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The Orientational Freedom of Molecules in Crystals

I—Joint Interpretation of Thermal and N.M.R. Data in an "All or Nothing" Correlation of Orientation Theory†

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Abstract—It is shown quantitatively that the Frenkel model (step reorientations among potential wells) is, in most cases, a very good approximation to the motion in crystals presenting a molecular orientational freedom. In contrast to n.m.r., thermodynamics is not sensitive to the dynamics of the motion, but rather to the appearance of the orientational disorder, whatever its rate of rearrangement. A classification accounting for the different observable temperature relations between n.m.r. line width narrowing and thermal data is proposed. This classification is based on the comparison between the symmetry of the molecule and the symmetry of its allowed orientations (potential wells). It applies to crystals of rigid molecules, in thermodynamic equilibrium, in which the correlation of orientation of the molecules is either very large (low temperature) or very small (high temperature).

The dynamics of crystals whose molecules possess orientational freedom may be treated according to two types of models, each about thirty years old, that of Pauling-Fowler[1, 2] and that of Frenkel.[3] In the first model, the molecules are in a state of rotation, if not strictly uniform, at least continuous. In the Frenkel model, however each molecule can take only certain orientations. This second model is presently considered to be the most realistic in the majority of cases. Possible exceptions are entities with no or a single heavy atom: H_2, ClH,..., SH_2,..., NH_3,..., CH_4,..., OH^- etc., where, because of their very small moment of inertia, the ground rotatory level may be close to the top of the potential

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barrier hindering the rotation, so that continuous rotation or fast tunnelling may occur.

In the present paper we have limited ourselves to heavier molecules. Although for these molecules the Frenkel model itself is generally accepted,[4] its consequences are sometimes overlooked.

Our purpose is to explore the consequences which arise from this model in a joint interpretation of calorimetric and n.m.r. data. We shall first recall briefly certain experimental results that lead us to adopt the model.

(1) Complete crystallographic studies show that the molecules occupy, most of the time, only a finite number of orientations,[5–7] hereafter called "allowed orientations". For example, in the case of 1,2-dichlorotetramethylbenzene, the molecule can take only six orientations;[5] at the position of each substituent, one observes an electronic density that is the weighted average of the chlorine atoms and of the methyl groups. As shown by dielectric measurements,[8] on the other hand, this disorder is dynamic, the rearrangement time being about 10^{-8} sec at $+20°$ C.

(2) Methods of studying orientational dynamics (dielectric relaxation, evolution of the n.m.r. line width, nuclear magnetic relaxation) allow one to determine an activation energy V for the molecular motion that is always much larger than kT: this excludes the possibility of free or even uniform rotation. Indeed, with the exception of the cases cited above, the moments of inertia are so large that the difference in energy ΔE between occupied levels is smaller than kT (these levels are, as we shall see, very close to being pure librational levels). So we have

$$\Delta E < kT < V$$

I. Detailed Description of the Model and Its Thermodynamic Consequences

We shall now describe in greater detail the model and its thermodynamic consequences. In the next section, we shall demonstrate its validity with two typical examples.

Each molecule spends most of its time in one of its allowed orientations; the time necessary to pass from one to another is very small, about 10^{-13} to 10^{-12} sec. These orientational jumps, fast and relatively rare, are caused by fluctuations of thermal energy, that is by the passage, at a given moment, of a certain number of phonons which have just the right amplitude, polarization and phase to enable the molecule to cross the barrier. The model does not imply that the librations are suppressed: during the entire period of time the molecule spends in one of its allowed orientations, it librates in the field of its neighbours. As a matter of fact, these neighbours also are in one of their allowed orientations and they produce, at the location of the particular molecule, a field (electrostatic, dispersive or repulsive) of fixed direction and intensity during the entire period during which they do not change their own orientation.

It is clear that the model is valid and leads to a simple quantitative interpretation only if the molecule spends, as stated above, most of the time in one or the other of its allowed orientations: the mean resting time τ_r in one of the allowed orientations must be much longer than the duration, τ_j, of a jump. This holds true even in extreme cases, as we shall see. As a consequence, the proportion of molecules in a state of jump at any given moment must also be small. The contribution of these molecules to the thermodynamic functions is therefore negligible or almost negligible: the thermodynamics are practically insensitive to orientational dynamics. Only the allowed orientations are important: if disorder can be defined for the molecules distributed in their allowed orientations, the thermodynamics will be sensitive to the existence of this disorder, but not to the dynamics of its rearrangement.

