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NMR Study of the FEP Film Covering a Maser Cavity

Correlation Between the Maser Behaviour and the Dynamic Parameters of the Film as a Function of Temperature

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SUMMARY :

NMR techniques have been used to characterize the transitions with temperature of a very thin film of a copolymer FEP wich had covered the walls of a maser cavity. Several points on the frequency-temperature chart have been obtained from a study of the temperature variation of the second moment and of the relaxation times T1 and T1ρ. They confirm that the transitions observed in the temperature dependence of the factors which control the maser stability are associated to very low frequency molecular motions.

INTRODUCTION

The stability in frequency of a hydrogen maser requires to minimize the interactions between the hydrogen atoms and the cavity walls. This can be achieved using a quartz cavity covered with a thin film of a non hydrogenated polymer such as polytetrafluoroethylene (PTFE)or its copolymers with hexafluoroisopropylene (FEP).

ZITZEWITZ and RAMSEY (1971) have first studied the temperature dependence of the frequency shift of such a maser. Their initial goal was to find a point where the mean dephasing of the magnetic moment of the hydrogen atoms due to their collision with the wall becomes equal to zero. Their results have revealed breaks in the slope of the temperature dependence of this mean dephasing at temperature generally associated with the α, β and γ relaxations of the material covering the cavity walls (PTFE 42 and FEP 120).

A more elaborate study of the interaction between the hydrogen atoms and the cavity walls of a maser covered with a FEP 120 film has been recently performed by DESAINTFUSCIEN et al. (1977). Not only the mean phase change per collision ($\Delta\phi$) but also the probability of escape of an atom during a collision and the rates of longitudinal and transverse relaxation of the proton spin have been measured between 77K and 373K.

The two breaks observed in the temperature dependence of $\Delta\phi$ (Figure 1) have been correlated, the first (at 296K) with a break found in the variation of the probability of escape versus temperature, the second (at 202K) with a break observed in the variation of the rates of relaxation of the proton spins.

A better understanding of the relation between the structure of the polymer covering the cavity walls and the absorption or relaxation of the hydrogen atoms depends on a precise characterization of the texture and the dynamics of the polymer film. Since FEP, as well as PTFE, is a semi-cristalline polymer, its morphological structure should very much depend on the

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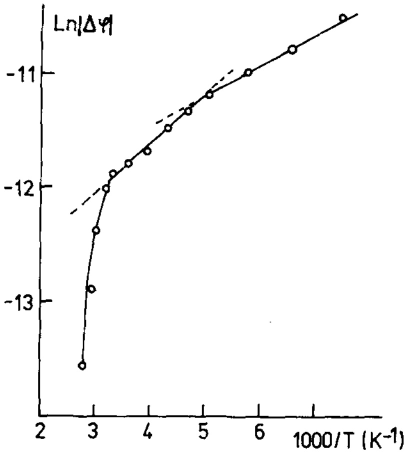

Figure 1 . Mean phase shift of the oscillating hyperfine moment per collision versus 1/T
After DESAINTFUSCIEN et al.(1977)

preparation and thermal history. The properties of a very thin film (1μ) may differ from those of a bulk sample. It is therefore important to directly characterize the thin film, peeled off the cavity walls. Due to the high magnetic moment of the fluorine atom, nuclear magnetic resonance is an efficient technique for the study of such a film. The simultaneous measurement of the second moment of the line shape, of the longitudinal relaxation time T1 and of the relaxation time in the rotating frame $T1\rho$ as a function of temperature provide several points on a relaxation frequency-temperature chart known as transition map. Order of magnitude of the frequencies of motions can then be associated with the temperature of transition in the maser behaviour.

