [5] suggest that the equal spin temperature assumption does not apply in this case, therefore its application in the nitrogen–proton system needs to be investigated.

The strength of the coupling between nuclear spin systems in a particular situation may be characterised by a thermal mixing time constant. If this is short compared with the time constant associated with any changes in polarisation then the nuclear spin systems will always be in thermal equilibrium. This may be tested by measuring the nitrogen polarisation as a function of proton polarisation over as wide a range of values as possible. The thermal mixing time constant may also be measured directly. This involves changing the polarisation of one of the nuclear species, for example by RF saturation of the appropriate nuclear resonance transition, and then observing the rate at which the system returns to its original state. Both techniques were used in this investigation.

3. Apparatus

The experimental data were obtained with an apparatus specifically designed and built to study the properties of materials suitable for dynamically polarised targets. This was effectively a small polarised target in which no provision was made for beam and scattered particle access [6].

The magnetic field was generated by an end corrected superconducting solenoid which provided a field uniformity of better than 1 in 10^4 over a volume of 1.2 cm^3 in the range 0.25–5 T. The target material was cooled with a vertical ^3He–^4He dilution refrigerator which had a maximum power capability of 9 mW at a temperature of 400 mK and a base temperature of 90 mK. This base temperature was sufficiently low to allow operation in frozen spin mode, which was essential for the nitrogen polarisation measurement (sect. 5). It was also possible to circulate pure ^4He to obtain stable operation at temperatures in the region of 1 K which was necessary for calibration of the NMR system used to measure the proton polarisation.

The microwave power necessary for the dynamic polarisation process was supplied by a klystron which had a tuning range of 1.3 GHz and a centre frequency of 71 GHz. This defined the magnetic field at which protons could be dynamically polarised as 2.53 T. It was also possible to make semiquantitative electron spin resonance measurements on the materials using this device, by scanning the field over a small range and detecting the change in power adsorption with the bolometric technique originally described by Niinikoski [7].

Two independent NMR spectrometers were incorporated in the apparatus. Both operated in frequency scan mode with a maximum scan width of 1% of the operating frequency, and used a constant current series tuned Q meter technique with real part signal measurement [8]. One system operating at 107 MHz was used exclusively for proton polarisation measurements. As the proton signals are large a low filling factor sampling coil was used. The second system operated at 12 MHz with a high filling factor sampling coil, as the nitrogen signals are very much smaller. Multipoint signal averaging was used with both systems to improve the signal to noise ratio.

4. Ammonia samples

Both the ^{14}N and ^{15}N containing materials were prepared using the slow freezing technique described by Meyer et al. [5]. The pieces of crushed solid ammonia were selected to have their largest dimension in the range 2–3 mm. The irradiation was carried out using a liquid nitrogen cooled irradiation facility at the Universities Research Reactor, Warrington, UK. The total

effective dose rate was approximately 7 Mrad h^{-1}, approximately one half of which was due to fission and thermal neutrons, the remainder being gamma radiation. The total dose given was approximately 180 Mrad and this produced materials with excellent polarisation properties, the proton relaxation time being 18 min at a temperature of 1 K in both cases. A sample volume of approximately 1 cm^3 was used for all measurements.

5. NMR measurement technique

The 107 MHz NMR spectrometer was used to measure the proton polarisation with the apparatus operating in either dynamic polarisation or frozen spin modes. It was calibrated using the standard thermal equilibrium signal technique. The statistical error in these measurements was less than $\pm 1\%$ but the overall uncertainty was $\pm 2\%$ at maximum polarisation due to systematic effects in the measurement of system gain and sample temperature at calibration.

The measurement of the ^{14}N polarisation was more complex. The resonance frequency is 7.78 MHz at 2.53 T and because of the quadrupole interaction which occurs with spin 1 nuclei in solids the line is very broad. In this case, as the solid is polycrystalline, the line has a characteristic two component shape with two sharp peaks separated by 2.37 MHz [9]. This combination of the low magnetic moment and large line width leads to very serious signal to noise ratio problems, with the consequence that it is not possible to observe or measure thermal equilibrium signals. Also as the line width is approximately 50% of the resonance frequency it is not possible to observe all of even a highly polarised signal using frequency scan. The method adopted was to use a 100 kHz frequency scan covering only the regions
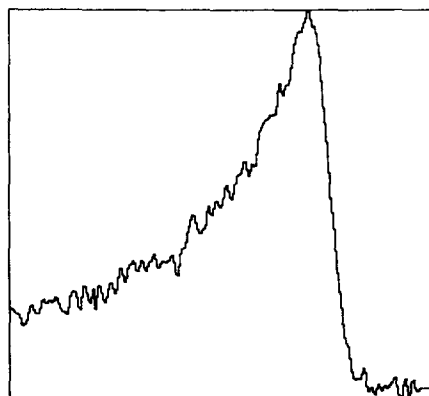

