

**RECENT NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS IN ROMANIA**  
**-A Felix Bloch Commemorative Lecture\*-**

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If one accepts science as a part of frontier life, that is — as strife and struggle, there seems to be no better and dignified way of paying tribute to pathfinders than talking of plain hard work. At four decades since its discovery, nuclear magnetic resonance spectroscopy is an almost basic tool, a most remarkable one, exceedingly pervasive by now in an astounding variety of fields. It is, perhaps, only its belonging to the high technology realm that hinders an even wider and quicker dissemination of its power in all the many areas of human endeavour where "knowing why" is an irreducible prerequisite of "knowing how."

The discovery by Bloch of magnetic resonance phenomena in 1945 had indeed a great impact on various branches of science like physics, chemistry, life sciences, etc. Today its applications range from fundamental research in physics (materials science, solid state structure, phase transitions, very low temperatures, etc., chemistry (molecular structure, chemical reactions), biology-biophysics (water and ionic diffusion across membranes, drug-membrane interactions, water ordering in biological systems) to many applied fields like the chemical industry — where it became a routine quality control technique, or agriculture (determination of content of oil, water or proteins in seeds and other products) or geology and oil technology (magnetometry, among others). Today one witnesses the penetration of NMR into clinical investigations, as a most fascinating and sophisticated development: the NMR imaging of the depths of the human body.

A glimpse at the whole development of the NMR field can bring us to better understand and properly appreciate the importance of Bloch's brilliant discovery that, in his original papers of

1946, he had called "nuclear induction." It should be stressed that many of the actual NMR achievements that followed over the years were proposed and predicted by Felix Bloch in these papers.

At the beginning of his research activity (Leipzig), he started as a theorist, developing the theory of electron conduction in metals. Later, in the U.S.A., he entered experimental physics, proposing a novel method for measuring the neutron magnetic moment (1936); the relevant experiment was carried out successfully in 1939. In fact, the ideas propelling this experiment induced him into believing that the change in orientation of nuclear magnetic moments should yield a measureable voltage signal in bulk matter. He proved it to be a fact after the war (1945) (1), when the radiofrequency techniques had been brought to an advanced level. In 1946 he published the extended paper on the theory of "nuclear induction" (2), followed by a second one (3), presenting the experimental evidence of the phenomenon.

Typically, Bloch acted as a brilliant theorist who had to grow as an ingenious experimentalist. It is interesting to note that this quality of the "father" of NMR eventually developed into a distinctive pattern of all subsequent important developments in NMR, related to such concepts and methods as spin temperatures, relaxation in solids, slow motions, double resonances, spin echos, multiple pulses, etc.; those who developed theories were eager to, and decisively instrumental in implementing the appropriate experimental approach to both prove them and put them to work.

Back to Bloch's first theoretical paper on NMR, it must be pointed out that, beside giving solution to the equations of the magnetization motion in the presence of the radiofrequency fields, he also recognized the importance of "thermal agitation" and "internuclear interaction" in shaping the NMR signal. In this context he gave a correct qualitative interpretation of the nuclear spin-lattice and spin-spin relaxation times  $T_1$  and  $T_2$  respectively, as characterizing

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the response of the spin system reaching thermal equilibrium. He also devised the phenomenological equations describing the change of magnetization due to relaxation processes. These equations, combined with the equation of motion of nuclear magnetization under the influence of magnetic fields lead to the famous Bloch equations. It is worth noting that such equations proved to describe a wider range of phenomena than NMR. The quantum mechanics calculation of the relaxation process in liquids fully proved the correctness of the relaxation equations introduced by Bloch (in solids only the "longitudinal" equation was confirmed). These theories revealed the connection between  $T_1$ ,  $T_2$  and the molecular motion in liquids and solids.

Determination of the temperature dependence of  $T_1$  and  $T_2$  became a powerful method to investigate molecular motion, thus confirming a prediction of Bloch's in his theoretical paper (1946). It should be noted that, in its conclusive lines, this paper hinted also at other important future developments in NMR, such as access to very low temperatures, the advent of new high precision magnetometers, or the use of paramagnetic impurities.

Bloch made an early observation that the paramagnetic impurities "in small percentage essentially act as catalysts and do not otherwise affect the nucleus under consideration." The full application of this idea, with most positive results, was only recently recognized when the paramagnetic impurities were used to label the intracellular or extracellular water in biological systems. This method, successfully applied in the case of erythrocyte membranes and phospholipid vesicle membrane, made possible the NMR investigation of water transport across the biological membranes and permitted the study of drug effects on membrane permeability or the change of permeability due to pathological alterations of the cells. The dynamic polarization of nuclei — that stands today as a valuable asset in both theoretical and experimental nuclear physics — is also worth highlighting in the fallout of the original recognition by Bloch of the potential importance of paramagnetic ions in a sample.

Today NMR — and all kinds of magnetic resonance techniques for that matter — is an established field, proud of its identity and prominence. Existence of the International Society of Magnetic Resonance — the ISMAR, and of AMPERE — the Atoms et Molecules par Etudes Radio-Electriques — ring the sound of a worldwide community and interaction. Our International Summer School of Magnetic Resonance in Mangalia, Romania (1969), that has grown since

into a series of regular AMPERE schools and colloques held in various countries over the Continent, and also the XVIth Congress AMPERE held in Bucharest (1970) — the first Colloque of this organization to be upgraded to a Congress — convincingly prove its importance.

The beginning of research on magnetic resonance phenomena in our country dates back to 1956 - 1957. A major impetus to this work came from meeting the discoverer of NMR in Princeton during my stay there. At this commemoration of Felix Bloch I must say that I owe much of my enduring involvement with magnetic resonance to meeting him in Princeton, thus getting first-hand insight into the matter, a flavor of how much can be done on it and an opening to how it can be done. His research style and work helped inspire us to establish in this country an active school of magnetic resonance, now endowed with modern labs and gathering fine experts in Bucharest, Cluj, Iassy, Timisoara, not to speak of the commercial facilities available for an increasing number of customers in industry, agriculture, health care, over the country.

It is with all of this in mind that I would like to speak now of some of our current work. I have neither the intention to give here a comprehensive historical appraisal of all our work over the years, nor am I able to cover the whole range of topics and projects under way. Compiling an exhaustive list of references would hardly help the scope of this commemorative lecture either; such lists are available from several review papers and books (4-7), most of them related to our work in Bucharest and Cluj. Because of my belief that NMR is now an established science, I will describe only two topics that I find both relevant and that we are *now* working on. These are (i) nuclear spin-spin and spin-lattice relaxation in  $UF_6$  — an isotope effect investigation; and (ii) nuclear spin-spin and spin-lattice relaxation in 1-X-adamantanes — the molecular dynamics in the vicinity of order-disorder phase transitions.

We shall be dealing, therefore, mainly with results of nuclear spin-lattice relaxation experiments on some molecular crystals. Recall that, as in many other fields, Bloch's and Purcell's ideas regarding the relaxation process in solids have found application in the investigation of molecular motion in this class of compounds. The NMR experiments were essential to determine the motional properties of the plastic phase in molecular crystals and helped in the understanding of the order-disorder phase transition in such compounds.