We now arrive at the definition of thermodynamic disorder. It is convenient (and it will be useful for the interpretation of the n.m.r. results) to define the orientation of the molecule by labelling each of its atoms.

The set of the allowed orientations is then a finite ensemble of triplets (θ, ϕ, ψ) (with no symmetry properties) for which at least one of the labelled atoms has a different spatial position. θ, ϕ and ψ are the Euler angles.

If the molecule itself has no element of symmetry other than identity, all these orientations are naturally distinguishable. If, on the contrary, the molecule has more than one element of symmetry, some of the orientations defined above will be indistinguishable if we suppress our labelling, i.e. from a thermodynamical point of view.

Finally, the extreme case is trivial, but interesting: the only allowed orientations which are observed are all indistinguishable without labelling: the symmetry group of the allowed orientations coincides with the effective point group of the molecule itself. No disorder exists from the thermodynamical point of view. This is the case for benzene; nevertheless, in this compound n.m.r. results[9] prove that orientational jumps exist between thermodynamically indistinguishable orientations.

In an orientationally disordered crystal—in other words in a crystal where the molecules, in a certain temperature range, may take on a set of several distinguishable allowed orientations (potential wells)—a thermal transition must exist at lower temperature since the third law of thermodynamics allows only one distinguishable configuration at 0° K. In the disordered phase, the total interaction energy is not minimized: the favourable conditions[10] of maximum close-packing, minimum repulsive energy and eventually minimum electrostatic potential energy cannot be achieved for each lattice site in the crystal. The energy difference in comparison with the ordered state of the low temperature phase represents the total latent heat ΔH of the thermodynamic transition.

On the other hand, if the allowed orientations are indistinguishable (as in benzene) no thermodynamic transition will appear (remembering of course that the molecules in a state of jump give a negligible contribution to the energy). In the limiting case where the allowed orientations are only slightly distinguishable (as for example in the case of symmetric molecules on which isotopic substitution has been made), the energy difference between the ordered state and the disordered one will be very small and the theoretical transition will occur at such a low temperature that it will surely not be observable for kinetic reasons. Consequently the expression "thermodynamically distinguishable" must in practice be understood as "energetically distinguishable".

Returning to the cases where a transition exists, we assume in the present paper that the order is almost perfect in the low temperature phase, and that the disorder is almost perfect in the high temperature phase. In other words, below the transition temperature, there is a complete correlation of orientations whereas above the transition temperature this correlation becomes immediately negligible.† Any progressive, cooperative establishment of the disorder is supposed to be absent. However we exclude neither the possibility that the kinetics, at the transition point itself, be cooperative, nor the possible existence of cooperative orientational jumps in the high temperature phase. Our present assumption is that the probability of *occupation* of the allowed orientations is either 1 (low temperature) or $1/n$ (high temperature); n is the number of allowed orientations. In the high temperature phase, the small differences which may exist at a given instant in the depth of the two potential wells accessible to a molecule, and which arise from the instantaneous orientational configuration of the neighbours, are supposed to be smaller than kT. However small, these differences can produce a relative displacement of the librational levels of the various molecules in the crystal. Consequently, although a librational motion exists just as in the low temperature phase, there occurs a statistical broadening of the observed libration band of the crystal. Moreover the potential wells of the high temperature phase are shallower than the unique accessible well of the low temperature phase. (This effect is specially marked if the transition involves a change in specific volume.) The accompanying decrease of the curvature of each occupied well produces an important red shift of the libration frequencies. Thus, the librational bands are both broadened and shifted; in some cases[11] they become, in the high temperature phase, unobservable by the neutron scattering method.

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† In the next paper of this series (Part II, to be published) we shall introduce some intermediate degree of correlation in both the low and the high temperature phases.

