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Molecular dynamics in liquid cyclopropane.
II. — Raman and magnetic nuclear resonance studies of orientational motion

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Abstract. — The orientational dynamics of liquid cyclopropane is studied by Raman spectrometry as a function of temperature (155, 300 K) and pressure (up to 3 kilobars). $^{13}$C and $^2$H nuclear magnetic resonance experiments are performed in the same temperature range. The isotropic and anisotropic Raman profiles associated to $A_i$ vibrational modes allow the determination of the orientational correlation function describing the reorientation of the molecular axis characterized by the diffusion coefficient $D_i$. The study of the anisotropic profile corresponding to a mode of $E'$ symmetry with a zero Coriolis constant describes the molecular axis spinning motion. NMR relaxation time $T_1$ of natural abundance $^{13}$C under proton decoupling conditions and nuclear Overhauser enhancement allow the determination of the $T_{1DD}$ relaxation time related to intramolecular dipolar relaxation processes. The validity of the decomposition of the $^{13}$C relaxation time is tested by comparison with the $T_1$ relaxation times of $^2$H; the quadrupolar coupling constant obtained is in agreement with other NMR measurement in nematic liquid crystal solution. Finally the evolution of $T_{1DD}$ with the temperature are in good agreement with the $D_i$ and $D_j$ deduced from the Raman profiles.

This justifies the approximations made in the analysis of the Raman data. This study shows that the orientational motion of the cyclopropane molecules in liquid state is very anisotropic. At low temperature the molecular axis

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Résumé. — La dynamique orientationnelle du cyclopropane liquide est étudiée par spectrométrie Raman dans une gamme de températures allant de 155 à 300 K et de pressions de 1 à 3 kilobars et par résonance magnétique nucléaire du carbone 13 et du deutérium dans la même gamme de températures. En diffusion Raman, les profils isotropes et anisotropes associés à un des modes de vibration de symétrie $A_i$ permettent de déterminer la fonction de corrélation orientationnelle décrivant la réorientation de l’axe moléculaire et le coefficient de diffusion $D_i$. L’étude du profil anisotrope correspondant à un mode de symétrie $E'$ dont la constante de Coriolis est nulle permet d’autre part d’évaluer une constante $D_j$ caractérisant le mouvement de rotation autour de l’axe moléculaire. En résonance magnétique nucléaire, les temps de relaxation longitudinaux $T_1$ du $^{13}$C en abondance naturelle dans les conditions de découplage protonique et le coefficient définissant l’effet Overhauser conduisent à la détermination du temps de relaxation $T_{1DD}$ lié aux processus de relaxation dipolaires intramoléculaires. La validité de cette décomposition du temps de relaxation du $^{13}$C est vérifiée par comparaison avec les temps de relaxation $T_1$ du deutérium ; la valeur de la constante quadrupolaire ainsi obtenue s’accorde avec les mesures faites antérieurement en milieu cristal liquide. Enfin la valeur de $T_{1DD}$ et son évolution en fonction de la température sont en excellent accord avec les constantes $D_i$ et $D_j$ déduites des profils Raman et justifient les approximations qui ont été faites dans l’analyse de ces derniers. Cette étude montre que le mouvement rotationnel des molécules de cyclopropane à l’état liquide est très anisotrope. A basse température la réorientation de l’axe moléculaire semble bien décrite par une rotation diffusionnelle. A plus haute température un modèle J semble mieux convenir bien que le temps moyen entre les chocs reste relativement petit. Par contre, la dynamique rotationnelle autour de l’axe moléculaire s’éloigne beaucoup du modèle diffusionnel à toutes les températures. Enfin, le rapport des constantes de diffusion translationnelle et rotationnelle est étudié ; il augmente nettement avec la température. Ce comportement qui est retrouvé pour plusieurs autres liquides non associés traduit une diminution plus rapide de la force quadratique moyenne s’exerçant sur le centre de gravité de la molécule que du couple quadratique moyen qui agit sur le mouvement de rotation et qui est probablement plus influencé par les forces à long rayon d’action.
1. Introduction. — Molecular motion in simple liquids has been the subject of various studies for fifteen years with the view of analysing the relaxation processes which may be obtained by different spectroscopic techniques and as a means to a better understanding of the liquid state. Some of these techniques are now well mastered making it possible to use them simultaneously to ensure more reliable results and to yield a more complete description of the molecular dynamics. Liquid cyclopropane seems to us a good subject of study; this molecule is a symmetric top and the liquid phase covers a large range of temperature (melting point 145.4 K) under few atmospheres (vapour pressure at room temperature # 7 atmospheres). In a recent paper [1], we have presented a study of the molecular motion of the centre of mass using incoherent neutron scattering and spin-echo nuclear magnetic resonance. The aim of this paper is to analyse the orientational fluctuations of this molecule using the results obtained by other techniques as well. Raman scattering and nuclear magnetic resonance are powerful and complementary tools to study such motion, in particular for symmetric tops [2]. From isotropic and anisotropic Raman profiles corresponding to a totally symmetric vibration it is possible to obtain the orientational correlation function of rank 2 describing the molecular axis reorientational fluctuations [2]. Information on the spinning motion around this axis can be obtained from the degenerate scattering profiles by making some simplifying assumptions and using modes with a zero Coriolis constant [3]. Nuclear magnetic relaxation \( T_1 \) longitudinal relaxation times measurement allows the evaluation of correlation times related to molecular reorientation. If the nucleus under consideration possesses a spin greater or equal to unity the origin of the relaxation process is mainly quadrupolar and if one knows the quadrupolar coupling constant and the asymmetry parameter it is possible to obtain the orientational correlation time [2, 4]. Half spin resonance study like proton or \(^{13}\)C provides an other way. For pure liquids, proton relaxation depends on intra and intermolecular contributions. On the other hand, \(^{13}\)C relaxation is mainly intramolecular but a number of other processes might also contribute including, dipolar relaxation, spin-rotation, and anisotropic chemical shift. Methods are proposed to separate these different contributions allowing the evaluation of the orientational correlation time \([5]\) from the dipolar relaxation term. It is customary however to neglect in these studies the dipolar cross-correlation terms. In a number of cases, these terms might be important and some authors have shown that for \(AX_2 \) [6, 7] or \(AB_2 \) [8, 9, 10] coupled systems, it is possible to extract all the parameters characterizing the dipolar relaxation process. We should point out that the orientational correlation times deduced by nuclear magnetic resonance depend in most cases on the orientational fluctuations around the different molecular axes and the determination of the constants corresponding to each motion is not always possible. This determination is possible by the simultaneous study of the correlation times of non-equivalent nuclei when this is allowed by the molecular structure or by a complete study of the dipolar relaxation in \(AX_2 \) or \(AB_2 \) systems taking into account the cross-correlation terms. Griffiths [11] proposed to evaluate the rotational diffusion constant \(D_2 \) of symmetric tops molecules from Raman data and used these results and a NMR relaxation time to deduce the rotational coefficient \(D_\eta \). In this paper, we use a slightly different approach evaluating as far as it is possible as much information as each technique allows, testing the consistency in each case.