More recently, interest in such NMR

investigations has increased once high resolution-very cold neutron experiments proved feasible and the theory of structural phase transition was developed for molecular crystals. This trend allowed a comparison of NMR and cold neutron data and a better understanding of the mechanism of molecular motion in different phases of molecular crystals.

### NUCLEAR SPIN-SPIN AND SPIN-LATTICE RELAXATION IN $UF_6$ - AN ISOTROPIC EFFECT INVESTIGATION

Utilization of NMR techniques in order to perform isotopic assays of  $^{235}U$  in the various chemical environments that accompany this relevant isotope all along its intricate path in the nuclear industries has long been seen as a challenge worth study in our labs in Bucharest and Cluj (8-14). The work was naturally targeted on  $UF_6$  - a compound of great importance in the nuclear fuel cycle (15).

Addressing head-on this task can hardly yield results of any practical value: direct detection of  $^{235}U$  by NMR is difficult indeed, due to the low sensitivity of this nucleus -  $2 \times 10^{-5}$  relative to protons at equal magnetic field; it would thus require very high fields and a large data acquisition capability. Direct detection would then appear as a time-consuming, infrastructure-intensive method - a fact that can make it prohibitive for current applications in nuclear technology.

To circumvent this difficulty, we proposed an indirect method that uses the detection of  $^{19}F$ . The presence of  $^{235}U$  is detected through recording changes in the  $^{19}F$  spin-spin relaxation time  $T_2$  that is due to  $^{19}F$ - $^{235}U$  indirect-scalar interactions. Such interactions, modulated by the strong quadrupolar relaxation of  $^{235}U$  leads to an additional relaxation mechanism for  $^{19}F$ . One can expect the effect is stronger in the liquid phase, where the dipolar interactions and the chemical shift anisotropy are reduced.

#### Samples and Experimental Procedure

Samples of uranium hexafluoride with different degrees of  $^{235}U$  enrichment ranging from  $I = 0.005$  to  $I = 0.93$  were obtained from two different sources.

Two sets of samples were supplied by British Nuclear Fuels Ltd. at nuclear purity and one set was prepared in our laboratory. The preparation methods were different for these two sources (10). For the home-made set the procedure kept the concentration of paramagnetic impurities at

the lowest possible level, in order to minimize their effects on  $T_2$  of  $^{19}F$ . The use of three sets of samples allowed us to set an upper limit of the errors introduced by paramagnetic impurities.

The NMR equipment used in this experiment was a variable frequency Bruker pulsed spectrometer (SXP 100). The same spectrometer was used in the FT mode, in order to obtain high resolution spectra of  $^{19}F$ .

The spin-lattice relaxation times  $T_{1Z}$  and  $T_{1D}$  were measured with the usual sequences (16-21):  $[(\pi/2)_0 - \tau - (\pi/2)_0]$  and  $[(\pi/2)_0 - T_2 - (\pi/4)_{90} - \tau - (\pi/4)_{90}]$  - respectively. In the case of liquid samples  $T_2$  was measured using the CPMG sequence (16).

#### Results and Discussion

The isotope effects are clearly observed in the liquid phase of  $UF_6$ . Figure 1 shows the dependence of  $T_2$  on  $^{235}U$  enrichment at differ-

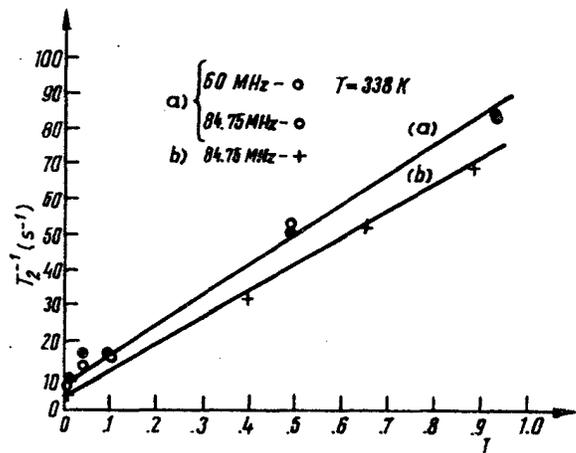


Figure 1.  $^{19}F$  transverse nuclear magnetic relaxation rate ( $T_2^{-1}$ ) versus  $^{235}U$  enrichment in liquid  $UF_6$  at  $T = 338$  K: a) the BMF -samples measured at  $H_0 = 60$  MHz and 84.75 MHz; b) the home-made samples measured at  $H_0 = 84.75$  MHz.

ent temperatures. It should be noted that the relaxation rate  $T_2^{-1}$  at the highest enrichment is about 13 times shorter than that at natural abundance of  $^{235}U$ . The experimental points lie on straight lines, indicating that the spin-spin relaxation time  $T_2$  of  $^{19}F$  depends linearly on

the  $^{235}\text{U}$  enrichment. This dependence was found in all three sets of samples used in the experiment. The relaxation times  $T_2$  measured at two different frequencies were identical within the limit of experimental errors.

These results were confirmed through a complementary approach, by high resolution  $^{19}\text{F}$  spectra in liquid  $\text{UF}_6$ . The spectra show a single line with no fine structure for all samples (Figure

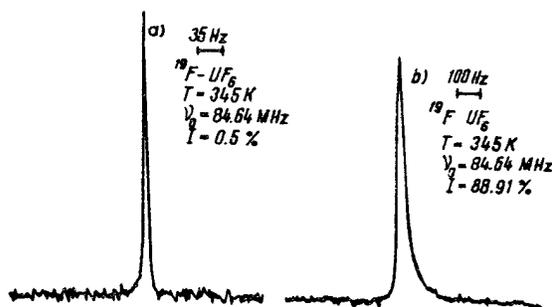


Figure 2.  $^{19}\text{F}$  high resolution NMR spectra in liquid  $\text{UF}_6$  recorded at  $H_0 = 84.63$  MHz and  $T = 345$  K. Spectra (a) and (b) correspond to the samples with the enrichments  $I = 0.007$  and  $I = 0.84$ , respectively.

2). The presence of the  $^{235}\text{U}$  isotope induces only a strong line broadening. At a high enrichment the linewidth reaches a value of 36 Hz, i.e. an increase by a factor of 9 as compared to the linewidth of the natural abundance samples ( $\approx 4$  Hz). The spin-lattice relaxation time  $T_1$  shows a weak dependence on  $I$  (Figure 3a, b) and no significant frequency dependence, even in the case of the highest enrichment.

The spin-lattice relaxation of the Zeeman reservoir ( $T_{1Z}$ ) and of the dipolar reservoir ( $T_{1D}$ ) were measured as a function of temperature and enrichment in the solid phase of  $\text{UF}_6$  (Figure 4a, b). No isotope effect on the relaxation rates was detected. The temperature dependence and the activation energy ( $E_a = 0.71$  eV) found in the solid phase of  $\text{UF}_6$  are in agreement with previous results obtained on natural  $\text{UF}_6$  (22).

### Relaxation Mechanisms

Previous investigations of  $\text{UF}_6$  (at natural abundance of  $^{235}\text{U}$ ) (23) have determined that

the main relaxation mechanism in the liquid phase of this compound is due to the spin-rotational interaction (SR), whereas in the solid phase the chemical shift anisotropy (CS) provides the dominant mechanism. In both cases the dipole-dipole interaction (DD) provides only a negligible contribution.