An important consequence of the lowering of the librational frequencies in the high temperature phase is that it produces a contribution to the entropy of transition. There can also exist, if the elastic constants are reduced above the transition, a contribution to this entropy arising from the translational modes of the crystal.

For a comparison with the experimental entropy of transition, both these contributions, which are difficult to evaluate, must be added[4,12] to the configurational entropy, which in the general case, is equal to $R \log N_{\mathrm{I}}/N_{\mathrm{II}}$† ($N_{\mathrm{I}}$ and N_{II} are the number of distinguishable allowed orientations in the high and low temperature phase respectively).

II. Illustration of the Realistic Character of the Model

In the previous section, we have presented qualitative arguments couched in the language of classical mechanics in favour of the adoption of the Frenkel model. It is perhaps worth while to give a more complete demonstration of its validity based on the theory of the hindered rotator and of its thermodynamical functions. In this section, we shall show in two physical cases that the corresponding hindered rotator has a mean energy and an entropy very close to that of the corresponding pure librator. This will show that the contribution to both energy and entropy of the molecules "in a state of jump" is negligible.

For the computation of the thermodynamic functions of our librator, we shall need its frequency of libration. In some cases (cf. benzene) this is known from spectroscopic measurements. In other cases only relaxation data are available, i.e., information about the variation with temperature of the mean frequency of jump $1/2\pi\tau_r$:

$$1/2\pi\tau_r = \nu_0 \mathrm{e}^{-V/RT}$$

As Waugh and Fedin[13] recalled recently, the pre-exponential factor ν_0 may *not* be identified with the librational frequency

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† As we shall see in Part II, if intermediate degrees of correlation exist, this value is reduced.

itself. ν_0 is actually determined by the difference between the entropy in the activated state (top of the barrier) and the entropy in the ground state (bottom of the well). The latter is closely related to the librational frequency, but the former involves the transverse width of the potential pass (the "top of the barrier" is in fact a pass, i.e. a saddle point of a three-dimensional surface in the space θ, ϕ, ψ, U). A detailed demonstration of this has been given by E. Bauer in 1944 in a paper[14] that is not widely known.

Because of our ignorance of the exact form of the potential surface, we shall rather rely only on the value V of the potential barrier. We shall assume that the potential presents a sinusoidal variation in θ, the values of ϕ and ψ being constant along the transition path.

The two examples chosen are representative of the wide field of validity of the model: They are benzene at 100° K and furan in its high temperature phase at 171° K. In the case of benzene, the orientational jumps are very rare so that the validity of the model is likely *a priori*. On the contrary, in the case of furan, jumps are very frequent but the calculation will show that the model is nevertheless an excellent approximation to physical reality.

BENZENE

To apply the existing theories, it will be assumed that the angular movement of the molecule occurs in a fixed crystalline potential. We shall take a mean potential whose barrier height is equal to the activation enthalpy of the orientational jumps. We therefore have:

$$U = \frac{V}{2}(1-\cos n\theta)$$

with $n=6$, and, from n.m.r. results,[9] $V = 3700$ cal/mole.

The Harmonic Librator Approximation

This approximation is that of the model because we neglect the levels lying in the vicinity of and above the top of the barriers, since they are not occupied. To obtain the frequency ν of the corresponding harmonic librator, we have to write the equation of motion, with the assumption of small θ's. We find for ν:

$$\nu = \frac{n}{2\pi}\sqrt{\frac{V}{2I}} = 2.05 \times 10^{12}\ \mathrm{sec}^{-1},\ \text{i.e. } 66\ \mathrm{cm}^{-1}$$

with I, the moment of inertia, $= 295 \times 10^{-40}$ (g/cm^2).

It is known that, because of intermolecular coupling, which has not been taken into account in the calculation, the librations in the crystal take the form of vibrational waves,[3,15] with some frequency distribution. However this distribution is probably narrow; the Raman-active frequencies are likely to be representative of the mean value of the distribution: In benzene two Raman lines attributed to the in-plane libration of the molecules have been observed.[16] At 100°K their frequencies are 59 and 100 cm^{-1}. The value we have obtained above using an average intermolecular field, lies correctly between those two figures.