EXPERIMENTAL PROCEDURES AND RESULTS

The film that we have studied has been provided by DESAINTFUSCIEN from the Laboratoire de l'Horloge Atomique at Orsay. It results from the coating of a maser quartz cavity with a FEP emulsion according to a procedure described elsewhere (DESAINTFUSCIEN 1975). It has been peeled off the walls using hydrofluoric acid, degazed under vacuum for 100 hours and sealed. From the Fourier transform of the free induction decay (FID) following a radiofrequency 90° pulse we have obtained, at 500K, a well resolved "high resolution" spectrum from which a 5.2% content in hexafluoropropylene units was determined.

All NMR measurements have been performed with a SXP Bruker spectrometer and a high resolution Varian V 3601 magnet stabilized by a 60 MHz proton external lock, with a corresponding resonance frequency of 56.4 MHz for the ^{19}F nucleus. The FID signal was digitalized using a fast Bruker BC104 converter with a sampling frequency up to 10 MHz and processed on line with a BNC12 Nicolet minicomputer. In all experiments the temperature of the sample was stabilized within ± 1°.

Second Moment

For polymers the evolution of the molecular mobility with temperature results in a decrease of the second moment of the spectral line, generally over a narrow temperature range. In many cases M_2 varies with temperature in several steps of amplitude ΔM_2 corresponding to different types of motions. Notwithstanding the complexity of the molecular motions it is generally possible to associate a motional frequency ν_c at the temperature corresponding to the middle of the step-wise transition in second moment. Following McCALL (1969) an approximate value of ν_c is then given by :

$$2\pi\nu_c = \gamma\,(\Delta M_2)^{1/2} \qquad (1)$$

The temperature dependence of the second moment of the FEP film is shown in Figure 2. At low temperatures (130K<T<230K) an oscillating behaviour of the FID reflects the dominating influence of the dipolar interaction of a small number of spins pairs. In this region of temperatures M_2 has been obtained from a fitting of the FID signal by an even polynomial (degree 14) using the middle of the 90° initiating pulse as zero time (VOLLMERS et al. 1978).

A strong decrease of M_2 is observed about 230K and the FID becomes gaussian up to 320K (region II in Figure 2). For this last temperature M_2 reaches the value 2.55 G^2 calculated by McBRIERTY et al. (1970) for a free rotation of the chain in the crystal. Here, the second moment was determined as before by fitting the FID signal, but also from the width δH at half height of the line obtained by Fourier transforming the FID (for a gaussian line $M_2 = (\delta H)^2/8\mathrm{Log}2$).

At still higher temperature (region III in Figure 2) the FID cannot be fitted by an even polynomial, its shape being intermediate between a gaussian and an exponential. M_2 was approximated in this region assuming a gaussian line shape.

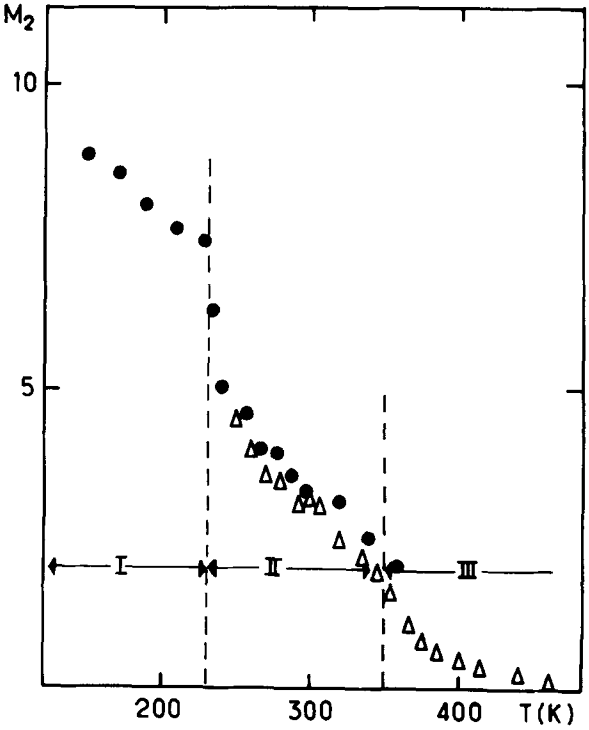

Figure 2. Second Moment (in gauss^2) of the FEP film versus temperature.