In these studies the F-U interactions were not taken into account, since  $^{235}\text{U}$  was at very low concentration and  $^{238}\text{U}$  has no magnetic moment.

When  $^{238}\text{U}$  is replaced by  $^{235}\text{U}$ , the nuclear  $^{19}\text{F}$ - $^{235}\text{U}$  indirect-scalar interactions become important and they may create a new relaxation path for  $^{19}\text{F}$ .

For the relaxation rates  $T_L^{-1}$  ( $L = 1, 2$ ) of  $^{19}\text{F}$ -nuclei in liquid  $\text{UF}_6$  we may consider the following equation:

$$T_L^{-1} = (T_L^{-1})_{\text{SR}} + (T_L^{-1})_{\text{CS}} + (T_L^{-1})_{\text{DD}} + (T_L^{-1})_{\text{Q}}$$

$(T_L^{-1})_{\text{Q}}$  accounts for the quadrupole relaxation process and is due to the large quadrupole moment of  $^{235}\text{U}$ .

The first three contributions do not explain the enrichment effect and should be discarded on the following grounds:

- the theoretical predictions for the frequency and temperature dependence of the relaxation rates  $T_1^{-1}$  and  $T_2^{-1}$  (8, 23) as determined by the chemical shift anisotropy or the dipole-dipole interactions are contrary to the experimental data;
- the relaxation through spin-rotational interaction might explain the observed temperature and frequency dependence. However, since the change in the inertial momentum of the  $\text{UF}_6$  molecule is negligible when  $^{235}\text{U}$  replaces  $^{238}\text{U}$ , the relaxation rate due to this mechanism should not change significantly and, therefore, it cannot explain the enrichment dependence.

Since the quadrupole momentum of  $^{235}\text{U}$  is relatively large, any distortion of the  $\text{UF}_6$  molecule leads to a large quadrupole interaction (24). Reorientation of the  $\text{UF}_6$  molecules provides a very strong relaxation mechanism for the  $^{235}\text{U}$  nuclei through their quadrupole interaction with the electric field gradients within the molecules. If  $\tau_{\text{q}}$  is the appropriate correlation time for the reorientation,  $e^2qQ/\hbar$  is the quadrupole coupling constant and  $\eta$  is the asymmetry parameter, then the relaxation times of  $^{235}\text{U}$ -nuclei in the extreme narrowing limit are given by (25):

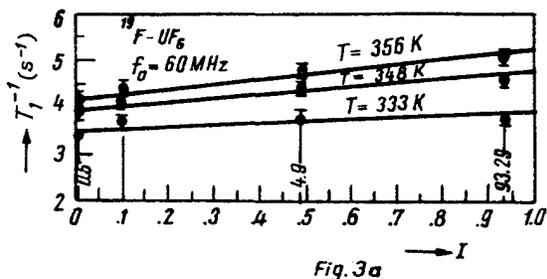


Fig. 3a

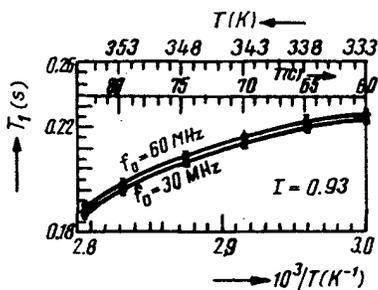


Fig. 3b

Figure 3. a) Longitudinal relaxation rate  $T_1^{-1}$  of  $^{19}\text{F}$  in  $\text{UF}_6$  vs. enrichment at three different temperatures and b)  $T_1^{-1}$  vs.  $T^{-1}$  at two different measuring frequencies for the highest enrichment.

$$T_{LQ}^{-1} = (1/98)(1 + \eta^2/3)(eqQ/h)^2 \tau_q$$

The rapid relaxation of the uranium nuclei induces rapidly fluctuating magnetic fields at the fluorine nuclei sites through the indirect-scalar coupling  $J I \cdot S$ ; this mechanism has been described in (25) as a type II scalar relaxation process. The contributions to the  $^{19}\text{F}$  relaxation rates are:

$$(T_1^{-1})_Q = (21/2)J^2 \frac{T_{1U}}{1 + (\omega_F - \omega_U)^2 T_{1U}^2} \quad (1)$$

$$(T_2^{-1})_Q = (21/4)J^2 \left[ T_{1U} + \frac{T_{1U}}{1 + (\omega_F - \omega_U)^2 T_{1U}^2} \right] \quad (2)$$

As  $\omega_U \ll \omega_F = 5 \times 10^8 \text{ s}^{-1}$  and  $T_{1U}$  is presumably longer than  $10^{-8} \text{ s}$ , the relation  $(\omega_F - \omega_U)^2 T_{1U}^2 \gg 1$  holds and eqns. 1 and 2

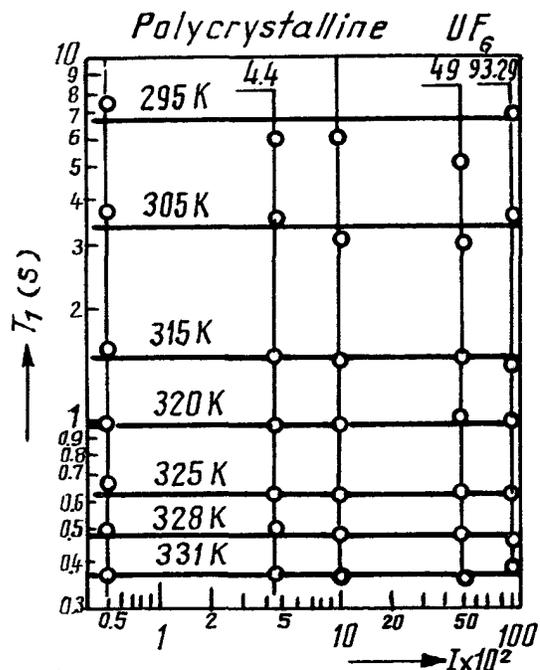


Fig. 4a

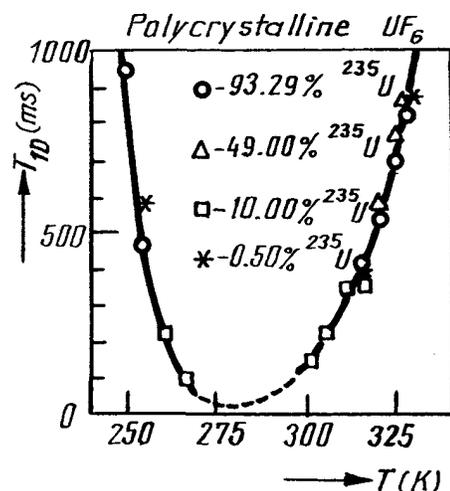


Fig. 4b

Figure 4. a)  $^{19}\text{F}$  longitudinal relaxation time  $T_1$  in solid  $\text{UF}_6$  at 60 MHz and b)  $^{19}\text{F}$  high field dipolar relaxation in solid  $\text{UF}_6$  at 60 MHz as a function of temperature.