The tables of thermodynamic functions of the harmonic oscillator[17] give, at 100°K, for the mean energy of our librator $\bar{E}_l = 119$ cal/mole and for its entropy $S_l = 2.16$ e.u. (There are six potential wells but the molecule having also a six-fold symmetry, there is no configurational entropy to be added.)

Calculation from the Exact Thermodynamic Functions of the Hindered Rotator

The problem of the hindered rotator has been studied by Pitzer *et al.*[18–20] in connection with internal rotation in molecules. Pitzer has treated, among others, the case of a molecule with a large moment of inertia (rigid frame) with an attached symmetrical top. This case is exactly ours: the molecule of benzene is the symmetrical top and the crystal is the rigid frame. Pitzer also assumes a sinusoidal potential with n wells, the symmetry number σ of the top being also equal to n. To use the table,[19] we must first calculate the partition function Q_F and the entropy S_F for free rotation of the top.

For benzene at 100°K, in terms of I in g/cm^2 and T in °K one obtains

$$\frac{1}{Q_F} = \frac{\sigma}{2.815} \times 10^{38}\, IT = 0.125$$

and

$$S_F = \frac{R}{2}+R\log Q_F = 5.11 \text{ e.u.}$$

The table gives then

$$\frac{\bar{E}}{T} = 1.22 \text{ e.u.} \quad \text{and} \quad S_F - S_{H.R.} = 2.91 \text{ e.u.}$$

The energy and the entropy of this hindered rotator are then

$$\bar{E}_{H.R.} = 122 \text{ cal/mole}^{-1} \quad \text{and} \quad S_{H.R.} = 2.20 \text{ e.u.}$$

These values are only 2% larger than those found for the harmonic librator. This small difference is not due to the contribution of the higher levels (molecules in a state of jump) but rather to the anharmonicity of the bottom of the potential wells in the sinusoidal potential model. Indeed, the proportion of molecules in levels higher than the height of the barrier is about

$$\mathrm{e}^{-V/RT} = 10^{-8}$$

The order of magnitude of this number can be also found in another way: the proportion of molecules in a state of jump at a given instant is equal to τ_j/τ_r. The duration τ_j of a jump can be roughly† evaluated, by assuming that the kinetic energy of the molecule is approximately equal to the height of the barrier

$$\frac{1}{2}I\overline{\left(\frac{\mathrm{d}\theta}{\mathrm{d}t}\right)^2} \simeq V$$

and with the further assumption that the molecule stops in the next potential well by yielding its kinetic energy to its neighbour

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} \simeq \frac{2\pi}{n\tau_j}$$

which gives

$$\tau_j \simeq 0.2\times 10^{-12} \text{ sec}$$

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† A more exact calculation could have been done, following De Micheli *et al.*[21]: There exists in fact a distribution of the τ_j's, whose most probable value does not differ much from our result.

A rough estimate of the resting time τ_r is to take it equal to three times[22] the n.m.r. correlation time

$$\tau_r = 3\tau_c = 3 \times 3.2\, 10^{-14}\, e^{3700/RT}$$

in the case of benzene.[9] At 100°K,

$$\tau_r = 10^{-5} \quad \text{and} \quad \frac{\tau_j}{\tau_r} \simeq 2.10^{-8}$$

i.e. the same order of magnitude as found by the Boltzman formula.

From these results, one can conclude that in the case of benzene, the molecules in a state of jump have a completely negligible influence on the thermodynamics of the crystal. Only the exact form of the potential in the vicinity of the bottom of the well plays a role (which, in fact, is itself rather small). Since this exact form is not exactly known,† the harmonic librator (parabolic potential) is an approximation as good as and easier to manipulate than that of the sinusoidally hindered rotator. We have chosen a temperature of 100°K because it is in this range that the existence of the orientational jumps was first detected by n.m.r. line-width narrowing. Up to the melting point, the thermodynamic contribution of the molecules in a state of jump should be also negligible (their proportion is less than 10^{-3}), if of course, the height of the barrier does not change.