2. Theoretical background. — 2.1 Theory of the Raman profiles in solution. — The work of Gordon [12] and Bratos and Maréchal [13] on the vibrational-rotational profile of a Raman band associated with a diatomic molecule in solution has been extended to the Raman spectrum of polyatomic molecules \([14, 15, 16]\). For a symmetric top molecule in solution the vibrational-rotational profile associated with a Raman band can be considered as a weighted sum of an isotropic profile and an anisotropic profile, respectively associated with the Fourier transform of the temporal correlation functions of the mean polarization \(\bar{z} \) and of the anisotropic polarizability \(\tilde{\beta} \) of the tensor \(\tilde{\alpha} \) of the vibrational transition:

\[
\hat{I}_{\text{isotropic}}(\omega) = \frac{1}{2 \pi} \int_{-\infty}^{+\infty} \frac{\langle \bar{a}(0) \bar{a}(t) \rangle}{\langle \bar{a}^2(0) \rangle} \exp(-i\omega t) \, dt
\]

\[
\hat{I}_{\text{anisotropic}}(\omega) = \frac{1}{2 \pi} \int_{-\infty}^{+\infty} \frac{\langle \text{Tr} \tilde{\beta}(0) \tilde{\beta}(t) \rangle}{\langle \text{Tr} \tilde{\beta}^2(0) \rangle} \exp(-i\omega t) \, dt
\]
where \( \hat{I}(\omega) \) are unit area normalized profiles. These profiles can be extracted from the experimental \( I_{\text{VV}}(\omega) \) and \( I_{\text{VH}}(\omega) \) obtained by illuminating the sample with a vertically polarized incident light and collecting either the vertical or horizontal scattered electric field components.

Assuming that there is no vibrational-rotational interaction and the absence of induced polarizability, the correlation function of the mean polarizability is the vibrational correlation function \( G_2(t) \) which expresses the fluctuation of the vibrational states resulting from intermolecular forces. The correlation function for the anisotropic polarizability part is given by \( G_{\text{ani}}(t) = G_v(t) G_{2m}(t) \), where \( G_{2m}(t) \) is the orientational correlation function. The ratio of the Fourier transform of the anisotropic spectrum to the Fourier transform of the isotropic spectrum allows the evaluation of the orientational correlation function. The correlation function \( G_{2m}(t) \) can be written:

\[
G_{2m}(t) = \sum_{m=-2}^{m=+2} \frac{\langle \alpha_{2m}(0) \alpha_{2m}^{*}(t) \rangle}{\sum_{m=-2}^{m=+2} \langle \alpha_{2m}(0) \alpha_{2m}^{*}(0) \rangle} \tag{3}
\]

where \( \alpha_{2m} \) is a component of the spherical irreducible traceless tensor \( \Phi \) associated with the vibrational transition. For highly symmetrical molecule this expression can be simplified according to the symmetry properties of each normal coordinate. Thus, for a symmetric top molecule such as cyclopropane belonging to the point group \( D_{3h} \), the Raman active vibrations belong to the \( A_1, E' \) and \( E'' \) representations of the group and the corresponding correlation functions are:

\[
G_{20}(t) = \frac{\langle \alpha_{20}(0) \alpha_{20}^{*}(t) \rangle}{\langle \alpha_{20}(0) \alpha_{20}^{*}(0) \rangle}, \tag{4}
\]

\[
G_{212}(t) = \frac{\langle \alpha_{212}(0) \alpha_{212}^{*}(t) \rangle}{\langle \alpha_{212}(0) \alpha_{212}^{*}(0) \rangle}, \tag{5}
\]

\[
G_{211}(t) = \frac{\langle \alpha_{211}(0) \alpha_{211}^{*}(t) \rangle}{\langle \alpha_{211}(0) \alpha_{211}^{*}(0) \rangle}. \tag{6}
\]

However, the evaluation of the vibrational correlation function presupposes the existence of an isotropic profile with non-zero intensity which is true only for vibrationally symmetric modes. Furthermore, for degenerate vibrations, the hypothesis of negligible vibrational-rotational interaction which allows the factoring of the correlation functions often fails due to Coriolis coupling.

The orientational correlation functions corresponding to the different tensorial elements, assuming fast modulation of the rotational states and for times greater than the correlation times of the angular velocities are exponential \([14, 15, 16]\)

\[
G_{2m}(t) = \exp \left\{ - \left[ (6 - m^2) D_\perp + m^2 D_\parallel \right] \frac{kT}{I_\perp} \right\} \tag{7}
\]

At very short times, less than the angular velocity correlation times, they are not exponential and approximate those of the free rotor. In particular, they are characterized by the second rotational moment:

\[
M_{2m} = m^2 \frac{kT}{I_\parallel} + \left( 6 - m^2 \right) \frac{kT}{I_\perp}. \tag{8}
\]

We have to point out that the diffusion constants must follow the fast modulation condition (see appendix) that is

\[
(6 - m^2) D_\perp + m^2 D_\parallel < \sqrt{M_{2m}}. \tag{9}
\]

In the previous development of the theory it was assumed that there was no phase relation between the vibrations of different molecules; it is only valid for dilute solutions. Its extension in the case of pure liquid has been treated recently [17]. Taking into account the effect of rapidly fluctuating intermolecular forces on the phase relaxation of oscillators, this work shows that two kinds of terms arise in the expression of the vibrational correlation functions. The former, which also appears in the dilute solution theory are not associated with vibrational energy transfer between molecules; the latter on the other hand, called exchange terms, are specific to the pure liquid and corresponds to a vibrational quantum moving from molecule to molecule, corresponding, in other words to vibrational coupling. Because of these exchange terms the isotropic Raman profile, the anisotropic Raman profile and that of the infrared belonging to the same molecular vibrational normal mode are not identical. However, for the \( A_1 \) vibration of a \( D_{3h} \) symmetry molecule such as cyclopropane the dipolar effects which are in general the most important terms of the exchange interactions are zero causing these modes to be infrared inactive. One can assume that the exchange effects are negligible, this hypothesis can be tested by the isotopic dilution technique [18]. For such a case, the pure liquid theory remains identical to the one for solutions.

### 2.2 Nuclear Magnetic Resonance

#### 2.2.1 \(^{13}\text{C} \) longitudinal relaxation time

The equations which describe the different aspects of the longitudinal relaxation of loosely coupled spin systems like AX\(_2\) have been developed in detail by D. M. Grant et al. in a series of papers [6, 7, 19, 20]. These authors have shown that when the multiplet structure of the spectrum is preserved, the cross-correlation terms play a fundamental role in the analysis of the temporal evolution of the magnetization associated to these multiplets. On considering only the intramolecular relaxation and treating the other relaxation mechanisms collectively as a local, fluctuating field, under the extreme narrowing condition, one shows that six spectral densities are necessary to describe completely the spin-lattice relaxation of a AX\(_2\) system. One
discerns two auto-correlation spectral densities $J_{\text{CH}}$ and $J_{\text{HH}}$ of the relaxation vectors CH and HH; two cross-correlation spectral densities $J_{\text{CHH}}$ and $J_{\text{HCH}}$ corresponding respectively to the vectors CH and HH and to the two vectors CH, finally, two spectral densities characterizing the random magnetic fields $J_{\text{c}}$ and $J_{\text{H}}$.