Fig. 1. The observed upper ^{14}N NMR line peak at a nitrogen polarisation of 10%, measured at a centre frequency of 12.17 MHz with 100 kHz scan width and at a field of 3.574 T. This signal was obtained by averaging over 4096 scans.

of the two peaks. A typical single peak signal obtained in this way is shown in fig. 1. This shows no structure and it was therefore assumed that the line shape may be calculated using the dipolar broadening and the peak separation as the only free parameters. The dipolar broadening was calculated by making a fit to the shape of the signal in the region of the peak. The area of the signal was then obtained by combining this result with measurements of the peak heights. To avoid the problems which arise from changes in NMR system gain with frequency, all these measurements were made at the same frequency. This is only possible if the nuclei are in the frozen spin state during the measurement period as it is then necessary to change the field. The frequency chosen should be as high as possible to maximise both the measurement sensitivity and the relaxation times, the upper limit being determined by the maximum available magnetic field. The frequency used was 12.2 MHz which resulted in the peaks being measured at fields of 3.6 and 4.3 T. It was then necessary to make corrections to the observed signal sizes to take account of the variation in measurement sensitivity with field. This system was calibrated using protons with previously measured polarisation and in the frozen spin state, by reducing the field to the value (0.28 T) at which the signal could be observed with the 12.2 MHz NMR system. The uncertainty generated by the fitting and signal reconstruction techniques resulted in a larger overall measurement error than was obtained with the proton measurements.

The ^{15}N nucleus has a resonance frequency of 10.9 MHz at 2.53 T and spin 1/2 so there is no quadrupole line broadening. The observed resonance signal width was 3 kHz and so the polarisation was measured using the standard technique at 10.9 MHz with calibration by the same proton signal transfer technique as described above. In this case the measurement errors were comparable with those obtained with the proton measurements.

6. Experimental results

With the ^{14}N sample the proton polarisation was enhanced to a given value and the microwave power was switched off so that the refrigerator rapidly cooled the sample to below 150 mK. The nitrogen polarisation could then be measured with the nuclei in the frozen spin state. This process was repeated a number of times with different values of both positive and negative polarisation. The data obtained is plotted in fig. 2.

The first stage of the measurement of the thermal mixing time constant was to obtain a high value of proton polarisation. The system was then put into the frozen spin state and the nitrogen polarisation reduced to a low level by RF saturation of the resonance transi-
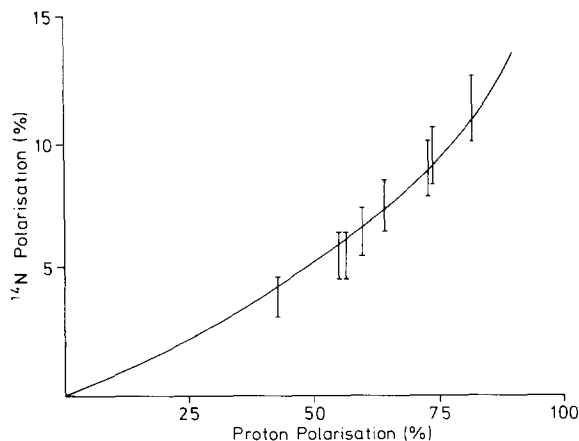

Fig. 2. The measured ^{14}N polarisation as a function of proton polarisation. The curve is the calculated relationship assuming spin temperature equilibrium.

tion. To do this a relatively high level 12.2 MHz voltage was applied to the high filling factor coil and the magnetic field was scanned over the range 3–5 T until there was no observable nitrogen resonance signal. The microwave source, set to the same frequency and power level used for dynamic polarisation, was switched on for a series of measured time intervals. The nitrogen polarisation was measured after each interval. The polarisation recovery was found to be exponential with a time constant of 6.7 min. No detectable growth of the signal was observed in the absence of microwave power and as a consequence the lower limit for this time constant was estimated to be 30 h.