The FID is :
-oscillatory in I
-gaussian in II
-nearly exponential in III

● M_2 determined by fitting the FID

Δ M_2 determined on the line obtained by Fourier transforming the FID

Relaxation time T1 and $T1_\rho$

Another evaluation of the temperature dependence of the molecular mobility can be obtained from the measurements of the relaxation times the first, T1, sampling the spectral density at the nuclear resonance frequency ($\omega_0 \sim 10^6 - 10^8$Hz) while $T1\rho$ is sensitive to much slower motion ($\omega_1 \sim 10^3 - 10^4$Hz). The temperature dependence of T1 and $T1\rho$ exhibit generally one or two minima from which is derived the temperature at which motional frequencies become of the order of ω_0 and ω_1. To discuss the values of T1 and $T1\rho$ at the minima and the activation energies associated with the temperature variation of these relaxation times it is necessary to assume a distribution of correlation times τ_c for the motions responsible for relaxation in the polymer. It is well known that the assumption of a single correlation time gives rise to too low *values* of T1 and $T1\rho$ at the minima and to activation energies that are low compared for example with those determined from dielectric studies on the same motion (BUR 1971). However, our central aim is to determine the mean correlation time and, fortunately, the *positions* of T1 and $T1\rho$ minima are fairly insensitive to the presence of distributions in τ_c and therefore we can use, according McCALL (1969), the following relations assuming a single correlation time τ_c :

$$(2\pi\nu_c)\text{T1 min} = \sqrt{2}\,\omega_0 \qquad (2)$$

$$(2\pi\nu_c)\text{T1}\rho\text{min} = \omega_1 \qquad (3)$$

assuming for $T1\rho$ that $H_I^2 >> M_2/3$ (JONES 1966).

The longitudinal relaxation time T1 has been obtained by the classical inversion-recovery sequence 180° - τ - 90°. For data acquisition and on line determination of the relaxation times a home-made computer program has been used.

In the whole temperature range the longitudinal magnetization has been found to decay monoexponentially. The temperature dependence of T1, as given in Figure 3, is very similar to that already observed on FEP (Mc BRIERTY et al. 1970) and also on the amorphous part of PFTE (McCALL et al. 1967) except for the strong rise that we observe at low temperatures which is probably due to the careful elimination of oxygen, made possible by the thinness of our sample. The minimum in T1 is rather broad and reflects the complexity of the molecular motion described by a distribution of correlations times. The value of T1 at the minimum (0.4s at 300K for $\omega_0/2\pi = 56.4$ MHz) is in excellent agreement with the value reported by McBRIERTY (0.2s at 228K for $\omega_0/2\pi = 30$ MHz) taking in account the ratio of the resonance frequencies. It is however much higher than the value 0.09s predicted for the free rotation of the chain around their axes which accounts well for the second moment decrease. A further indication of a distribution of correlation times results for the difference in slopes of the low and high temperature lines of LogT1 versus 1/T with apparent activation energies of 4 and 2 kcal/mole.

The rotating frame relaxation time $T1\rho$ has been measured using a 90° pulse followed by a 90° phase shifted pulse of duration τ of the rf field H_1, for two amplitudes of H_1 : 3 and 9 gauss. The relaxation is monoexponential in the whole temperature range. In their study of FEP and PTFE samples, McBRIERTY et al. (1970) described a relaxation appearing to be the superposition of two exponentials attribued to the amorphous and crystalline parts of the sample. Such a behaviour is not found with our sample.