These considerations cause Grant and coworkers to propose a method consisting of studying the relaxation of the different lines of the $^{13}\text{C}$ triplet for different conditions of preparation of the system. Unfortunately it was not possible to use this method for cyclopropane since it does not constitute a true AX$_2$ system causing fine structure due to the different CH$_2$ spin coupling to be present. So far we are left with the study of the $^{13}\text{C}$ relaxation under proton decoupling conditions [20]. This allows one to simplify the spectrum as a result of the removal of the triplet structure of the $^{13}\text{C}$ resonance line, and to increase the sensitivity, and offers the advantage of removing the spectral densities $J_{\text{HH}}$ and $J_{\text{CHH}}$. Thus, we are left with a system of two coupled differential equations which can be written using Grant's notations as follows:

$$\frac{d}{dt} \begin{bmatrix} y_2(t) \\ y_3(t) \end{bmatrix} = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{12} & \Gamma_{22} \end{bmatrix} \begin{bmatrix} y_2(t) \\ y_3(t) \end{bmatrix} + \begin{bmatrix} \Gamma_{13} \\ \Gamma_{23} \end{bmatrix}$$

(10)

where

$$y_2(t) = \langle I_z(t) \rangle - \langle I_z \rangle,$$

$$y_3(t)$$

is a linear combination of diagonal matrix elements corresponding to the population of the different levels under proton decoupling conditions.

$$\langle I_z(t) \rangle$$ is the $^{13}\text{C}$ magnetization at time $t$ along the $z$ axis under proton decoupling conditions.

$$\langle I_z \rangle$$ is the $^{13}\text{C}$ magnetization along the $z$ axis at thermal equilibrium without proton decoupling conditions.

The matrix elements $\Gamma_{ij}$ are connected to the spectral densities, by a term $1/T_{1C}$ which describes the contribution of the non intramolecular dipolar relaxation processes and by the gyromagnetic ratios $\gamma_H$ and $\gamma_C$ of proton and $^{13}\text{C}$. The matrix elements are:

$$\Gamma_{11} = \frac{20}{3} J_{\text{CH}} + \frac{1}{T_{1C}}$$

$$\Gamma_{12} = \frac{20}{3} \sqrt{3} J_{\text{HCH}}$$

(11)

$$\Gamma_{22} = \frac{40}{9} J_{\text{CH}} - \frac{20}{9} J_{\text{HCH}} + \frac{1}{T_{1C}}$$

(12)

$$\Gamma_{13} = -\frac{10}{3} J_{\text{CH}} \frac{\gamma_H}{\gamma_C} \langle I_z \rangle$$

$$\Gamma_{23} = -\frac{10}{3} \sqrt{3} J_{\text{HCH}} \frac{\gamma_H}{\gamma_C} \langle I_z \rangle.$$  

(13)

For a symmetric top molecule, in the rotational diffusion limit, the spectral densities are given by [21]:

$$J_{\text{CH}} = \frac{3}{10} \frac{\gamma_H^2 q^2 h^2}{r_0^2} \tau_{\text{CH}} (\text{HCH})$$

$$J_{\text{CH}} (\text{HCH}) = \frac{3}{10} \frac{\gamma_H^2 q^2 h^2}{r_0^2} \tau_{\text{CH}} (\text{HCH})$$

and

$$\tau_{\text{CH}} (\text{HCH}) = \frac{1}{24 D_1} \pm \frac{3 \sin^2 \theta \cos^2 \theta}{5 D_1 + D_{||}} + \frac{3 \sin^2 \theta}{4(2 D_1 + 4 D_{||})}$$

(15)

where the plus and minus signs correspond respectively to $\tau_{\text{CH}}$ and $\tau_{\text{HCH}}$ and $\theta$ is the angle between the relaxation vector CH (of length $r_{	ext{CH}}$) with the molecular axis. From the equation system (10) one can deduce a solution at steady state:

$$\langle I_z \rangle = \frac{\Gamma_{11} \Gamma_{23} - \Gamma_{22} \Gamma_{13}}{\Gamma_{11} \Gamma_{22} - \Gamma_{12} \Gamma_{12}}.$$

(16)

For a purely intramolecular dipolar relaxation, this steady state solution allows one to write:

$$\eta = \frac{\langle I_z \rangle_d - \langle I_z \rangle}{\langle I_z \rangle} = \frac{\gamma_H}{2 \gamma_C}$$

(17)

where $\langle I_z \rangle_d$ is the $^{13}\text{C}$ magnetization along the $z$ axis at thermal equilibrium under proton decoupling conditions.

One finds the nuclear Overhauser effect (NOE), characterized by the parameter $\eta$ and which gives the enhancement of the intensity of the $^{13}\text{C}$ resonance line when the proton transitions are irradiated.

In the absence of cross-correlation effects, if a further relaxation mechanism exists in addition to dipolar one, the value of $\eta$ become:

$$\eta = \frac{\gamma_H}{2 \gamma_C} \frac{T_1}{T_1}$$

(18)

where

$$\frac{1}{T_1} = \frac{1}{T_{1p}} + \frac{1}{T_{1C}}$$

(19)

with

$$\frac{1}{T_{1p}} = \frac{20}{3} J_{\text{CH}}$$

(20)

one sees that the integration of the coupled differential equations system (10) leads to a bi-exponential evolution of the $^{13}\text{C}$ magnetization $y(t)$. In the case of negligible cross-correlation terms ($J_{\text{HCH}} \neq 0$) this law becomes a single exponential.

2.2.2 Deuteron longitudinal relaxation time. — For molecules having nuclei whose spins are $\geq 1$ the coupling between the quadrupolar moment of the nucleus and the electric field gradient produced at the nucleus site by the electronic charges distribution, yields an efficient relaxation of the system. The measurement of the spin lattice relaxation time allows the evaluation of $T_{1Q}$ which is given in the extreme narrowing condition by [22]:

$$\frac{1}{T_{1Q}} = \frac{3 \pi^2}{10} \frac{2 I + 3}{I(I-1)} \left(1 + \frac{x^2}{3}\right) \left(\frac{e^2 q Q}{h}\right)^2 \tau_Q,$$

(21)
$I$ is the nuclear spin, $e^2 Q / h$ is the quadrupolar coupling constant, $\chi$ the asymmetry parameter of the tensor associated with the electric field gradient. For a symmetric top, in the rotational diffusion limit, the orientational correlation time $\tau_\theta$ is given by the expression (15) corresponding to $\tau_{CH}$ where the angle $\theta$ is the angle between the molecular axis and the principal axis of the tensor characterizing the electric field gradient.

3. Experimental conditions. — 3.1 COMPOUNDS. —
The cyclopropanes $C_3H_6$ and $C_3D_6$ used are commercial products of Matheson with a purity greater than 99.5% and of Merck with a purity of 98%.