have the approximate form:

$$(T_1^{-1})_Q = 0, \quad (3)$$

$$(T_2^{-1})_Q = (1029/2)J^2[(1+\eta^2/3)(eqQ/h)^2]\tau_q^{-1}$$

Eqn. 3 explains why  $T_1^{-1}$  does not depend on the presence of  $^{235}\text{U}$  while  $T_2^{-1}$  depends on it via  $(T_2^{-1})_Q$  contribution. The temperature dependence predicted by eqn. 3 is correct as long as the usual assumption  $\tau_q = \tau_q^0 \exp(E_a/kT)$  is valid. One should note that in the limiting cases  $I = 0$  and  $I = 1$ , the relaxation rates are  $(T_L^{-1})_0 = (T_L^{-1})_{\text{SR}}$  and  $(T_L^{-1})_1 = (T_L^{-1})_{\text{SR}} + (T_L^{-1})_Q$ . These values are obtained from Figure 1 by extrapolation:

$$(T_2^{-1})_0 = 4.2 \text{ s}^{-1} \quad (T_2^{-1})_1 = 78.4 \text{ s}^{-1}$$

For intermediate enrichments  $I = x$ ,  $xN$  molecules will relax with  $(T_L^{-1})_1$  and the others  $(1-x)N$  with  $(T_L^{-1})_0$ . In this case, if there is no intermolecular exchange the decay of  $^{19}\text{F}$ -transverse magnetization should be the sum of two time-dependent exponentials with decay constants  $(T_2^{-1})_0$  and  $(T_2^{-1})_1$  and the FT spectra should be the superposition of two lines with different line broadenings.

For all values of  $I$  we have observed only a single exponential decay and FT spectra do not reveal the superposition of two lines. Consequently, we concluded that in the liquid phase of  $\text{UF}_6$  an intermolecular mechanism spreading magnetic information over the whole nuclear magnetic system should exist. In this case one observes a single exponential decay (a single line in the FT spectrum) with an effective relaxation rate:

$$(T_2^{-1})_{\text{eff}} = (1-I)(T_2^{-1})_{\text{SR}} + I(T_2^{-1})_Q \quad (4)$$

Eqn. 4 gives a reasonable explanation of the linear dependence of the observed relaxation rate  $T_2^{-1}$  on the  $^{235}\text{U}$  enrichment.

Since we found that  $(T_2^{-1})_{\text{SR}} \ll (T_2^{-1})_Q$  from eqn. 4, it follows that for a relatively high enrichment ( $I \geq 0.8$ ),

$$(T_2^{-1})_{\text{eff}} \approx I(T_2^{-1})_Q \sim \tau_q$$

The semilogarithmic plot of  $(T_2^{-1})_{\text{eff}}$  against  $T^{-1}$  at  $I = 0.89$  is linear (Figure 5), with an activation energy  $E_a = 0.072 \text{ eV}$  — a value close to that found in natural  $\text{UF}_6$  (23) using  $T_1$  measurements. This indicates that the quadrupole relaxation of  $^{235}\text{U}$  in liquid phase of  $\text{UF}_6$  involves the same type of molecular collisions

(i.e. the same correlation time) as the spin-rotational mechanism.

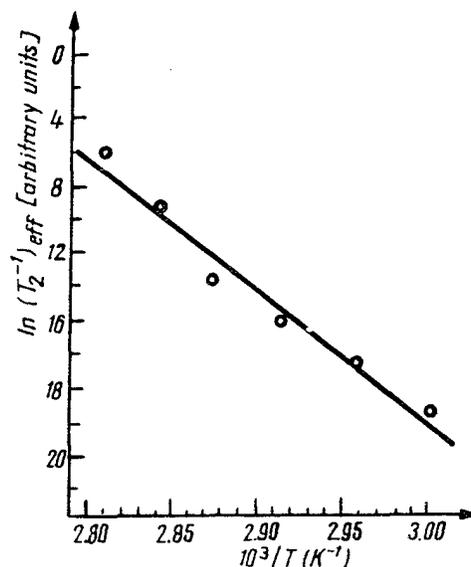


Figure 5. Semilogarithmic plot of the  $(T_2^{-1})_{\text{eff}}$  relaxation rate versus the reciprocal temperature.

tional mechanism.

The quadrupolar mechanism assumed above is confirmed by the high resolution spectra. The nuclear scalar coupling  $^{19}\text{F}$ - $^{235}\text{U}$  should lead to a multiplet structure. In the case of a sample with  $I = 0.89$  the  $^{19}\text{F}$  spectrum should reveal a central line corresponding to molecules with  $^{235}\text{U}$  ( $S = 0$ ) and eight symmetrical satellites of about the same intensity corresponding to the molecule with  $^{235}\text{U}$  ( $S = 7/2$ ). Experimentally this pattern could not be detected, since the rapid fluctuation of  $^{235}\text{U}$ -magnetic moment induced by the strong quadrupolar relaxation leads to the collapse of the multiplet structure, the emerging spectrum being a single broad line (Figure 2).

We note that in similar compounds, such as  $\text{MoF}_6$  and  $\text{WF}_6$  the coupling constant  $J$  is 47 Hz and 44 Hz respectively (26).

Assuming that  $J$  is about the same for  $\text{UF}_6$  too, one can obtain the order of magnitude of  $T_{1U}$  from eqn. 3. Using  $(T_2^{-1})_Q = 78 \text{ s}^{-1}$  and  $J = 47 \text{ Hz}$  one obtains  $T_{1U} \approx 6 \times 10^{-3} \text{ s}$  and  $J T_{1U} = 0.3 < 1$ .

The absence of a narrow line due to the  $^{235}\text{U}$ -molecules suggests again the existence of a

mechanism to convey the magnetic information between  $^{238}\text{U}$  and  $^{235}\text{U}$  molecules. Such a mechanism may be generated either by an intermolecular indirect-scalar interaction F-U, or by an intermolecular atomic exchange. The latter possibility is suggested by the fact that it was observed in compounds of the form  $\text{UR}_4$  (27).

The relaxation rates  $T_{1Z}^{-1}$  and  $T_{1D}^{-1}$  in the solid phase of  $\text{UF}_6$  do not depend on  $^{235}\text{U}$  isotopic abundance (9). The frequency and temperature dependence agrees with previous results on natural  $\text{UF}_6$  (22). The dominant relaxation mechanism is due to the modulation of the anisotropic chemical shift by the molecular reorientations.

NMR spectra and longitudinal relaxation rates of  $^{19}\text{F}$  isotope in saturated vapors of uranium hexafluoride have been measured as a function of  $^{235}\text{U}$  enrichment, temperature and Larmor frequency (13, 14). The linewidth and  $T_1$  values show a pronounced dependence on  $^{235}\text{U}$  enrichment. The temperature dependence of longitudinal relaxation rate in saturated vapors of  $\text{UF}_6$  (0.7%  $^{235}\text{U}$ ) is similar to that of other molecular compounds ( $\text{SF}_6$ ,  $\text{WF}_6$ ,  $\text{MoF}_6$ , etc.). The " $T_1^{-1}/\rho$ " law is not recognized in the case of enriched  $\text{UF}_6$ . This fact, corroborated with the homogeneous broadening of  $^{19}\text{F}$  absorption line in the high temperature domain, proves that  $^{19}\text{F}$ - $^{235}\text{U}$  scalar coupling modulated by time-fluctuating quadrupole interaction of U is the dominant relaxation mechanism.