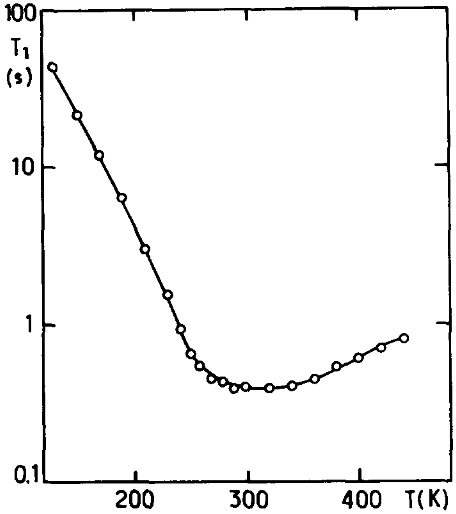

Figure 3 . Experimental value of T1 versus temperature

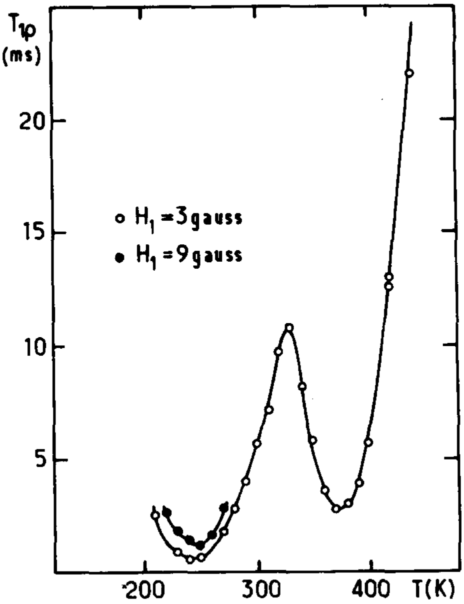

Figure 4 . Experimental values of $T1\rho$ versus temperature for two values of the initiating field H_1

The temperature dependence of $T1\rho$ is given in Figure 4 for the two value of H_1. Two minima are observed ($T1\rho$ = 0.6ms at T ∿ 245K and $T1\rho$ = 2.7ms at T ∿ 370K for H_1 = 3G; $T1\rho$ = 1.1 ms at T ∿ 245K for H_1 = 9G). The presence of two minima is in good agreement with the existence of two steps in the temperature dependence of M_2. The value of the low temperature minimum for H_1 = 3G should not be considered since $H_1 \simeq \sqrt{M_2}$, but the value for H_1 = 9G at 245K is again about five times higher than the value 0.21ms predicted for a free rotation of the chains.

DISCUSSION

As already announced the above results can be used to characterize the temperature dependence of the mean motional frequency ν_c. The second moment decrease can be decomposed in two steps centered at 230K and 350K of respective amplitudes $\Delta M_2 \sim 4G^2$ and $\Delta M_2 \sim 2.5G^2$. One calculates from relation (1) :

$$\nu_c(230K) = 1.27 \times 10^3 Hz \qquad \nu_c(350K) = 1 \times 10^3 Hz$$

From the position of the significant minima in the temperature dependence of the relaxation times, using relations (2) and (3) one gets :

$\nu_c \simeq 8 \times 10^7 Hz$ at 300K from T1
$\nu_c \simeq 5.1 \times 10^4 Hz$ at 245K from $T1\rho$ (H_1 = 9G)
$\nu_c \simeq 1.7 \times 10^4 Hz$ at 370K from $T1\rho$ (H_1 = 3G)

We have plotted the set of values thus obtained on a log ν_c versus 1/T plot (Figure 5) on which have been also plotted -- the log ν_c versus 1/T lines for the β, the cristalline and the γ relaxation of PTFE as deduced from a large number of mechanical, dielectrical, acoustical and NMR measurements (BUR 1972) -- the dotted line (a) obtained from dielectric relaxation measurements on FEP with a 10.7% content in HFP by EBY and WILSON (1962). Our points are in satisfactory agreement with the previous works, especially with the results obtained by EBY and WILSON on the bulk FEP sample. There is a clear difference between the γ relaxation of PTFE and FEP, relaxation associated with the motion of few segments in the non crystalline regions . The activation energies, deduced from the slopes of the lines, are about 18kcal/mole for the "cristalline" and 33kcal/mole for the γ relaxation. They are much higher than the apparent activation energies obtained from the logT1 versus 1/T lines, pointing out once again to the complexity of the spectral density.

