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Spin-lattice relaxation measurements and spin conversion in methane below 1 K (*)

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Résumé. — La conversion de spin résonnante sur les sites ordonnés de CH_4 a été observée et contrôlée par l'évolution de T_1 avec le temps. L'accroissement de l'écart entre les niveaux A et F, à basse concentration P_F d'espèce F, a été vérifié. La conversion résonnante $E \rightarrow F$, pour la première fois observée, a fourni une valeur de l'écart $E \rightarrow F$. La dépendance de T_1 avec la température à P_F fixée a été suivie jusqu'à 80 mK, pour P_F comprise entre 9×10^{-4} et 2×10^{-2} .

Abstract. — Resonant spin conversion on the ordered sites has been observed in CH_4 through the time dependence of T_1 at 0.18 K. The increase in the A-F level splitting at low F-species concentration P_F has been confirmed. Resonant $E \rightarrow F$ conversion has given a direct measurement of the $E \rightarrow F$ level splitting. T_1 at fixed P_F has been measured as a function of temperature to 80 mK for $9 \times 10^{-4} < P_F < 2 \times 10^{-2}$.

1. Introduction. — Solid CH_4 in phase II, below 20.4 K, has two kinds of orientational sites : One fourth are almost free rotor sites of symmetry O_h (FR), while on the remaining sites, of symmetry D_{2d} , the molecules oscillate about fixed orientations (OM). After cooling to helium temperatures, the FR molecules relax relatively quickly (in a few hours) to their ground state of symmetry A (rotational quantum number $J = 0$, total nuclear spin $I = 2$), since the first excited FR state ($J = 1$, $I = 1$) is at 12 K [1] and transitions between these states ($\equiv$ spin conversion) are sufficiently fast [2]. According to the extended James and Keenan model (EJK) [3], the ground torsional manifold of the OM is split into three levels : a five-fold degenerate ground level of symmetry A ($\bar{A}_2$ B) and spin $I = 2$, a F level of spin $I = 1$ which in turn is very slightly split into $\bar{F}_1$ A_2 and $\bar{F}_1$ E with degeneracies 3 and 6 respectively and a doubly degenerate E level with zero spin (¹). Transitions between these levels (intrinsic spin conversion) are much slower than for the FR [4] and it is therefore not easy to study pure CH_4 in thermal equilibrium below 4 K.

Paramagnetic impurities are able to induce spin conversion through their magnetic field gradient.

Resonant conversion has been shown to occur between F and A levels of the OM if the Zeeman energy of the impurities in an applied magnetic field H equals the torsional level splitting $\Delta_{AF} = E_F - E_A$. Conversion rate measurements as a function of H then yield direct information on Δ_{AF} as well as on the level widths. Such measurements have been reported [5] for CH_4 with a F-species population (P_F) corresponding to a temperature between 1 K and 4 K. The result ($\Delta_{AF}/k_B = 1.7$ K) was in good agreement with inelastic neutron scattering on equilibrium CH_4 at 4.2 K [1] which gave $\Delta_{AF}/k_B = 1.66$ K.

In the present letter, we report measurements on Δ_{AF} down to very small P_F ($\geq 5 \times 10^{-4}$), corresponding to an equilibrium at 0.25 K. The EJK model predicts a weakening of the molecular field as a result of the depopulation of the F-species. This leads to an increase in Δ_{AF} [3]. Such an increase has been inferred from specific heat measurements [6] and, very recently, its onset has been observed directly by neutron scattering [7] on equilibrium CH_4 down to 1 K. We also report observation of the resonant conversion of the E-species, which enabled us to measure the splitting Δ_{FE} .

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(¹) We have found it convenient to use F instead of T for the three-dimensional representation of the group T_d , in order to avoid an overuse of the letter T (temperature, relaxation time, symmetry).

2. The paramagnetic impurities. — Oxygen is always present as an impurity in methane but the properties of small quantities of O_2 in CH_4 (clustering, energy levels, etc...) are not well known [8, 9] ; further-

more the conversion mechanism due to O_2 [4] is not understood. It may be worth mentioning that we have induced spin conversion in three samples of CH_4 , containing 50, 300 and 1 200 ppm O_2 (the concentration of O_2 is measured around the solidification point, following the method developed in [10]). In all three cases, the spin-lattice relaxation became strongly non exponential. A possible explanation would be a macroscopic concentration gradient for O_2 in the solid, leading to different conversion rate in different parts of the sample. For the above reasons, our measurements were done on a sample containing CH_3 and $H^\bullet$ radicals created by γ -irradiation at 4.2 K (15 Mrad., Co^{60}). The radical concentration (800 ppm, if we extrapolate the figures known for CD_4 [11]) was sufficient for their influence to be dominant over that of the 50 ppm O_2 impurities found in the liquid sample before irradiation.

