Molecular motion in some solid hydrocarbons

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Résumé.

Les auteurs ont déterminé jusqu'à des températures aussi basses que 20° K la variation avec la température de la forme de la raie d'absorption des protons en résonance magnétique nucléaire du pentane normal, de l'hexane normal, de l'octane normal et du cyclopentène.

Pour les trois paraffines, on voit que la réorientation des groupes méthyl se produit dans tout l'intervalle de température étudié.

Dans le cas du cyclopentène, on a établi la nature non planaire de la molécule et montré que la réorientation moléculaire se produit au-dessus de 85° K. Un processus de self-diffusion a été mis clairement en évidence juste au-dessous du point de fusion.

On donne également des résultats préliminaires du temps de relaxation spin réseau de l'octane normal jusqu'à 20° K.

Abstract.

The variation with temperature of the nuclear magnetic resonance absorption line-shapes for *n*-pentane, *n*-hexane, *n*-octane and cyclo-pentene have been measured down to 20° K. For the three paraffins it appears that methyl group reorientation occurs over the whole temperature range. In the case of cyclo-pentene, the non-planar nature of the molecule is established and molecular reorientation is shown to occur above 85° K. Strong evidence is also found for a self-diffusion process just below the melting point.

Preliminary measurements of the spin-lattice relaxation times for *n*-octane down to 20° K are also reported.

1. Introduction.

The measurements reported are part of a series of investigations into the nuclear magnetic resonance absorption line-shapes and spin-lattice relaxation times of hydrocarbons carried out in this laboratory. The apparatus consists of a twin-T bridge followed by a radio-frequency amplifier, commercial receiver and phase-sensitive detector. The magnetic field of 5260 oersted is provided by a large permanent magnet. A cryostat

enables temperatures from 20° K upwards to be maintained. (Lawrenson and Rushworth, 1958.)

2. N-PENTANE, N-HEXANE AND N-OCTANE.

Measurements of the absorption spectra and spin-lattice relaxation times for n-pentane and n-hexane at temperatures from 70° K to the melting points have been reported previously (Rushworth, 1954). The second moments of the absorption spectra were found to be smaller than the calculated values for rigid lattices over this temperature range, and these reduced values were explained on the basis of reorientation of the methyl groups about the end C-C axes. Measurements of the absorption spectra have now been extended down to liquid hydrogen temperatures, and at 20° K the second moments of the absorption line for n-pentane was found to be 21.2 ± 0.6 gauss^2 and for n-hexane 21.4 ± 0.8 gauss^2. These values are larger than those found at 120° K, as might be expected due to normal lattice contraction, but are still some 12 gauss^2 less than the theoretical rigid lattice values. This suggests that reorientation of the methyl groups is still occurring even at 20° K.

The spin-lattice relaxation times in this lower temperature range have not yet been measured, but in view of the interesting T_1 variation for n-octane reported below it is hoped to make these measurements.

Since it appeared that reorientation in n-pentane and n-hexane still occurred at 20° K, it was thought that an investigation of the higher homologue n-octane would be of interest. The higher melting point gives a greater temperature range in the solid state, with presumably more chance of the motion being frozen out at the lowest temperatures currently available. The second moments of the absorption line for n-octane at 20° K, 90° K and 120° K are shown in table 1 together with the corresponding values for n-pentane and n-hexane.

TABLE 1.

Second moment values in gauss^2.

(The uncertainties have been omitted for clarity.)

	20° K	Experimental 90° K	120° K	Calculated 120° K
n-pentane	21.2	18.6	16.7	31
n-hexane	21.4	19.4	18.8	31
n-octane	21.4	20.5	18.8	30

As will be seen from the table, the experimental second moment of n-octane at 120° K is 11.2 gauss^2 smaller than the rigid lattice value. Some type of reorientation is therefore occurring and must still be taking place at 20° K.

The calculation of the rigid lattice second moment for n-octane follows the lines of the calculation for n-pentane and n-hexane (Rushworth, 1954). The intramolecular contribution is 20.4 gauss^2 and the same estimation of 9.6 gauss^2 for the intermolecular contribution was used. This was calculated by Andrew and Eades (1953) for n-hexane and should be reasonably correct for n-octane since their method becomes more accurate the longer the molecule.

Reorientation of the n-octane molecule about its long axis reduces the intramolecular contribution by 14.9 gauss^2, which is greater than the total reduction to be explained. Since the intermolecular contribution will also be reduced, this type of motion appears improbable. Methyl group reorientation is again the most likely cause of the narrowing. This motion reduces the intramolecular contribution by 6.4 gauss^2 to 14.0 gauss^2, and it seems reasonable for the intermolecular contribution to be reduced to 4.8 gauss^2, about half its estimated rigid lattice value. Although only one third of the protons in each molecule are involved in the reorientation process, the methyl group protons of the neighbouring molecules are in very close proximity to each other and so will represent an appreciable part of the rigid 9.6 gauss^2.

The spin-lattice relaxation time for n-octane was measured from 20° K to 90° K and affords additional information about the relaxation process. As the temperature was lowered from 90° K, the relaxation time increased sharply but at 70° K the curve began to flatten out and the relaxation time remained relatively constant down to 20° K. These measurements were difficult to make and it is planned to repeat them in a series of T_1 measurements for all three paraffins. These preliminary results, however, show that above 70° K the T_1 variation follows the normal pattern and can be connected with a single correlation time τ_c according to the picture first proposed by Bloembergen, Purcell and Pound (1948). Assuming a Boltzmann distribution in the population and a barrier height of V_0, then, as in the cases of n-pentane and n-hexane, a plot of log T_1 against $1/T$ should be a straight line. This is found to be the case, and from a least squares analysis of the slope the barrier height V_0 is found to be 2600 cal per mole. This is in good agreement with barrier heights found for other paraffins.