FURAN

The example of furan in its high temperature phase is, *a priori*, one of the best tests of the limit of validity of the Frenkel model. As a matter of fact the reorientation frequency from dielectric measurements[26] is among the highest frequencies ever observed in solids: 6000 Mc/s at 171°K, with a low activation energy $V = 2000$ cal/mole. To make the calculation possible, we shall approximate the molecule by a regular pentagonal molecule with the same moment of inertia as furan ($I = 179.64 \times 10^{-40}$ g/cm^2).[27] The complete crystallographic study of the high temperature phase has

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† It is worth to note, however, recent calculation on this question by Kitaigorodskii *et al.*[23] and Craig *et al.*[24, 25]

not yet been done; we shall assume that five allowed coplanar orientations exist with the symmetry C_5 (if there are only four of them, as for thiophene,[28] our results will be only little modified).

The Harmonic Librator Approximation

For the corresponding librator, the frequency is found to be:

$$\nu = \frac{5}{2\pi}\sqrt{\frac{V}{2I}} = 1.57\times 10^{12}\ \mathrm{sec}^{-1},\ \text{i.e. } 52.5\ \mathrm{cm}^{-1}$$

Unfortunately, no far infra-red studies are available to compare with this value.

The tables[17] give for the mean energy at 171°K:

$$\bar{E}_l = 270\ \text{cal/mole}$$

and for the libration entropy for one of the potential wells: 3.61 e.u. to which we shall add $R\log 5 = 3.20$ e.u. because the molecule has not an effective C_5 symmetry. We get $S_l = 6.81$ e.u.

Calculation Using the Exact Thermodynamic Functions of the Hindered Rotator

The same tables of Pitzer *et al.*[19] will be used as for benzene. As the thermodynamic functions are given for symmetric top molecules, we must[20] add to the entropy of the tables $R\log n$ to obtain the entropy of the corresponding asymmetric top molecule (real $\sigma = 1$). With the same notation as above, we obtain:

$$\frac{1}{Q_F} = 0.10 \quad S_{F_{\mathrm{sym}}} = 5.54\ \text{e.u.}$$

$$\bar{E}_{H.R.} = 296\ \text{cal/mole} \quad S_{H.R.} = 7.11\ \text{e.u. at } 171°\mathrm{K}$$

With regard to the harmonic oscillator, we obtain an increase of 9% for the energy and 4.5% for the entropy. The proportion of molecules in a state of jump is estimated to be about 0.3% by the Bolzmann formula and 1% using τ_j/τ_r.

Assuming this last value, and because of the fact that the molecules in a state of jump have an energy roughly six times greater than those which are in the wells, we obtain at most 6%

for their additional contribution to the energy, that is about 18 cal/mole. ΔH, the heat of the transition taking place at 150°K is equal to 490 cal/mole[29]: the energy of the molecules in a state of jump represents only 4% of the energy involved by the presence of the disorder.

We can conclude from these results that, even in such an extreme case as furan, the thermodynamics is almost insensitive to the rearrangement dynamics of the disorder. Only the fact that this disorder exists is important.

III. Systematics of the Relation Between Thermal and N.M.R. Narrowing Results

It is well known that the n.m.r. line-width and observed second moment are sensitive to the dynamics of reorientation in the crystal, if rapid enough. The narrowing of the line-width occurs as soon as the correlation time τ_c becomes shorter than the inverse of the line-width of the "rigid" lattice. To define the movement in the case of molecular reorientations, the position of the atoms, at a given moment, must be referenced, that is labelled, as in Section I. Here, in contrast to the thermodynamical point of view, the quantized state of the nuclear spins provides a natural "labelling" for the atoms and this explains why n.m.r. can reveal orientational jumps, even if they are relatively rare ($\tau_j/\tau_r = 10^{-8}$) between orientations which are thermodynamically indistinguishable.