Summing up the results we arrive at the following conclusions:

- (a) the isotope effect, studied for the first time on  $\text{UF}_6$  follows a linear dependence of the  $^{19}\text{F}$  transverse relaxation rate on the U-enrichment in the liquid phase of  $\text{UF}_6$ ; a similar isotope effect was observed in  $\text{UF}_6$  saturated vapors;
- (b) the frequency and temperature dependence as well as the isotope effect can be explained by taking into account the selective contribution of the quadrupole relaxation of the  $^{235}\text{U}$  nuclei to the relaxation rates  $T_1^{-1}$  and  $T_2^{-1}$  of F-nuclei.
- (c) this contribution is dominant over dipole-dipole and spin-rotational interactions for the transverse relaxation rate. Our data allowed a study of the temperature dependence of the quadrupolar contribution. The activation energy obtained from these data is very close to that found through  $T_1$  measurements in natural  $\text{UF}_6$ . Therefore, we conclude that the quadrupole relaxation of  $^{235}\text{U}$  is generated by the same type of molecular collisions as in the case of the

spin-rotational mechanism;

(d) the high resolution spectra of  $^{19}\text{F}$  show a collapse of the multiplet structure, thus confirming the assumed model;

(e) the existence of a single transverse relaxation rate at different enrichments suggests the presence in the liquid phase of an intermolecular mechanism that spreads magnetic information over the entire system of spins;

(f) under certain conditions (inter alia — availability of a small specialized spectrometer) the isotope effect may be used as a fast NMR method to determine the  $^{235}\text{U}$ -isotopic abundance.

Our current work aims at (i) a fully developed theory of the isotope effect in NMR on gaseous  $\text{UF}_6$  and (ii) establishing whether or not an isotope effect is identifiable in the solid phase of  $\text{UF}_6$ ; to this end, the use of nuclear double resonance is envisaged. These topics, which are potentially relevant for monitoring production and safeguards in some nuclear industries, enjoy also the interest and support of the International Atomic Energy Agency.

#### **NUCLEAR SPIN-SPIN AND SPIN-LATTICE RELAXATION IN 1-X-ADAMANTANES — MOLECULAR DYNAMICS IN THE VICINITY OF ORDER-DISORDER PHASE TRANSITION**

The molecular crystals may be characterized by strong intramolecular forces of covalent nature and weak intermolecular forces. As a consequence, the molecules in crystals behave like rigid bodies executing librations and/or reorientation jumps against the weak intermolecular forces.

For many purposes these forces were successfully described by atom-atom interaction potentials of the exponential-6 type function (28).

Many molecular crystals undergo structural phase transitions. A special class of them are the molecular crystals with a plastic phase. This class has a very low fusion entropy indicating that the crystal has lost a part of ordering already before the melting point. The low fusion entropy is due to the fact that in the plastic phase the crystal is orientationally disordered (i.e. the molecules may occupy several orientations in the crystal).

At lower temperature the plastic crystals undergo a solid-solid phase transition with an orientational ordering of the molecules in the low temperature phase.

The studies of these phase transitions,

undertaken by different methods (X-ray, NMR, neutron diffraction) on some compounds considered as models (adamantane,  $\text{NH}_4\text{Cl}$ ,  $\text{CH}_4$ ) has established that the transition is of a dynamical type. Therefore the investigation of molecular motion above and below the transition temperature is essential in order to describe the mechanism of such transitions.

The great variety of results regarding the properties of plastic phases (e.g. entropy of transition, plastic range) in different compounds could not be reconciled through attempts to relate in an empirical way the measured quantities with the shape and symmetry of free molecules (29, 30). On the other hand, theoretical calculations have shown that such differences as those between adamantane ( $\text{C}_{10}\text{H}_{16}$ ) and hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ), molecules with similar structure and shape, could not be explained only by the variation of atom-atom potentials due to the replacement of C by N (28).

All of these results suggest that, in order to reveal the role played by different factors, a valuable approach is to study a group of similar compounds with slightly different molecular properties — like the molecular symmetry, electric dipole or the nature of the substituent.

In order to provide, through such an approach, some new information about the molecular motion and the order-disorder phase transition, we undertook an NMR investigation of 1-Cl, 1-Br, and 1- $\text{NH}_2$ -adamantanes (31, 32). Their molecular structures are closely related to each other and to that of adamantane ( $T_d$  symmetry). On the other hand, when scanning the above sequence of compounds one notes that some of their properties depart gradually from those of adamantane; thus

- (i) the symmetry is increasingly lower: the first two compounds ( $C_{3v}$  molecules) have only one  $C_3$ -molecular symmetry axis, while the third compound has no molecular symmetry axis at all (Figure 6);
- (ii) the Van der Waals radii are increasingly larger, as well as the electric dipole;
- (iii) the atom-atom potential is gradually changed.

### Experimental Results

The temperature dependence of the proton spin-spin relaxation time ( $T_2$ ), of the spin-lattice relaxation of the Zeeman reservoir ( $T_{1Z}$ ) and of the dipolar reservoir ( $T_{1D}$ ) on powder samples are shown in Figures 7, 8a, b, c.  $T_2$  was defined as the time when the FID signals decay to half of their initial values.

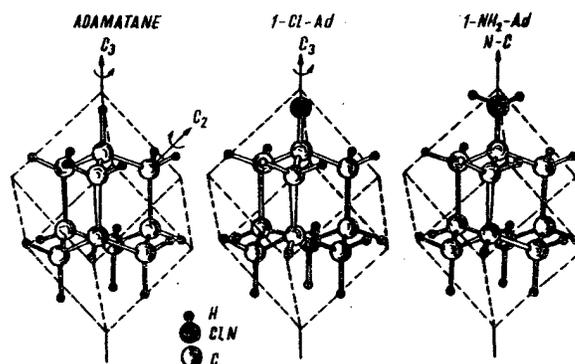


Figure 6. Molecules of adamantane, 1-Cl, 1-Br and 1- $\text{NH}_2$ -adamantanes.

The main results may be summarized as follows:

1. In each of the three compounds there is a certain temperature  $T_1$  where  $T_2$  becomes shorter, indicating a motional line-narrowing process. For 1-Cl and 1-Br-ad, these temperatures coincide with the reported transition temperatures determined by d.s.c. measurements (29).

2. At the same temperatures  $T_{1Z}$  has a strong anomalous decrease (or increase). Below these temperatures, the temperature dependence of  $T_{1Z}$  is of V-type (B.P.P), indicating a relaxation process due to an energy-activated molecular motion. The activation energy and the correlation times were obtained from a least squares fit of experimental data (solid lines in Figure 8) to the usual expression of  $T_{1Z}$ :

$$T_{1Z}^{-1} = C \left[ \frac{\tau_c}{1 + (\omega_0 \tau_c)^2} + \frac{4\tau_c}{1 + 4(\omega_0 \tau_c)^2} \right] = C f(\tau_c) \quad (5)$$

and  $\tau_c = \tau_0 \exp(E_a/kT)$ .