3.2 RAMAN SPECTROSCOPY. — 3.2.1 Choice of the studied profiles. —
Cyclopropane is an oblate symmetric top belonging to the $D_{3h}$ point group with rotational constants which are respectively

$$A = 0.42 \text{ cm}^{-1} \quad \text{and} \quad B = 0.67 \text{ cm}^{-1} \quad [23, 24].$$

It has 21 internal degrees of freedom which span the irreducible representations of the point group $D_{3h}$ as: $3 A_1^I + 1 A_2^I + 1 A_2^I + 2 A_2^I + 4 A' + 3 E'$. The $A_1^I$, $E'$ and $E''$ modes are Raman active, the $A_2^I$ and $E''$ modes are infrared active. Its spectroscopy is the subject of a large number of investigations among those some are recent [25, 35]. The main attributes of the liquid Raman spectrum (Fig. 1) known for twenty years [23, 24] are still valid.

We have to point out that the existence of an accidental degeneracy between the $v_3$ mode of $A_1^I$ symmetry at 1188 cm$^{-1}$ and the $v_{13}$ mode of $E''$ symmetry [23, 35, 36] has been clearly stressed. Among the three $A_1^I$ vibrations, only, the $v_3$ band at 1188 cm$^{-1}$ has sufficient intensity and is well enough separated from neighbouring bands to allow a study of its profile. We studied this band in spite of the accidental degeneracy with the $v_{13}$ mode assuming that the $v_{13}$ mode whose intensity is weaker than the former's has no influence on its profile. The gas Raman spectrum at 1188 cm$^{-1}$ (Fig. 2) which is very close to the pure rotational Raman spectrum seems in our opinion, to support this assumption. The intensity of the $v_{13}$ mode can be evaluated to be less than 10% that of $v_3$. For the profiles corresponding to degenerate vibration we choose to study the $v_{12}$ $E''$ profile at 3080 cm$^{-1}$ because this band is the only one with a zero Coriolis constant [33, 36].

We have to emphasize that none of these profiles contain hot bands, the lowest vibrational energy level of cyclopropane is located at 740 cm$^{-1}$.

3.2.2 Apparatus. — A Coderg PHO spectrometer was used with two Ebert-Fastier monochromators with serial gratings having 1800 lines/mm and a blaze wavelength of 550 nanometers. The light source was the 488 nm line of a Spectra-Physics Argon-ion laser with a power of approximately 500 mW. The spectral width used was 1.4 cm$^{-1}$.

The cyclopropane sample was contained in a glass tube of 4 mm inner diameter.

The recorded scattering profiles are $I = I_{VH} + I_{VH}$ and $I = I_{HV} + I_{HV}$. They are obtained by collecting the two components of the 90° scattered light by the sample using an incident electric field vector whose direction is respectively perpendicular or parallel to the plane done by the direction of propagation of the incident light and the scattered light. A quarter wave plate is used to circularly polarize the radiation entering the spectrometer. For the studies at different temperatures and at different pressures we have used respectively a Coderg cryostat and the apparatus designed and built in our laboratory [37].

![Raman spectrum of liquid cyclopropane at room temperature. Herzberg's notation is used for the bands assignment.](image1)

![Comparison of the $I_{WH}$ Raman profile at 1188 cm$^{-1}$ (A) with the Rayleigh depolarized profile (B) corresponding to the pure rotation for gaseous cyclopropane under 3 atmospheres. The experimental width is 6 cm$^{-1}$, 488 nanometers laser line, 1.5 W.](image2)
Isotropic and anisotropic profiles normalized to unit area for $\nu_3$ $A_i$ at 1188 cm$^{-1}$.

Fig. 3. — Isotropic and anisotropic profiles normalized to unit area for $\nu_3$ $A_i$ at 1188 cm$^{-1}$.

Fig. 4. — $A_i$ band at 1188 cm$^{-1}$ at room temperature. Vibrational correlation function $G_v(t)$; Correlation function associated to the anisotropic profile $G_{a\text{iso}}(t)$; Orientational correlation function $G_{2\text{iso}}(t)$. The curve (0) represents the orientational correlation function calculated with the J model ($r_J = 0.065$ ps). Logarithm of the correlation function $G_{2\text{iso}}(t)$. The temporal resolution represented by $-\infty$ is 0.11 ps.

Fig. 5. — Anisotropic profile of the $\nu_{12}$ E" band at 3080 cm$^{-1}$ at room temperature.

Fig. 6. — Correlation function (0) $G_{\nu_{12}\text{iso}}(t)$ associated to the E" band at room temperature. The temporal resolution is represented by $-\infty$ and is 0.08 ps. The free rotor orientational correlation function for the Raman E" profile of a symmetric top (ref. [16]) is represented by (0).
3.3 Nuclear Magnetic Resonance. — 3.3.1 $^{13}$C longitudinal relaxation time measurement. — The $^{13}$C relaxation longitudinal times $T_1$ of cyclopropane were measured at 22.63 MHz on a Bruker HX 90 spectrometer coupled to a Nicolet 1080 computer. The sample is enclosed in a glass tube of 10 mm inner diameter containing the cyclopropane in natural abundance and approximatively 10\% in volume of C$_3$D$_6$ for locking the magnetic field. The $[180^\circ\tau-90^\circ]$ sequence of measurement is used. A first $180^\circ$ radio frequency pulse invert totally the nuclear magnetization; then after a time $\tau$ a 90° radio frequency pulse brings the magnetization into the measurement plane. Four free induction decay signals were accumulated to improve the sensitivity. The NMR spectrum is then calculated in a spectral range of 600 Hz by Fourier transforming the resulting free induction decay signal. The waiting time between two sequences of measurement is approximately 5 $T_1$. During the complete measurement, the saturation of the proton resonances is realized at 90 MHz by means of a Bruker model BSV3P broadband decoupler.

We have to emphasize that the measurement of the thermal equilibrium $^{13}$C longitudinal magnetization under proton decoupling conditions is done at the beginning of the experiment and after five measurements of the magnetization at different $\tau$. The values of the magnetizations measured at time $\tau$ are then corrected by linear interpolation from the equilibrium values which connect them.

3.3.2 Measurement of the $^{13}$C Overhauser effect. — The evaluation of the nuclear Overhauser enhancement is done in two steps. The integrated intensity of the $^{13}$C thermal equilibrium resonance line when proton resonances are irradiated is first evaluated using the sequence $[90^\circ\text{-acquisition-}T]$. Then, the integrated intensity of the $^{13}$C thermal equilibrium resonance is measured with the gated decoupling sequence $[D_{on-90^\circ\text{-acquisition-}}D_{off-}T]$. D symbolizes the change of state of the decoupler which works only during the free induction decay acquisition period. This allows an easy integration of the resonance line, hence the removal of the triplet structure; the waiting time $T$ is fixed at a value of 10 $T_1$. During the complete measurement, the deuteron resonances is realized at 90 MHz by means of a Bruker model BSV3P broadband decoupler.

For these measurements, the number of accumulations is four. At each temperature the measurement of $\eta$ is done several times which allows the evaluation of a mean value of this quantity with a relative uncertainty of approximately 5\%.