Let us review briefly how the n.m.r. second moment can give information about the nature of the reorientation motion. Two classes of motion must be considered:

> For a fast enough reorientation about an axis C_n, the value of the second moment S for a rigid lattice, as calculated from the Van Vleck formula,[30] is reduced by a certain easily computable factor either[31] in the case $n = 2$ or[32] in the case $n \geqslant 3$.
>
> For a rapid enough spherical rotation, the intramolecular part S_1 of the second moment is averaged out. But free spherical rotation probably never occurs. There exists however a physical case where $S_1 = 0$: it is when there exists a finite set of equally

probable allowed orientations having the endospherical symmetry, i.e. the reorientations point towards the vertices of a regular polyhedron.[33] Here again, the flipping rate of the molecules among these orientations must be fast enough. It is convenient then to use the term "quasi-isotropic reorientation". It is worth recalling that the n.m.r. method can distinguish only with difficulty (through S_2) either between free axial rotation and C_n reorientations[34] (excepted the case $n=2$), or between free spherical rotation and endospherical reorientations.[35] Such distinctions are made on the basis of energetic arguments or using X-ray data.

At this point it is possible to propose the following systematic classification of the relationship between the calorimetric data and the n.m.r. narrowing results:

(1) We have seen in Sections I and II that, if the allowed orientations have the same symmetry group as the molecule itself, the molecular reorientation, with a consequent n.m.r. narrowing, does not necessarily imply a thermal transition. Two typical examples exist:

Benzene,[9] for the case of reorientation about an n-fold periodic potential barrier (axis C_n).

Hexamethylenetetramine,[36] of endospherical symmetry T_d ($\bar{4}3m$) for the quasi-isotropic reorientation.

(2) If the molecule has a lower symmetry than that of its allowed orientations, a thermal transition is, in principle,† necessary to liberate the reorientation.

(a) If then, in the high temperature phase, the potential barrier V is low enough that immediately above the thermal transition, the orientational jumps are frequent, an abrupt n.m.r. narrowing will coincide with the thermal transition point.

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† As in the example of isotopic substitution cited above, some cases may exist where the transition would be unobservable because its kinetics would be too slow. This could happen if ΔH were small, which would imply a low transition temperature, although the potential barrier would still be high. The crystal would then be frozen in a disordered state until 0°K, being a practical exception to the Nernst principle. This is perhaps the case of some hexasubstituted benzenes.[37, 38]

(b) If, in the high temperature phase, V is large enough, the orientational jumps may be rare just above the transition temperature. In this case, the narrowing of the n.m.r. spectrum will only appear with the acceleration of the movement at higher temperatures.

The phenomena (a) or (b) may appear in both of the cases considered, *reorientation over an n-fold periodic axis* and quasi-isotropic reorientation.

(1′) In case (1) a transition may exist which induces, in addition to indistinguishable orientations relative to the actual symmetry group of the molecule, other allowed orientations, these latter being distinguishable from the original n-indistinguishable orientations. In such a case, the second moment may not be modified at the thermal transition if the narrowing of the line width caused by jumps among indistinguishable orientations has already taken place at lower temperatures. For example, a molecule with C_3 symmetry reorienting fast enough around a three-fold symmetry axis may, after a transition, reorient over the same axis but with three more allowed orientations (C_6 axis). The reduced second moment is the same for a fast C_3 reorientation below the transition point or a fast C_6 reorientation above.

The preceding considerations are illustrated in Table 1. This table allows a systematic classification of the examples found in the

TABLE 1 Symmetry of Orientations

	C_n	Endospherical
The molecule possesses the symmetry of the allowed orientations	(1) benzene, quinuclidine, triethylenediamine, NF_3, cyclohexane (1′) t-butylchloride	(1) hexamethylenetetramine (1′) adamantane, neopentane, P_4, CF_4
The molecule possesses a lower symmetry than the allowed orientations	(2a) furan, cyclohexene (2b) bicyclo-222-octa-2-ene, cyclopentene	(2a) quinuclidine, bicyclo-222-octa-2-ene, triethylenediamine, cyclohexane, d-camphor (2b) perfluorocyclohexane

literature. Some compounds are present in several places in the table, when orientational degrees of freedom are successively liberated at increasing temperatures. The table, of course, is not exhaustive because in many cases thermal and n.m.r. data are not available simultaneously. Some translational diffusion often occurs in plastic crystals before the melting point; sometimes the diffusion takes place just at the thermal transition as in cyclopentane,[39] both quasi-isotropic reorientation and diffusion occurring simultaneously. In other cases, the further n.m.r. narrowing corresponding to a diffusion occurs after a plateau corresponding either to a C_n reorientation as in cyclobutane,[40] furan,[41] cyclopentane,[42] or to a quasi-isotropic reorientation as in cyclohexane,[43] succinonitrile,[44] d-camphor[45] etc.