The relative lack of variation of T_1 between 70° K and 20° K has to be explained from another viewpoint. Powles and Gutowsky (1955) and Das (1957) have compared classical reorientation with quantum mechanical tunnelling. It is shown that whereas the classical reorientation term is strongly dependent on temperature due to the Boltzmann exp $(- 1/T)$ term, the tunnelling term is much less dependent on temperature. As the temperature decreases, therefore, and the upper energy levels become depopulated, the tunnelling term becomes dominant and this may explain the lack of variation with temperature below 70° K. A further analysis will be published elsewhere when the T_1 measurements in all three paraffins are complete.

One useful result from the fact that T_1 does not continue to increase as T decreases is that the onset of saturation is avoided, and absorption curves can be taken. If T_1 continued to increase as T decreased then the permitted r.f. voltage across the coil would soon reach the limit imposed by signal-to-noise considerations.

3. CYCLO-PENTENE.

Measurements of the absorption line-shape of cyclo-pentene have been made from 20° K to the melting point of 138° K. Specific heat data reported by Huffman, Eaton and Oliver (1948) show a specific heat transition at 87° K and another slight anomaly at 54° K which they attributed to the possible release of a frozen-in mode of motion. Provided this motion is fast enough, it should have an effect on the nuclear magnetic resonance line-shape, as also should the much larger transition at 87° K.

The mean experimental second moment at 20° K is 19.6 ± 0.25 gauss^2 and remains effectively constant up to 85° K, apart from a small gradual change attributable to thermal expansion of the lattice. The second moment then falls gradually to a value of 7.6 ± 0.2 gauss^2 at 110° K, remains constant for about 14° K and then undergoes a rapid narrowing until at 128° K, 10° below the melting point, the experimental second moment is smaller than the value due to field inhomogeneity.

The crystal structure of cyclo-pentene is not known, but two molecular models have been discussed by Beckett, Freeman and Pitzer (1948). One model has a planar carbon skeleton and the other model a non-planar skeleton, with one carbon atom out of the plane of the other four by 0.3 A. The intramolecular contribution to the second moment for the planar

model is 12.9 gauss² and for the non-planar model 13.0 gauss². This leaves about 6.6 gauss² for the intermolecular contribution, which seems reasonable on comparison with estimations made for similar hydrocarbons. The lattice is therefore rigid below 85° K and there is no change of line-width or second moment at 54° K corresponding to the anomalous effect mentioned above.

An explanation of the second moment value of 7.6 ± 0.2 gauss² from 110° K to 124° K has to be looked for on the basis of reorientation of the molecule about an axis perpendicular to the plane containing five (or four) carbon atoms. Calculations show that in the planar case, the intramolecular contribution is only reduced from 12.9 gauss² to 9.4 gauss². The dominant contribution comes from the individual methylene groups, and as these interproton vectors are parallel to the axis of rotation there is no reduction in their contribution to the second moment. The planar model cannot explain the results since the reduced intra-molecular contribution alone is greater than the total reduced experimental second moment. Motion about the diad axis is also found to give insufficient reduction. In the non-planar case the reduced intramolecular contribution is 6.7 gauss². Comparison with intermolecular contributions to the second moments of other substances when motion is occurring leads to a rough value of 1.6 gauss² for this part. The total reduced second moment of 8.3 gauss² is subject to a large uncertainty, but is in much better agreement with the experimental value than in the planar case. We are thus enabled to distinguish between the two molecular models in favour of the non-planar one.

The further reduction in second moment at 128° K can only be explained by introducing a more random motion. Free spherical rotation of the molecules would reduce the second moment to about 1 gauss², and so we must assume a self-diffusion process similar to that discussed by Andrew (1954). This motion below the melting point is not, however, reflected in the heat of melting, which is about 7 times the heat of transition. In the case of cyclo-pentane (Rushworth, 1954) a similar type of motion occurred but in this instance the heat of melting is considerably smaller than the heat of transition.

REFERENCES

ANDREW, E. R. (1954), *Report of the Conference on Defects in Crystalline Solids* (London: Physical Society).
—— and R. G. EADES (1953), *Proc. Roy. Soc., A 216,* 398.

BECKETT, C. W., N. K. FREEMAN and K. S. PITZER (1948), *J. Amer, Chem. Soc.*, *70*, 4227.

BLOEMBERGEN, N., E. M. PURCELL and R. V. POUND (1948), *Phys. Rev.*, *73*, 679.

DAS, T. P. (1957), *J. Chem. Phys.*, *27*, 763.

HUFFMAN, H. M., M. EATON and C. D. OLIVER (1948), *J. Amer. Chem. Soc.*, *70*, 2911.

LAWRENSON, I. J. and F. A. RUSHWORTH (1958), *Proc. Phys. Soc.*, *72*, 791.

POWLES, J. G. and H. S. GUTOWSKY (1955), *J. Chem. Phys.*, *23*, 1692.

RUSHWORTH, F. A. (1954), *Proc. Roy. Soc.*, *A 222*, 526.