3.3.3 Deuteron longitudinal relaxation time measurement. — The deuteron longitudinal relaxation time of C$_3$D$_6$ were carried out on Bruker HX90 multi-resonance spectrometer. The sample container is a glass tube of 10 mm inner diameter containing approximately 10\% in volume of C$_3$D$_6$ in C$_3$H$_6$. The deuteron resonance of heavy water is used to lock the magnetic field.

The sequence of measurements is based on the sequence $[180^\circ\tau-90^\circ\text{-acquisition-}T]$. The frequency of the study is 13.82 MHz. The waiting time $T$ is of the order of 25 s. Four free induction decay signals are accumulated at room temperature and one at the others temperature.

4. Results. — 4.1 Raman Spectrometry. —

4.1.1 A$_1$ band. — The measured depolarization ratio

$$\rho = \frac{\int I_{VV}(\theta) d\theta}{\int I_{VV}(\theta) d\theta} = 0.08 \pm 0.01$$

does not vary with temperature and pressure within the experimental uncertainty.

The high frequency side of the isotropic profile varies in a monotonic way with frequency (Fig. 3) and is very nearly Lorentzian. The dilution of the isotopic compound has little influence on this profile (Fig. 7) whose width varies from 5.5 cm$^{-1}$ to 4.5 cm$^{-1}$ showing that the exchange effect on the vibrational relaxation is weak and that the dilute solution approximation can be used. Furthermore, the anisotropic profile which is situated at the same frequency, as the isotropic profile (Fig. 3), 1188 cm$^{-1}$, is also nearly Lorentzian. It was not possible to evaluate the second moment of these profiles at all temperatures since the function

$$F(\Omega) = \int_0^{+\Omega} \omega^2 I(\omega) d\omega$$

did not converge in the investigated spectral range which extends from the band centre to +150 cm$^{-1}$. The correlation functions corresponding to the high frequency side of these profiles and the orientational correlation function are quasi exponential (Fig. 4) if one excludes the short time range between 0 and

![Raman spectrum comparison](image-url)
0.3 ps. It seems difficult to give a physical significance to the behaviour of the correlation function in this time range, which is not very different from the resolution namely 0.1 ps. Furthermore, for the orientational correlation function the signal to noise ratio becomes very bad for times greater than 1.5 ps.

The vibrational correlation time obtained by integrating the corresponding correlation function or by the fit of this function to an exponential is the same within the experimental errors that one can estimate to be of the order of 10%. It varies from 2.0 ps at room temperature to approximatively 3.5 ps at 155 K. These values are not corrected for the experimental resolution but this effect is relatively weak. Clearly the correlation time rises when the temperature decreases which is contrary to some results obtained in solution [40] but similar to results obtain on other pure liquids [3, 38]. We attribute these vibrational correlation times to phase relaxation [41].

The orientational correlation times \( \tau_{20} \) were also evaluated by integration or by fitting the correlation function with an exponential. The results are the same within the experimental error estimated to be 15-20% (Table I). We have to stress that the evaluated orientational correlation times \( \tau_{20} \) are not affected by the instrumental resolution which affects the isotropic and anisotropic profiles in the same way. Assuming the rotational diffusion limit, we have evaluated the rotational diffusion constant \( D_1 \); its variation versus temperature which follows approximately the Arrhenius law allows the evaluation of an activation energy of 0.8 kcal.mole\(^{-1}\). On the other hand, we note that the diffusion constant decreases when the pressure increases but the activation volume of about 10 cm\(^3\) that we have evaluated is very imprecise.

### 4.1.2 E\(^\prime\) band.

The function

\[
F(Q) = \int_0^{+\infty} I(\omega) \omega^2 d\omega
\]

converges in the studied spectral range when the temperature is greater than or equal to \(-50°C\), which allows the evaluation of its second moment (Table II). Finally the global correlation time \( \tau_{\text{aniso}} \) was evaluated by integration of the correlation function (Table II).

The Coriolis coupling constant which is near zero allows one to write the correlation function as a product of a vibrational correlation function by an orientational correlation function \( G_v(t) G_{2\pm1}(t) \), this last one corresponding to the rotation of the tensors elements \( \alpha_{2\pm1} \). Furthermore the values of the measured second moment which are not really different from the theoretical one suggest that the profile is mainly due to the rotational relaxation; \( G_v(t) \) decreases with time more slowly than does \( G_{2\pm1}(t) \).

We shall try to evaluate a rotational diffusion constant \( D_\parallel \) using the rotational diffusion hypothesis and making a correction for the vibrational relaxation.

### Table I. — Orientational correlation time \( \tau_{20} \) and diffusion constant \( D_1 \) versus temperature and pressure for the \( A_1 \) Raman profile. \( D_1^* \) is the product of the diffusion constant \( D_1 \) by \( \sqrt{l_J/kT} \).

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( P ) (atm.)</th>
<th>( \tau_{20} ) (ps)</th>
<th>( D_1 ) (ps(^{-1}))</th>
<th>( D_1^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>7</td>
<td>0.42</td>
<td>0.40</td>
<td>0.128</td>
</tr>
<tr>
<td>253</td>
<td></td>
<td>0.75</td>
<td>0.22</td>
<td>0.076</td>
</tr>
<tr>
<td>233</td>
<td></td>
<td>0.83</td>
<td>0.2</td>
<td>0.072</td>
</tr>
<tr>
<td>220</td>
<td></td>
<td>1</td>
<td>0.17</td>
<td>0.063</td>
</tr>
<tr>
<td>203</td>
<td></td>
<td>1.03</td>
<td>0.16</td>
<td>0.062</td>
</tr>
<tr>
<td>185</td>
<td></td>
<td>1.2</td>
<td>0.14</td>
<td>0.057</td>
</tr>
<tr>
<td>172</td>
<td></td>
<td>1.42</td>
<td>0.12</td>
<td>0.050</td>
</tr>
<tr>
<td>155</td>
<td></td>
<td>2.1</td>
<td>0.08</td>
<td>0.035</td>
</tr>
<tr>
<td>298</td>
<td>825</td>
<td>0.45</td>
<td>0.37</td>
<td>0.12</td>
</tr>
<tr>
<td>—</td>
<td>1500</td>
<td>0.65</td>
<td>0.26</td>
<td>0.083</td>
</tr>
</tbody>
</table>

### Table II. — Experimental second moment and theoretical rotational second moment; correlation time \( \tau_{\text{aniso}} \), \( D_\parallel \) diffusion constant, versus temperature and pressure for the \( E'' \) Raman profile. \( D_\parallel^* \) is the product of the diffusion constant \( D_\parallel \) by \( \sqrt{l_J/kT} \).