To end this section, we shall recall that the proposed classification is established with the following assumptions:

(1) The molecules have rigid skeletons: we exclude molecules with internal rotations. We however admit molecules with $-CH_3$ groups: this is well justified because often these groups are already rotating at very low temperatures.[46] Their rotation is always very fast because of the tunnelling effect due to the very low moment of inertia of these groups: they can often be considered as spherical entities for the symmetry classification of the molecule. However, in the cases of neighbouring CH_3 groups (hexamethylbenzene)[47,48] their rotation may be coupled in a "cog-wheel" manner. In such a case, their effective contribution to the molecular symmetry is difficult to determine and thus the corresponding cases are difficult to classify.

(2) The Frenkel model is the basis of this classification scheme. It is, as we have seen, an excellent approximation, even if the molecular reorientations are frequent. In each particular case, if the complete crystallographic structure is not known, its validity can be verified by comparison of the activation energy with kT.

(3) Metastable thermodynamic phases are excluded (cf. footnote, page 313).

(4) We do not claim that in all the examples given in the table the "all or nothing" correlation model strictly applies. Our point

is that if deviations to this model exist, these deviations are too small to affect the expected relation between thermal and n.m.r. data.

IV. Comments on the Examples of the Table

REORIENTATION ABOUT AN AXIS $C_n \geqslant 3$

(1) *Benzene* (see Section II), *Quinuclidine* (1-azabicyclo-222-octane)[49] and *Triethylenediamine* (1,4-diazabicyclo-222-octane)[50] below their transition to plastic crystals (198 and 351°K respectively)[12,51]

The n.m.r. narrowing of the line-width occurs in these compounds around 140 and 190°K respectively, far below the thermal transition. At these temperatures, the orientational jumps among indistinguishable C_3 orientations are rapid enough to reduce the line-width: these jumps take place about the $N\ldots C_{tert}$ axis for the quinuclidine and about the N...N axis for the triethylenediamine. Well-defined plateaus in the second moment follow the narrowing, indicating that while the same molecular motion is accelerating, no other type of motion appears until the thermal transition.

Nitrogen trifluoride NF_3[52] below the thermal transition at 56.6°K

This is analogous to the preceding case: since the molecule itself has C_3 symmetry, a C_3 reorientation takes place between three indistinguishable positions and this explains the n.m.r. narrowing at about 35°K. The thermal transition at 56.6°K liberates a more general motion.

Cyclohexane[43] below the transition to a plastic crystal (186°K)

The n.m.r. narrowing between 155 and 180°K is quantitatively consistent with orientational jumps about a three-fold axis C_3, corresponding to the molecular symmetry (chair conformation). As predicted by the model, no thermodynamic transition exists at these temperatures.

Cyclobutane[40] below the thermal transition at 146°K

The molecule is probably planar with D_{4h} symmetry. No thermodynamic transition is necessary to liberate the reorientation about the corresponding four-fold axis: its mean frequency is effective for a narrowing of the n.m.r. line width between 130 and 140°K.

(1′) t-*Butylchloride*[46] under 220°K

The $-CH_3$ groups rotate even at very low temperature. As shown by dielectric measurements,[53] the C—Cl axis is fixed up to 220°K. The n.m.r. narrowing observed at about 100°K reveals reorientations about this axis; but below the transition at 183°K, the only allowed orientations are the three indistinguishable orientations, probably belonging to one of the groups T_d or C_{3v}. On the other hand, above this temperature the molecule can take all six orientations, distinguishable two by two, of the combined group $T_d + C_{3v}$.[4,54] The C_3 reorientation being already rapid before the transition at 183°K, the C_6 reorientation which appears at this transition point does not introduce any additional reduction of the second moment.