The same procedure was used in the high temperature phase ( $\alpha$ -phase) of 1-Cl-ad which displays a  $T_{1Z}$  minimum in this phase too. 1-Br-ad and 1- $\text{NH}_2$ -ad do not have such a minimum in the  $\alpha$ -phase and no independent information about  $\tau_0$  and C could be obtained if one

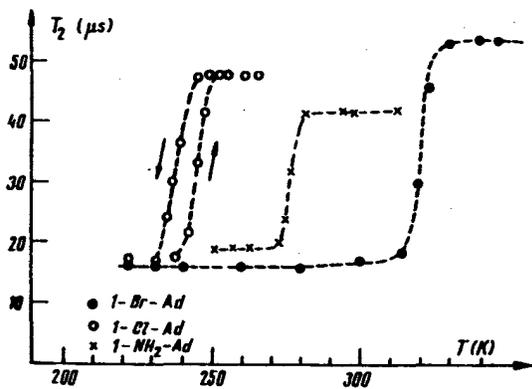


Figure 7. Temperature dependence of  $T_2$ .

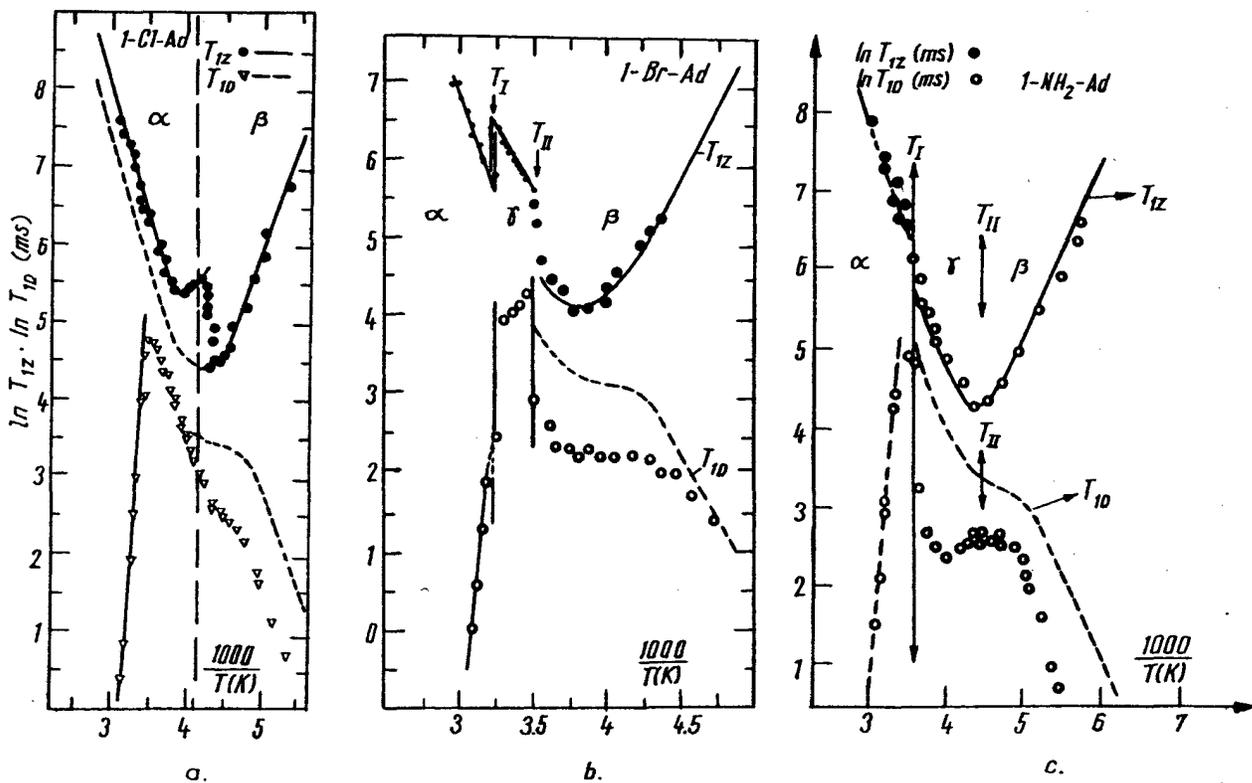


Figure 8. Semilogarithmic plot of  $T_{1X}$  (●) and  $T_{1D}$  (○) versus  $T^{-1}$ . The solid and dashed lines are a least squares fit of eqns. 5 and 6 to experimental data.

TABLE 1

	Ordered $\beta$ -phase		Disordered $\alpha$ -phase					
	$\tau_o$ (s)	$E_a$	$d^*(s)$	$d_o(s)$	$E_a$	$E_D$	$T_m - T_I$	$\Gamma$
1-Br-Ad.	$8 \cdot 10^{-16}$	7.4	$7 \cdot 10^{-3}$	$10^{-21}$	8.5	27	86	3.17
1-Cl-Ad.	$8.3 \cdot 10^{-15}$	6.85	$10 \cdot 10^{-3}$	$10^{-21.8}$	6.85	29	198.3	4.23
1-NH <sub>2</sub> -Ad.	$6.9 \cdot 10^{-15}$	5.4	$27 \cdot 10^{-3}$	$2 \cdot 10^{-18}$	5	23	209	4.6
Adamantane	$10^{-15}$	6.5	$1.6 \cdot 10^4$	$1.6 \cdot 10^{-21}$	3	36	331.4	12

\* Calculated at  $T = 312$  K with p of a f. c. c. structure.

Fusion temperatures  $T_m$  taken from Ref. 29 and adamantane data from Ref. 35  
 $E_a$  and  $E_D$  are given in Kcal/mol.

TABLE 2

	$(K_n)_{ij}$	$(K_3)_{ij}$	$K_n \sim \sum_{i < j} (K_n)_{ij} / S$	$K_3 \sim \sum_{i < j} (K_3)_{ij} / S$
A	$(1 - 3\cos^2 \theta_{ij})^2 / 4r_{ij}^6$	$(\frac{1}{8}\sin^4 \theta_{ij} + \frac{1}{4}\sin^2 \theta_{ij}) / r_{ij}^6$	0.3	0.185
B	$(1 - 3\cos^2 \theta_{ij})^2 / 4r_{ij}^6$	$\frac{1}{8}\sin^4 \theta_{ij} / r_{ij}^6$	0.3	0.555
C	$(1 - 3\cos^2 \theta_{ij})^2 / 4r_{ij}^6$	$(\frac{1}{4}\sin^4 \theta_{ij} + \frac{8}{3}\sin^2 \theta_{ij}) / r_{ij}^6$	0.3	0.12
D	$(1 - 3\cos^2 \theta_{ij})^2 / 4r_{ij}^6$	$(\frac{1}{8}\sin^4 \theta_{ij} + \frac{7}{72}(1 - 3\cos^2 \theta_{ij})^2 + \frac{1}{18}) / r_{ij}^6$	0.3	0.222
E	$K_{ij}(\text{isotropic}) = r_{ij}^{-6}$		$K(\text{iso}) \sim \sum_{i < j} K_{ij}(\text{iso}) / S = 1$	
C <sub>3</sub>	$K_{ij}(C_3) = 1 - \frac{1}{4}(1 - 3\cos^2 \theta_{ij})^2 / r_{ij}^6$		$K(C_3) \sim \sum_{i < j} K_{ij}(C_3) / S = 0.7$	

$\theta_{ij}$  is the angle between C<sub>3</sub>-symmetry axis of molecule and the vector  $r_{ij}$  connecting the spins i and j.

relies only on  $T_1$  data.