3. Spin-lattice relaxation. — In order to follow the conversion to very low concentrations P_F , the proton spin-lattice relaxation T_1 can be used. T_1 depends strongly on P_F , since the A-species are not coupled directly to the lattice by $\mathcal{H}_{intra}^d$ and relax *via* the F-species [12]. We can thus write, in terms of specific heat or in terms of populations

$$(T_1)^{-1} = (T_1^F)^{-1} (C_F / (C_A + C_F)) \quad (1)$$

$$= (T_1^F)^{-1} (P_F / (3 P_A + P_F))$$

where T_1^F is the relaxation time of an F-molecule. The above model, with a constant T_1^F , seemed to work quite well down to 1 K, i.e. for not too low lattice temperatures and appreciable F-concentrations. It is then straightforward to extract P_F from the T_1 measurements.

For low P_F , we may still keep the model of equation (1), but T_1^F can be expected to depend both on lattice temperature and on P_F :

$$T_1^F = f(P_F, T). \quad (2)$$

This is confirmed by experiment. Temperature dependent relaxation times T_1 have been found previously between 0.1 K and 0.5 K by Vinegar [13] for different samples of CH_4 with, probably, different degrees of conversion. We have initiated a systematic study of the temperature dependence of T_1 as a function of P_F . This can be done in the following way: A given P_F is obtained in a few hours by resonant conversion. The d.c. field is then shifted far away from resonance, where conversion is negligible during the time necessary to measure T_1 as a function of temperature. Figure 1 shows the results, which lead to the following qualitative conclusions: the temperature dependence of T_1 and, through equation (1) of T_1^F , is weak at high P_F and becomes stronger with decreasing P_F . At the same time, our measurements reveal a dependence of T_1^F on P_F . To obtain a rough value of P_F given in figure 1 for each run, we have measured

Fig. 1. — Spin-lattice relaxation time T_1 as a function of inverse temperature for several concentration of F-species; magnetic field fixed at 5.3 kG far from resonance. The equilibrium T_{1eq} is shown.

T_1 at thermal equilibrium down to 250 mK ($T_{1eq} \sim 1700$ s was reached in several days); a smooth curve through the experimental values is shown in figure 1. At the points of intersection, P_F is known from the Boltzmann distribution

$$P_F / P_A = 9/5 \exp(-\Delta_{AF}/T);$$

$\Delta_{AF}(P_F)$ is approximated according to [3]. The dependence of T_1^F on P_F is weak at 470 mK becoming stronger with decreasing temperature. At 80 mK, T_1^F increases by a factor of 5 when P_F varies from about 2×10^{-2} to 9×10^{-4} .

The data seem to suggest the existence of two relaxation mechanisms: i) Temperature dependent relaxation of isolated F-molecules and ii) concentration dependent and temperature independent relaxation within clusters of F-molecules (adiabatic molecular reorientation [12]). The first is dominant at high temperatures and low P_F while the second dominates for the opposite conditions. (We neglect throughout the contribution to T_1 of the paramagnetic impurities. It decreases exponentially with T as $\exp(-\mu H/kT)$ and can thus safely be neglected at the temperatures and fields used in our measurements).

4. Resonant conversion $F \rightarrow A$. — Starting from thermal equilibrium at 1.2 K, the CH_4 sample is cooled in a few minutes to 180 mK and, at $t = 0$,

the magnetic field is set at a fixed value close to the value for resonant conversion. The time dependence of T_1 is then monitored, either by standard pulse techniques ($\pi/2 - \tau - \pi/2$) for short T_1 or by saturation-recovery with a low-level Q -meter, more convenient for long T_1 . Figure 2 shows three runs at different fields. Two behaviours can be distinguished.

Fig. 2. — Resonant conversion $F \rightarrow A$: spin-lattice relaxation time T_1 versus time spent in a given field ; lattice temperature fixed at 180 mK ; initial condition : equilibrium at 1.2 K at $t = 0$.