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( P ) (atm.)</th>
<th>( M_{2\pm1}^{(2)} ) (cm(^{-2}))</th>
<th>( M_{2\pm1}^{(1)} ) (cm(^{-2}))</th>
<th>( \tau_{\text{aniso}} ) (ps)</th>
<th>( D_\parallel ) (ps(^{-1}))</th>
<th>( D_\parallel^* )</th>
<th>( \tau_{\text{aniso}}^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>7</td>
<td>1920 ± 300</td>
<td>1558</td>
<td>0.20 ± 0.03</td>
<td>2.4</td>
<td>0.97</td>
<td>1.49</td>
</tr>
<tr>
<td>253</td>
<td></td>
<td>1950 ± 300</td>
<td>1323</td>
<td>0.26 ± 0.03</td>
<td>2.2</td>
<td>0.96</td>
<td>1.78</td>
</tr>
<tr>
<td>223</td>
<td></td>
<td>1610 ± 250</td>
<td>1166</td>
<td>0.30 ± 0.03</td>
<td>1.9</td>
<td>0.88</td>
<td>1.93</td>
</tr>
<tr>
<td>185</td>
<td></td>
<td>non conv.</td>
<td>1009</td>
<td>0.37 ± 0.04</td>
<td>1.4</td>
<td>0.70</td>
<td>2.22</td>
</tr>
<tr>
<td>155</td>
<td></td>
<td>non conv.</td>
<td>810</td>
<td>0.53 ± 0.05</td>
<td>0.9</td>
<td>0.50</td>
<td>2.84</td>
</tr>
<tr>
<td>298</td>
<td>50</td>
<td>1910 ± 300</td>
<td>1558</td>
<td>0.20 ± 0.02</td>
<td>2.4</td>
<td>0.97</td>
<td>1.49</td>
</tr>
<tr>
<td>—</td>
<td>800</td>
<td>2080 ± 300</td>
<td>—</td>
<td>0.23 ± 0.02</td>
<td>1.9</td>
<td>0.77</td>
<td>1.71</td>
</tr>
<tr>
<td>—</td>
<td>2000</td>
<td>2010 ± 300</td>
<td>—</td>
<td>0.25 ± 0.03</td>
<td>2.1</td>
<td>0.85</td>
<td>1.86</td>
</tr>
<tr>
<td>—</td>
<td>3000</td>
<td>1750 ± 250</td>
<td>—</td>
<td>0.27 ± 0.03</td>
<td>—</td>
<td>—</td>
<td>2.00</td>
</tr>
</tbody>
</table>
A way derived from Rakov’s method [42] consists of studying the quantity
\[ \log \left[ \frac{1}{\tau_{\text{aniso}}} - 5 D_1 - \frac{1}{\tau_y} \right] = \log D_\parallel \]
as a function of \(1/T\) [3]. The value of the vibrational correlation time which is assumed to be temperature independent is selected by trying to obtain approximately a straight line, the slope of which gives the activation energy corresponding to the spinning motion around the symmetry axis. A value of \(\tau_y\) corresponding to a Lorentzian vibrational profile of 6 cm\(^{-1}\) of full width at half height seems acceptable (Fig. 8). The results for the parameter \(D_\parallel\) are given in table II, the associated activation energy is 0.7 kcal. mole\(^{-1}\).

![Fig. 8. — Evolution of the logarithm of \(D_\parallel\) versus the reciprocal temperature.]

We have to stress that the acceptable values of \(\tau_y\) have little effect on the high temperature result, but this correction technique can lead to important errors in the parameter \(D_\parallel\) at low temperature and on the activation energy. Finally, one can notice a very weak dependence of \(D_\parallel\) with pressure.

**4. 2 \(^{13}\text{C}\) AND DEUTERON NMR RELAXATION TIMES.**

The behaviour of the logarithm of the magnetization corresponding to the \(^{13}\text{C}\) resonance line is linear for all the temperatures, which allows the evaluation of the \(T_1\) relaxation times (Table III). We note that this linearity persists for times much greater than the \(T_1\) relaxation time (Fig. 9) which shows that the cross-correlation effects are negligible [20].

The values of \(\eta\) characterizing the nuclear Overhauser effect are given on table III. Assuming that the cross-correlation effects are negligible, it is possible to evaluate \(T_1^{\text{DD}}\) characterizing the purely dipolar correlation time and \(T_{1\text{C}}\) which corresponds to the other relaxation processes (Table III). In this table, we have reported the measurement done at room temperature by Roberts et al. [43] on a 50% W/W sample of cyclopropane in CDC\(_3\).

One sees that:

i) Within the experimental errors, our value of the room temperature relaxation time is very near that of Roberts.

ii) The efficiency of the relaxation processes other than the intramolecular dipolar one increases with temperature. One can conclude that among these

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(T_1) (s)</th>
<th>(\eta)</th>
<th>(T_1^{\text{DD}}) (s)</th>
<th>(T_{1\text{C}}) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 (*)</td>
<td>36.7</td>
<td>1.0</td>
<td>72.2</td>
<td>74.6</td>
</tr>
<tr>
<td>300</td>
<td>42.5</td>
<td>0.96</td>
<td>88</td>
<td>82</td>
</tr>
<tr>
<td>281</td>
<td>34</td>
<td>1.04</td>
<td>65</td>
<td>72</td>
</tr>
<tr>
<td>265</td>
<td>31.5</td>
<td>1.1</td>
<td>57</td>
<td>71</td>
</tr>
<tr>
<td>254</td>
<td>31.5</td>
<td>1.24</td>
<td>51</td>
<td>84</td>
</tr>
<tr>
<td>243</td>
<td>30.5</td>
<td>1.33</td>
<td>46</td>
<td>92</td>
</tr>
<tr>
<td>223</td>
<td>30.6</td>
<td>1.42</td>
<td>43</td>
<td>107</td>
</tr>
<tr>
<td>190</td>
<td>27.5</td>
<td>1.56</td>
<td>35</td>
<td>128</td>
</tr>
<tr>
<td>173</td>
<td>21.5</td>
<td>1.62</td>
<td>26</td>
<td>116</td>
</tr>
</tbody>
</table>

![Fig. 9. — Evolution of \(\text{Log}(R)\) with \(R = \frac{\langle I_x \rangle_a - \langle I_x(0) \rangle}{2 \langle I_x \rangle_a}\) versus time for liquid cyclopropane.]

Table IV. — Evolution of the deuteron longitudinal relaxation time \(T_1^D\) for the cyclopropane \(d_6\) molecule versus temperature.

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(T_1^D) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>6.5</td>
</tr>
<tr>
<td>223</td>
<td>3.6</td>
</tr>
<tr>
<td>193</td>
<td>2.8</td>
</tr>
<tr>
<td>173</td>
<td>2.12</td>
</tr>
</tbody>
</table>
5. Coherence of the measurements. — 5.1 Internal coherence of NMR measurements. — The measurement of the dipolar relaxation time $T_{1DD}^0$ and of the $T_1^0$ relaxation time allows the evaluation of the quadrupole coupling constant of $C_3D_6$. The formulas (14), (20) and (21) allow to write:

$$\frac{T_{1DD}^0}{T_1^0} = 7.402 \frac{\tau_{CH}^0 (1 + x^2/3)}{4/3 \gamma_2^0 \hbar^2} \left(\frac{e^2 q Q}{h}\right)^2 \tau_Q / \tau_{CH}.$$ (23)

We have done the following hypothesis which involves $\tau_Q = \tau_{CH}$.

i) The principal axis of the gradient electric field tensor is along the CD bond of $C_3D_6$.

ii) The deuteration of the cyclopropane molecule does not change its orientational dynamic. We have also neglected the asymmetry parameter, a theoretical study [44] shows that its value was very small $-0.073$. Taking $r_{CH} = 1.089$ Å [45] we have deduced from the ratio $T_{1DD}^0/T_1^0$ a value of $(192 \pm 20)$ kHz for the quadrupole coupling constant whatever the temperature is. This value is in very good agreement with a recent measurement [46] in a nematic liquid crystal which gives $(184 \pm 20)$ kHz.