3. For all three compounds,  $T_{1D}$  in the high temperature phase is much shorter than  $T_{1Z}$  and has a reversed temperature dependence. The low values of  $T_{1D}$  and the high activation energy  $E_D$  indicate that the relaxation mechanism of the dipolar reservoir in the  $\alpha$ -phase is due to a slow-motion process.

Below the phase transition temperature  $T_I$  the dipolar relaxation time  $T_{1D}$  has a totally different temperature dependence, one that is much more reflective of a fast molecular reorientation mechanism. If the dipolar reservoir is relaxed by the same molecular motion as the Zeeman reservoir, then an approximate expression of  $T_{1D}$  is given by (33):

$$T_{1Z}^{-1} = C[\tau_c + \frac{3\tau_c}{1 + (\omega_0\tau_c)^2} + \frac{6\tau_c}{1 + 4(\omega_0\tau_c)^2}] \quad (6)$$

The relaxation times  $T_{1D}$ , given by eqn. 6, are shown as dashed lines in the  $\gamma$ -phases.  $T_{1D}$  was calculated using  $E_a$ ,  $\tau_0$  and  $C$  obtained from  $T_{1Z}$  data. The experimental values are systematically lower than the values predicted by eqn 6, even for low temperatures.

4. The phase transition at  $T_I$  is accompanied by thermal hysteresis of the relaxation times in the case of 1-Cl, and 1-Br-ad. There is no such effect in the case of 1-NH<sub>2</sub>-ad.

5. The NMR relaxation data clearly show that there is a second phase transition in 1-Br-ad at  $T_{II} = 253$  K. There is also evidence that a second transition might take place at  $T_{II} = 217$  K in 1-NH<sub>2</sub>-ad too. The phases between  $T_I$  and  $T_{II}$  were labeled at  $\alpha$ -phase.

Some of the experimental results are given in Table 1.

### Discussion

The high values of  $T_2$  in  $\alpha$ -phases of all these compounds correspond to a motional line-narrowing process. If we assume a Gaussian line, the values of  $T_2$  can be exactly related to the second moment  $M_2$ . On this assumption for 1-Cl, 1-Br and 1-NH<sub>2</sub>-ad, we obtained for  $M_2(\alpha)$  the values 0.88, 0.72, and 1.09 G<sup>2</sup> respectively.

The low values of  $M_2$  (the expected values of the rigid second moment is about  $M_{2R} \approx 20$  G<sup>2</sup>) in  $\alpha$ -phases can be explained only by either a isotropic reorientation of the molecule, or by a jump reorientation about several axes. The increase of  $M_2$  (decrease of  $T_2$ ) below  $T_I$  ( $M_2(\beta) = 7.0, 7.5, 5.4$  G<sup>2</sup>) reflects a restricted molecular motion in ( $\alpha$ )-phases. The number of

orientations the molecule may take in the  $\beta$ -phase decreases, and the second moment is no longer averaged to zero (the intramolecular part of it). Nevertheless, the motion in the  $\beta$ -phase produces a significant reduction in the second moment. The values of  $T_2$  and its temperature dependence above and below  $T_I$  prove that the molecules lose a part of their degree of orientation as the  $\alpha$ - $\beta$  transition takes place — which agrees with the high entropy of transition found by d.s.c. measurements (29) in 1-Cl and 1-Br-ad.

Usually, for molecules which possess a symmetry axis (e.g. the adamantane or NH<sub>4</sub>Cl) the reorientation takes place about these axes and the molecule fluctuates between *indistinguishable* orientations, even at a very low temperature. In the case of 1-Cl-ad and 1-Br-ad the molecule (C<sub>3v</sub>) has a C<sub>3</sub>-symmetry axis. The reorientation about this axis leads only to a partial reduction in the second moment. The strong decrease of  $M_2$  in the  $\beta$ -phase can be explained by the set-in of a new molecular motion that, alone or combined with the reorientation about the C<sub>3</sub>-axis, strongly reduces the effective dipolar interactions. Since the molecule has no other symmetry axes, we assume the new motion that sets-in in the  $\alpha$ -phase to be a jump reorientation of the molecule between several *distinguishable* orientations (the C<sub>3</sub>-axis changes its orientation in time). On the other hand, the gap between  $T_{1Z}$  above and below  $T_I$  in 1-Cl-ad can be explained only by a decrease (a factor of 4) in the  $\alpha$ -phase, of the parameter  $C$  in eqn. 5.

In order to explain these results we have proposed (32) the following model:

(a) the molecule performs two independent jump reorientations: one about the C<sub>3</sub>-axis with correlation time  $\tau_3$ , the other between  $n$  distinguishable orientations with correlation time  $\tau_n$ ;

(b) the fluctuations between distinguishable orientations are allowed only in the  $\alpha$ -phase. This reorientation process slows down in the vicinity of  $T_I$  and disappears in the  $\alpha$ -phase leading to an orientational ordering in this phase.

Calculations of correlation functions according to this model lead to the following form of  $T_{1Z}$  (32):

$$T_{1Z}^{-1} = K_3 f(\tau_3) + K_n f(\tau_n) + Kf(\tau)$$

with  $\tau^{-1} = \tau_3^{-1} + \tau_n^{-1}$ .

This model allowed us to test different possibilities of reorientation in the  $\alpha$ -phase, on the assumption of a f.c.c. structure. The results are given in Table 2 for the following cases:

A. four reorientations parallel to (111, -111, 1-11, -1-11) directions;

- B. eight orientations parallel to the three-fold cubic axes;
- C. four orientations parallel to (111, -1-11, -11-1, 1-1-1);
- D. six orientations parallel to (100, -100, 010, 0-10, 001, 00-1)
- E. isotropic reorientation and  $C_3$  – the case when the reorientation takes place only about a  $C_3$ -symmetry axis of the molecule (the case of  $\beta$ -phases).

From all these possibilities, the most appropriate one to account for the experimental results in 1-Cl-ad is the case A, since assuming  $\tau_n(\alpha) \ll \tau_3(\alpha)$  it gives

$$C(\beta) : C(\alpha) \approx K(C_3) : K_3 = 3.85$$

which is indeed very close to the reported value of 4. According to this result, the phase transition does not change essentially the  $C_3$ -reorientations, but strongly changes  $\tau_n$  (i.e. the intermolecular potential barrier which opposes the reorientations between distinguishable orientations).

Due to the high activation energy and the low values of  $T_{1D}$  at high temperatures, we are lead to identify the slow-motion process that relaxes the dipolar reservoir as being the translational diffusion of molecules.

The strong-collision theory (34) relates the mean time of molecular jumps to a vacancy  $\tau_d$  to  $T_{1D}$  by

$$T_{1D}^{-1} = 2(1 - p)\tau_d^{-1}.$$

The temperature dependence of  $T_{1D}$  shows that  $\tau_d$  is of the form  $\tau_d = \tau_{d0} \exp(E_D/kT)$ .