(2a) *Furan*[41]

The high temperature line width and the second moment are consistent with a reorientation about an axis perpendicular to the molecular plane. The line-width narrowing is abrupt at the thermodynamic transition as predicted by the short τ_r, previously found by dielectric measurements.[26]

Cyclohexene[55]

If the crystal is in thermodynamic equilibrium the n.m.r. narrowing does not appear below the transition at 139°K and is very sharp at this point. The high temperature plateau of the second moment is due to the onset of a reorientation about an axis C_n, with $n > 2$, perhaps $n = 6$, with $\tau_r < 10^{-6}$ sec.

(2b) *Bicyclo*-222-*octa*-2-*ene*[49] below 175°K

In contrast to quinuclidine or triethylenediamine, the molecule does not possess trigonal symmetry. A C_3 reorientation (about the axis $C_{tert} \cdots C_{tert}$) then involves a thermal transition at lower temperature than the observed n.m.r. narrowing (130°K): in our opinion, this transition is the one observed by E. F. Westrum[12] at 111°K; it liberates the orientational disorder, the motion being slow at the beginning. Only at about 130°K is the C_3 reorientation fast enough to reduce the n.m.r. second moment to an incipient plateau of about 7 gauss^2, corresponding to a reorientation about the pseudotrigonal axis of the molecule.

Cyclopentene[42]

Since a non-planar model is assumed (a planar model would not account for the experimental values of the n.m.r. second moment), the molecule has no symmetry axis: any n.m.r.-active reorientation involves a previous thermodynamic transition and effectively this transition exists at 87°K.[56] The n.m.r. narrowing begins at this temperature ($\tau_r \simeq 10^{-5}$ sec) but it is not sharp as it is in furan. It is complete at about 110°K. The incipient plateau at 110°K is consistent with a reorientation about an axis perpendicular to the plane of the four coplanar carbons (allowed orientations with perhaps C_5 symmetry).

Quasi-Isotropic Reorientation

(1) *Hexamethylenetetramine*[36]

This molecule has endospherical symmetry (group T_d); it may present a quasi-isotropic reorientation without thermodynamic transition; effectively no thermal transition has been detected (measurements have been performed up to 513°K),[57] although the narrowing of the n.m.r. line-width takes place between 340 and 420°K, (S_1 vanishes above 420°K). This implies reorientation among the twelve indistinguishable orientations of the group T_d.[35] The observed high potential barriers (18 kcal/mole) are due to hydrogen bonding. We have here a typical example of the nonequivalence of the terms: "quasi-isotropic reorientation" and "free rotation".

(1′) *Adamantane*,[58] *Phosphorus* P_4,[59] *Carbon tetrafluoride* CF_4,[60] *Neopentane*[46]

These molecules have tetrahedral symmetry: n.m.r. narrowing may occur without any previous thermal transition if the rotational motion takes place among the twelve indistinguishable orientations of the group T_d. The line narrowing begins at about 140°K for adamantane, 100°K for P_4, 55°K for CF_4 and 73°K for neopentane (in this compound, the effective molecular symmetry is also T_d because the methyl groups are rotating even at very low temperature). The thermal transition observed at higher temperature in these compounds probably introduces more allowed orientations: in adamantane, for example, recent X-ray measurements[6] have shown that in the high temperature phase the molecules are randomly distributed among two distinct T_d sets, which are related to each other by a 90° rotation about a line joining two opposite methylene groups. This transition has also been observed from a discontinuity in the spin-lattice relaxation time.[61]

(2a) *Quinuclidine,*[49] *Bicyclo-222-octa-2-ene,*[49] *Triethylenediamine,*[50] *Cyclohexane,*[43] *d-Camphor*[45]

These molecules do not have endospherical symmetry. At the transition to the plastic crystal (the higher temperature transition for bicyclo-222-octa-2-ene) they take on a set of orientations with endospherical symmetry, since the intramolecular second moment is reduced to zero. Frequent jumps among these distinguishable orientations take place.

(2b) *Perfluorocyclohexane* C_6F_{12}[62]

In the solid state, the molecule has either the chair or boat form, but in any case not endospherical symmetry. S_1 is found equal to zero above 185°K, implying a quasi-isotropic reorientation of the molecules. The thermal transition necessary for the reorientation process has been detected at 168°K, but the narrowing of the n.m.r. line is not immediate: until about 175°K, the orientational jumps are still rare and become more frequent at higher temperature.

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