5.2 Agreement between the Raman and NMR measurements. — On figure 10, we have reported the logarithm of the correlation time $\tau_{CH}$ of the relaxation vector CH versus the temperature. It was deduced on the one hand from $^{13}$C relaxation time and deuteron relaxation time and computed on the other hand from $D_\perp$ and $D_\parallel$ deduced from the Raman measurements. One sees that the points lie on the same curve and that the agreement between all the techniques is fairly good. One can notice that this correlation time does not follow an Arrhenius law in the temperature range investigated. This good agreement between NMR and Raman gives some validity to the method of evaluation of the parameter $D_\parallel$ that we have used in this last technique. We have to stress, as was pointed out elsewhere as well [4] that the correlation time $\tau_{CH}$ is not very greatly influenced by the value of $D_\parallel$ near $\theta = 32.45$ degrees, the angle between the relaxation vector CH and the symmetry axis of cyclopropane. An error of $\pm 20\%$ on $D_\perp$ and $10\%$ on the correlation time $\tau_{CH}$ leads to a value of the reorientational anisotropy $D_{\parallel/\perp}$ between 5 and 12. In spite of these large errors, a large rotational anisotropy of the cyclopropane molecule is sure.

6. Discussion of the rotational model. — 6.1 Orientation dynamical of the molecular axis. — The rotational diffusion model which allows us to evaluate $D_\perp$ was suggested by the quasi-exponential behaviour of the orientational correlation function. However, this criterion is not sufficient. The evaluated $D_\perp$ must fulfill the fast modulation condition (cf. appendix) that can be written:

$$D_\perp^* < 1/\sqrt{6}$$ (24)

with

$$D_\perp^* = D_\perp \sqrt{\frac{T}{kT}}.$$ (25)

One can see in table I that this condition is always true. However a deeper analysis seems necessary. Let us recall that the strict rotational diffusion hypothesis leads to the verification of Hubbard's [47] relation:

$$D_\perp^* = \tau_{CH}^* \tau_{CH}^* = \tau_{CH}^* \sqrt{\frac{kT}{T}}$$ (26)

where $\tau_{CH}^*$ is the correlation time of the component of the angular velocity in the plane perpendicular to the molecular axis. Gordon's J model [48] which has been extended to symmetric tops [49] is more general. It assumes free rotor steps, interrupted by instantaneous collisions, perturbing both the orientation and magnitude of the angular momentum, and allows one to go from a quasi-free rotation for high angular momentum correlation time $\tau_j$ values, to the rotational diffusion limit in the opposite extreme. The calculations show that when $\tau_j^* \neq \tau_{CH}^* \neq 0.05$, Hubbard's relation is verified with a precision better than $5\%$ and the ratio of the vectorial correlation time to the second order tensorial one associated with the
motion of the molecular axis is \( \geq 2.93 \) instead of 3 as in the strict rotational diffusion limit. Thus, the condition \( D^{*} \leq 0.05 \) seems to constitute a good criterion of rotational diffusion hypothesis. This corresponds approximately to the \( \chi > 5 \) condition of the Gillien and Noggle test [50]. One sees in table I that this condition is fulfilled for temperatures less than 185 K. For greater temperatures the J model seems to be more adapted. Thus, at room temperature the correlation function computed from the ratio of the inertial moment of cyclopropane with \( \tau_{\text{rot}} = 0.2 \) is very near the experimental correlation function in a time range of the order of 1.5 ps (Fig. 4). It appears that the experimental constant \( D_{\perp} \) is not a real rotational diffusion constant but a parameter which is a function of \( \tau_{\text{rot}} \), \( D_{\perp} = f(\tau_{\text{rot}}) \tau_{\text{rot}} \). The quantity \( f(\tau_{\text{rot}}) \), near unity at low temperature, where the rotational diffusion model seems valid, falls to about 0.75 at room temperature.

6.2 ORIENTATIONAL DYNAMICS AROUND THE MOLECULAR AXIS. — If one equates the correlation time \( \tau_{\text{aniso}} \) associated with the anisotropic correlation function of the E" band, to an orientational correlation time, the vibrational relaxation effect being relatively small, the fast modulation condition (cf. appendix) is written:

\[
\tau_{\text{aniso}} > 1
\](27)

with

\[
\tau_{\text{aniso}} = \tau_{\text{aniso}} \left( \frac{5kT}{I} + \frac{kT}{I_{\perp}} \right)^{1/2} .
\](28)

Table II shows that this condition is fulfilled, the width of the band being less than the square root of its second moment. However, the values of

\[
D^{*} = D_{\perp} \sqrt{\frac{I_{\perp}}{kT}}
\]

are near 1 which excludes a rotational diffusion model for the motion of the molecule around its axis. One can show (Fig. 6) that within about 0.3 ps the experimental correlation function is very nearly the free rotor orientational function for a E" Raman band [16]. In this time range, the orientational dynamics around the axis seems to be a quasi-free rotation, and it is not possible to take into account such dynamics with a J model; indeed, the \( I_{\parallel} \) inertial moment of cyclopropane, greater than the \( I_{\perp} \) moment, should lead to rotational dynamics around the axis slower than the molecular axis itself, because the \( \omega_{\parallel} \) and \( \omega_{\perp} \) velocities are modulated by the same angular momentum correlation time \( \tau_{\text{rot}} \). This relatively free character of the rotation around the symmetry axis arises more probably from the symmetry of the intermolecular potential. The studies of the orientational dynamics of small oblate or prolate symmetric tops in the liquid state by NMR or, using Griffith’s method by NMR and Raman [11] leads generally to \( D_{\perp} \) and \( D_{\parallel} \) diffusion constants exhibiting the same characteristics as those of liquid cyclopropane, namely:

\[
D_{\parallel} > D_{\perp} \quad 0.2 \leq D^{*} \leq 1 .
\](29)

The rotational motion around the molecular axis which appears more free than the molecular axis itself does not follow the fast modulation condition and is qualified as an inertial rotation. We must emphasize the non-consistency of these kinds of results with the theoretical relations which allowed us to obtain them and which are based on the diffusion model. This inconsistency affects our work as well. Unfortunately, only the diffusion and J models are easily tractable. The development of theories better adapted to the description of the orientational dynamics of symmetric tops seems to us very desirable.