The ^{15}N measurements were much simpler and quicker to make because there was no need to move into the frozen spin mode to measure the polarisation. The
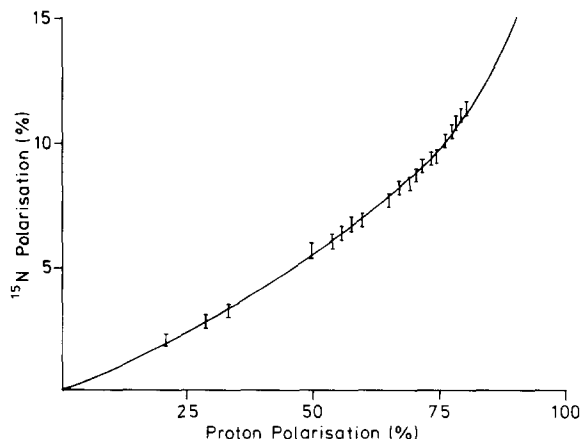

Fig. 3. The measured ^{15}N polarisation as a function of proton polarisation. The curve is the calculated relationship assuming spin temperature equilibrium.
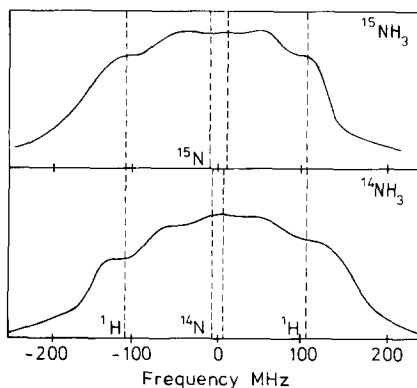
Fig. 4. The observed ESR spectra in irradiated $^{14}NH_3$ and $^{15}NH_3$ at a temperature of 1 K. The measurements were made at a constant frequency of 71 GHz by scanning the magnetic field, but are plotted in terms of frequency. The dashed lines show the positions of the three nuclear resonance frequencies involved relative to the line centre frequency.

data are plotted in fig. 3. The thermal mixing time constant was 6.1 min. The characteristic time associated with proton polarisation growth was measured to have a minimum value of 20 min, and this combined with the good agreement between the static nitrogen polarisation values and theory confirms the existence of spin temperature equilibrium. This implies a relatively strong coupling between the two nuclear spin systems, which is reasonable since the measured ESR line width, as shown in fig. 4, is sufficiently large to give considerable overlap between the nuclear Zeeman and the electronic non-Zeeman spectra.

It may be concluded, that in a dynamically polarised target using ammonia made with either ^{14}N or ^{15}N, which is operating under standard conditions at a field of 2.5 T, the nitrogen polarisation is calculable from the measured proton polarisation. It should be noted that with higher operating fields this may not be true as the ESR line width is likely to remain constant while the

nuclear resonance frequency will increase with field, leading at some point to the situation where there is no spectral overlap. It has also been demonstrated that if the presence of nitrogen polarisation causes serious experimental problems, then with targets operating in the frozen spin mode, it may be reduced to a very low level by RF saturation of its resonance transition, with negligible effect on the proton polarisation.

Acknowledgments

References

[1] A. Abragam and M. Goldman, Nuclear Magnetism Order and Disorder (Oxford University Press, London, 1982) ch. 6 and references therein.
[2] M. Borghini and K. Scheffler, Phys. Rev. Lett. 26 (1971) 1362.
[3] M. Borghini and F. Udo, Phys. Lett. 43A (1973) 93.
[4] W. De Boer, M. Borghini, K. Morimoto, T.O. Niinikoski and F. Udo, J. Low Temp. Phys. 15 (1974) 249.
[5] W. Meyer et al., Nucl. Instr. and Meth. 227 (1984) 35.
[6] G.R. Court, P. Harrison and W.G. Heyes, Proc. 4th Int. Workshop on Polarised Target Materials and Techniques (1984) Universität Bonn Physikalisches Institut, p. 122.
[7] T.O. Niinikoski and J.M. Rieubland, Phys. Lett. 72A (1979) 141.
[8] D. Gifford, Proc. 2nd Int. Workshop on Polarised Target Materials (1979) Rutherford Laboratory, RL-80-080, p. 85.
[9] J.M. Lehn and J.P. Kintzinger, Nitrogen NMR, eds., M. Witanowski and G.A. Webb (Plenum, New York, 1973) p. 80.