At short times (T_1 a few seconds, P_F a few percent), T_1 varies approximately as $t^{3/8}$. This behaviour may be understood in the following way. The dipolar field gradient responsible for conversion varies as r^{-4} , where r is the distance from the impurity. The conversion rate thus varies as r^{-8} . Integration over the whole sample, with a one centre model, leads to a $t^{3/8}$ dependence of P_F [13]. An analogous calculation applies for nuclear relaxation by fixed paramagnetic impurities in absence of spin diffusion [14]. In the derivation of the $t^{3/8}$ law for conversion, the absence of diffusion among tunnelling states (conversion diffusion) is assumed. It should be noted however that an inhomogeneity of conversion on a scale of the mean distance R between the paramagnetic impurities ($R \approx C^{1/3} \approx 10$ lattice spacings) does not lead to a non exponential nuclear relaxation, T_1 is long compared to the spin-diffusion time over the distance R , but not the conversion time. If one neglects the weak P_F dependence of $T_1^F(3P_A + P_F)$, T_1 should increase as $t^{3/8}$. This dependence has already been observed for resonant conversion at 1.2 K [15] and it seems to account for the evolution at 180 mK up to $T_1 \approx 3$ s. This would mean that conversion diffusion is negligible during the first hour, in contradiction with theoretical estimates [4]. Later, T_1 increases faster, like t^α with $\alpha \gtrsim 2$. This is partly due to the dependence of T_1^F on P_F . The increase of Δ_{AF} with decreasing P_F is clearly demonstrated by the cross-over of the $T_1(t)$ curves at different fields. In figure 3, the times t_{T_1} needed to reach a given T_1 is plotted as a function of field

(i.e. Zeeman energy of the impurity), showing again an increase of 6% in Δ_{AF} for P_F decreasing from 10^{-1} to 9×10^{-4} .

Fig. 3. — $F \rightarrow A$ resonance curve : time required to reach a spin-lattice relaxation time T_1 equal to 1.5 s (●) and 500 s (○) versus field (kG) and corresponding energy (K) ; the shift corresponds to an increase of the splitting $F-A$ during the conversion.

In order to determine the equation of evolution $P_F(t)$ from the measured $T_1(t)$, one needs to know the importance of conversion diffusion. If it is fast and therefore the sample homogeneous it is sufficient to know Δ_{AF} as a function of T for equilibrium CH_4 and, from there, T_1^F as a function of both T and P_F . One is then able to infer P_F from a measured T_1 through equation (1). If, on the other hand, conversion diffusion is slow, as seems to be the case at the beginning of conversion, equation (1) is meaningless since the resonant conversion speed is locally P_F -dependent through $\Delta_{AF}(P_F)$.

5. Resonant $E \rightarrow F$ conversion. — Although the E-species have zero nuclear spin, it is possible to observe resonant conversion $E \rightarrow F$ by T_1 measurements in the following way : A sample is cooled from thermal equilibrium at 1.2 K to 180 mK and left at this temperature in a field of 13.5 kG in order to induce the $F \rightarrow A$ resonant conversion. After 15 hours, the F level is almost empty ($T_1 \approx 500$ s), but we still have the high temperature population in the E level. If the field is now quickly shifted to 7 kG, resonant $E \rightarrow F$ conversion sets in which fills up the F level. This is seen by a spectacular drop in T_1 as seen on a typical curve in figure 4. At the beginning, it is difficult to measure T_1 since its rate of change $dT_1/dt \gg 1$. After one hour the variation is much slower and T_1 much shorter. Figure 5 shows the field dependence of $d(\log T_1)/dt$, which is a (non linear) measure of the conversion speed $E \rightarrow F$. The pronounced peak

Fig. 4. — Resonant conversion E → F : spin-lattice relaxation time T versus time spent at 6.7 kG ; at $t = 0$ the F levels are nearly empty ; lattice temperature fixed at 180 mK.

corresponds to a level splitting $\Delta_{EF}/k = 0.96$ K in good agreement with neutron scattering results [1] ($\Delta_{EF}/k = 0.85$ K), specific heat measurements [6] (0.94 K) and with calculations based on the EJK model [3] which lead to a splitting varying from $\Delta_{EF}/k = 0.94$ K for equilibrium populations at 4 K to $\Delta_{EF}/k = 1.14$ K at absolute zero.

6. Conclusion. — We have been able to convert CH_4 close to its ground state by resonant conversion with paramagnetic impurities. The field dependence of the conversion speed gives a measure of the tunnelling splittings Δ_{AF} and Δ_{FE} . Δ_{AF} has been found to increase slightly with decreasing F-concentration, in agreement

Fig. 5. — E → F resonance curve : E → F conversion rate $\Delta \log T_1 / \Delta t$ versus field (kG) and corresponding energy (K) in a linear approximation as it is shown on figure 4 ; the peak is centred around 0.96 mK.

with an earlier molecular field model calculation. These results clearly show for the first time that phase II in CH_4 is stable to ~ 100 mK and for a F-concentration of $\sim 9 \times 10^{-4}$.

Apart from being a convenient and sensitive tool to monitor spin-conversion, T_1 is interesting by itself. The knowledge of its temperature and concentration dependence is an important step towards the understanding of the molecular dynamics in CH_4 at low temperatures.

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