The values of  $\tau_{d0}$  and  $E_D$  are given in Table 1 assuming a f.c.c. structure for all compounds ( $p = 0.223$  (35)).

Finally, we mention that we did not try at present to give a full interpretation of  $T_{1D}$  results in  $\beta$ -phases. One reason is that the form of eqn. 6 of  $T_{1D}$  is valid only when the dipolar energy resides in intermolecular dipolar interaction (33). Nevertheless, in the  $\gamma$ -phase of 1-Br-ad this approximation is valid and we assumed it true below  $T_{II}$ , at least in its vicinity. The lower value of  $(T_{1D})_{\text{exptl}}$  is caused by an additional relaxation mechanism which we assume to be due to the dipolar proton-bromine coupling. Its contribution to the relaxation rate shown in Figure 9 was obtained as

$$(T_{1D}^{-1})_Q = (T_{1D}^{-1})_{\text{exptl}} - (T_{1D}^{-1})_{\text{rotation}}$$

Assuming a short relaxation time for the

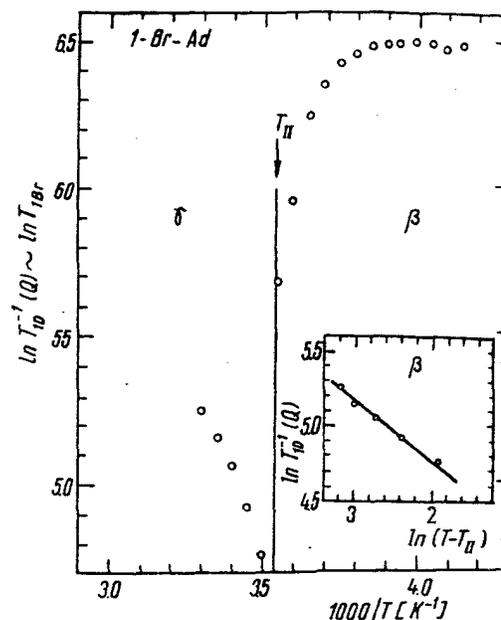


Figure 9. Temperature dependence of  $(T_{1D}^{-1})_Q$  in the vicinity of  $T_{II}$  for 1-Br-adamantane.

quadrupole nucleus Br ( $T_{1Br} < T_2$ ), the weak collision theory predicts  $(T_{1D}^{-1})_Q \sim T_{1Br}$ . The temperature dependence of  $(T_{1D}^{-1})_Q$  reflects that of  $T_{1Br}$ . Above  $T_{II}$ ,  $T_{1Br}$  decreases as  $T_{1Br} \sim (T - T_{II})^\beta$  with  $\beta = 0.43$ . Below  $T_{II}$ ,  $T_{1Br}$  has a large increase and tends to reach a plateau. The temperature dependence of  $T_{1Br}$  displays a critical behavior similar to that found in some ferroelectrics (36). A check of this rather speculative result may be provided by a direct measurement of  $T_{1Br}$ .

Finally, we observed that this is a correlation between the reorientation motion and the translational diffusion. Clear evidence for this correlation is obtained if one introduces the parameter  $\Gamma = E_a(\text{rotation})/E_D(\text{diffusion})$ . Experimentally one finds (see Table 1) that the plastic range ( $T_m - T_c$ ) is a decreasing function of  $\Gamma$ . This result agrees with the prediction of the theory developed by L. M. Amzel and L. N. Becka (37) which establishes the connection between the translational disorder (fusion,  $T_m$ ) and the orientational ordering (solid-solid) transition,  $T_I$  in a

molecular crystal. Although this theory may give a qualitative explanation of our data, it is not entirely adequate for this class of compounds, since the activation energy  $E_D$  as measured by the NMR method is different from the diffusion used in ref. (37). In fact,  $E_D$  is the sum of two contributions: the activation energy of migration  $E_m$ . Only the last term is taken into account in ref. (37).

Summing up, we arrive at the following conclusions:

1. The temperature dependences of  $T_2$ ,  $T_{1Z}$  and  $T_{1D}$  show that all three investigated compounds undergo an orientational order-disorder phase transition at  $T_I$ .

2. In the high temperature disordered phase ( $\alpha$ -phase) the molecule should reorient between several distinguishable orientations. At the same time the molecules perform strong translational diffusion. The molecular motion process in this phase is similar to that found in the disordered phase of adamantane, placing this phase in the class of plastic phases.

A model of motion was introduced based on  $T_{1Z}$  data in 1-Cl-ad. According to this model, the isotropic motion is very improbable in the disordered phase.

3. The  $\alpha \leftrightarrow \beta$  ( $\gamma$ ) transition is accompanied by a "freezing-in" of the reorientation between distinguishable orientations ( $\tau_n \rightarrow \infty$ ) and a blocking of translational diffusion.

4. In the low temperature phase ( $\beta$ ) the molecules continue to reorient between a reduced number of orientations. The results in 1-NH<sub>2</sub>-adamantane show that such a motion exists even when the molecule has no symmetry axis. In fact, it can be argued (38) that 1-NH<sub>2</sub>-ad has an effective C<sub>3</sub>-axis (C-N) since the two protons of the NH<sub>2</sub> group have a negligible effect on the intermolecular potential.

5. When compared to adamantane, the results obtained on the compounds under consideration in this section show that substituents produce a shift towards high temperatures of transition and a reduction of the plastic range ( $T_m - T_c$ ). The high symmetry of adamantane molecule allows it to preserve a high possibility of reorientation in the ordered phase (35). At the transition point the second moment is not changed, which is not the case for 1-Cl, 1-Br, and 1-NH<sub>2</sub>-adamantanes.

Faithful to my original claim of selective description, let me choose a single theme for a concluding remark. As it happens with many mature fields in physics, NMR today is moving in two directions: increased sophistication/increased relevance. While these may come

together, more often than not they may not.

The first trend is encouraged heavily by both the rapid progress of the instrumentation (increased availability and large-scale automation of standard equipment and novel, improved ones) and the vast possibilities of associating various kinds of resonance techniques (ENDOR, nuclear-nuclear double resonance, solid effect, optical-nuclear double resonance, etc.). Ever better hardware creates addiction; temptation is great, particularly where the high technology is readily accessible. There is little doubt that magnetic resonance studies facilitated by mere possession of diverse and effective instrumentation will eventually yield new results — just as access to personal computers opened new prospects to approaching stability theory (turbulence, strange attractors, etc.) On the other hand, there is even less doubt that a careful selection of jobs to be assigned to NMR — and other resonance techniques — can only maximize the scientific and practical benefits of the efforts and cost invested in them. With few exceptions — and NMR tomography is, of course, a strikingly good example of the best in hardware and software development — I do not feel that everything has yet been done to complete this process.

Admittedly, the topical sampling in this lecture may not be the most convincing one. Yet, we do hope to improve ourselves in being able to pick the most relevant issues and to give them the most technically appropriate and cost-effective treatment.

As I knew him, I am sure that Felix Bloch would have liked it.

And I am confident that, together, we can do it.

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