If we report on the transition map the temperatures corresponding to a transition in the temperature dependence of the maser parameters (dashed area in Figure 5), we find motional frequencies of the order of 10^{-1} Hz at 296K and 10^2Hz at 202K.

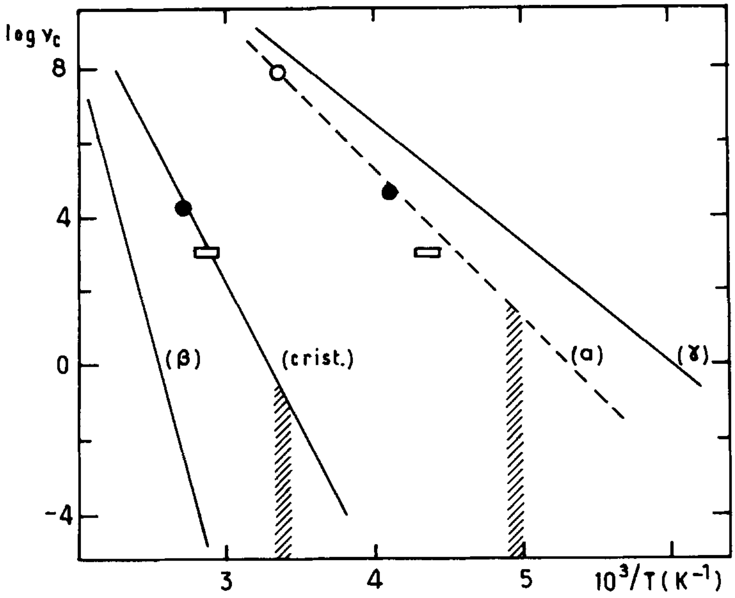

Figure 5 . Polymer transition map.
straight line : mean of other measurements on PTFE (BUR 1972)
dotted line : dielectric measurements on FEP (EBY and WILSON 1972)
o our result from T1 minima
● our results from $T_{1\rho}$ minima
▭ our results from M_2 transitions

The dashed area corresponds to the transitions observed on the maser by DESAINTFUSCIEN (1977).

Although these two transitions correspond to a change in the temperature dependence of two very different physical quantities (relaxation rates of the atomic proton spins at 220K and escape probability of an atom during a collision at 296K) they both are associated to slow molecular motions in the polymer coating the walls of the maser cavity. DESAINTFUSCIEN'S (1975) observation that the interaction between the hydrogen atoms and the walls at T < 202K is typical of an interaction with a rigid solid is in agreement with the fact that at those temperatures the second moment remains practically equal to that calculated for the rigid lattice. If it is difficult to understand the influence of the first slow motions on the relaxation rates of the atomic spins it is easier to imagine that the slow motions appearing at 296K and influencing the escape probability could be linked to an increase hydrogen permeability of the film.

On the other hand, since NMR techniques are sensitive to motions at frequencies in the range 10^4 - 10^9Hz, it is impossible to detect motions associated to β relaxation which should reach this frequency range at temperature of the order of 500K.

CONCLUSION

The use of NMR techniques has made it possible to characterize the molecular motions in the film covering the walls of a maser cavity. The motional frequency - temperature chart,thus obtained,confirm that the breaks in the temperature dependence of the maser parameters are associated with very low frequency molecular motions. Since a shift of these frequencies can eventually be produced by crosslinking of the film and characterized by NMR, these findings can be useful in the design of coatings with improved maser stability at a chosen temperature.

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