7. Comparison of the translational diffusion coefficient with the rotational diffusion coefficient versus the temperature. — The ratio of the translational diffusion coefficient \( D_{\text{trans}} \) to the rotational one \( D_{\perp} \) for cyclopropane increases strongly with temperature (Fig. 11). Such a behaviour is found for a number of simple liquids and is contrary to the one observed for strongly associated liquids (Fig. 11). It is important to try to extract a physical significance. Two different approaches were proposed in order to analyse the diffusion constants. The first, based on the hydrodynamic model, uses the Stokes-Einstein relation for the translational diffusion and the corresponding relation due to Debye [51] for the rotational diffusion; these relations connect the diffusion cons-
tants to the viscosity of the medium. However, these theories appear poorly adapted to the analysis of the motion of a molecule whose shape is of the order of magnitude of the surrounding molecules [52]. Thus, in the translational diffusion case one is led to introduce an empirical parameter, the so-called microviscosity coefficient, which allows one to correct the Stokes-Einstein relations [53, 54]. In the rotational case, the same approach leads to the use of an adjustable parameter [53, 55, 56]. These different corrections are formally related to the boundary conditions used to solve the Navier-Stokes: stick [57] or slip [58, 59] conditions. The existence of these adjustable parameters makes difficult the analysis of the evolution of the ratio of the diffusion coefficients $D_{\text{trans}}/D_{\perp}$.

The second is a microphysical approach. It is based on the extension of Enskog’s theories [60, 61] where molecules are supposed to be hard spheres suffering non-correlated instantaneous binary collisions. They assume that the repulsive part of the interaction potential plays a major role in the liquid dynamics. However, this model although well adapted to spherical molecules has not been extended to the symmetric rotors case.

We have to point out that recently one has tried to use the two kinds of approach simultaneously, the first model taking in account the effect of the far solvation layers, the second the effect of nearest neighbours [52].

Fortunately, one can try to analyse the evolution of the ratio $D_{\text{trans}}/D_{\perp}$ versus temperature without referring to these models. Indeed, one knows that:

$$D_{\text{trans}} = \frac{kT}{M} \tau_v$$

(30)

where $\tau_v$ is the linear velocities correlation time. In the strict rotational diffusion limit for a symmetric top molecule, a relation of the same kind connects the diffusion constant $D_{\perp}$ to the angular correlation velocities $\tau_{ao}$:

$$D_{\perp} = \frac{kT}{I_{\perp}} \tau_{ao}.$$  

(31)

On the other hand, the linear velocities correlation time can be connected in the Langevin model to the mean square force $\langle F^2 \rangle$ which acts on the particle and to the correlation time of this force $\tau_F$ [56, 62]:

$$\tau_v = \frac{kTM}{\langle F^2 \rangle \tau_F}.$$  

(32)

For a linear or a spherical top, there is a relation of the same kind between $\tau_{on}$ the mean square torque $\langle \Gamma^2 \rangle$ and the torque correlation time $\tau_F$ [56, 62]:

$$\tau_{ao} = \frac{kTI}{\langle \Gamma^2 \rangle \tau_F}.$$  

(33)

For the correlation time $\tau_{ao}$ of a symmetric top, one must add to previous equation a term containing the precession frequency of the angular momentum around the molecular axes, however, in the fast modulation limit, $\tau_{ao}$ is generally shorter than the mean free precession time, which allows one to consider the previous expression as a good approximation of $\tau_{ao}$ [56]. Thus,

$$D_{\text{trans}}/D_{\perp} = \frac{\langle \Gamma^2 \rangle \tau_{\perp}}{\langle F^2 \rangle \tau_F}$$

(34)

and if we assume as Kivelson et al. [56] that $\tau_F \simeq \tau_F$ one finds finally that

$$D_{\text{trans}}/D_{\perp} = \frac{1}{f(\tau^2)} \frac{\langle \Gamma^2 \rangle}{\langle F^2 \rangle}.$$  

(35)

This relation holds only for a diffusional motion of the molecular axis. However, if the rotation is not too far from a diffusional model, one can use the $f(\tau^2)$ factor computed with the J model which allows one to connect more precisely the $D_{\perp}$ parameter to the correlation time $\tau_{ao}$. Thus,

$$\frac{D_{\text{trans}}}{D_{\perp}} = \frac{1}{f(\tau^2)} \frac{\langle \Gamma^2 \rangle}{\langle F^2 \rangle}.$$  

(36)

For cyclopropane, $f(\tau^2)$ is a correction factor whose variation with temperature is very much less than the evolution of the ratio $D_{\text{trans}}/D_{\perp}$. So, the increase of the ratio when the temperature rises (Fig. 11) indicates a greater diminution of the mean square force than the mean square torque. This could result from a relatively more important role of the long range intermolecular forces in the $\langle \Gamma^2 \rangle$ term while the quadratic force remains dominated at all temperatures by the short range repulsive forces.

Recent findings indicate that the product $\tau_{20} D_{\text{trans}} = \frac{D_{\text{trans}}}{6 D_{\perp}}$ for cyclohexane increases with temperature. Arndt and McClung [67] concluded that the $\kappa$ parameter of Kivelson et al. [56] increases. This conclusion is in good agreement with ours because

$$\kappa = \frac{3}{4} \frac{\langle \Gamma^2 \rangle}{\langle F^2 \rangle};$$  

(37)

where $r^2$ is the hydrodynamic radius of the molecule. We have to point out finally that the fact that the ratio $D_{\text{trans}}/D_{\perp}$ increases with temperature can be associated with the result of Alms et al. [68, 69] showing that $\tau_{20}$ varies linearly with the viscosity but is not proportional to this value. Indeed, if $D_{\perp}$ was, as $D_{\text{trans}}$ inversely proportional to the viscosity, the hydrodynamic model should lead to a constant ratio of $D_{\text{trans}}/D_{\perp}$ if the other parameters-radius of the spherical molecule $\kappa$ and microviscosity parameter were also constant.
Acknowledgments. — The authors thank Dr Canet for the helpful discussion and assistance in the NMR measurements at the Nancy University. One of us (MB) thanks particularly Dr Canet for his kind hospitality. The help of Dr Lalanne, of the Dr Brevard and of the Société Bruker, Spectrospin (Wissembourg) for the deuteron NMR experiments was very much appreciated.

We thank also MM. Cavagnat, Cornut and Devaure for their technical assistance.

Finally, we acknowledge Dr Leicknam for his suggestions and for providing to us the computed free rotor Raman profile.

Appendix. — The rotational correlation function corresponding to an irreducible spherical tensor element $a_{lm}$ can be written:

$$G_{lm}(t) = \langle a_{lm}^*(0) a_{lm}(t) \rangle . \quad (A.1)$$

Taking the time derivative, one has:

$$\dot{G}_{lm}(t) = -i \langle a_{lm}^*(0) \omega(t) J a_{lm}(t) \rangle . \quad (A.2)$$

where $J$ is the rotational operator (angular momentum in h units) and $\omega$ the instantaneous angular velocity. After a simple transformation connecting $a_{lm}(t)$ with $a_{lm}(0)$ and $\omega(t)$ one obtains:

$$\dot{G}_{lm}(t) = - \langle a_{lm}^*(0) \rangle \int_0^t d\tau \langle \omega(t), J \rangle \langle \omega(\tau), J \rangle a_{lm}(\tau) \rangle . \quad (A.3)$$

This expression allows one to compute easily the second moment of the profile associated with $a_{lm}(t)$:

$$\ddot{G}_{lm}(0) = - \langle a_{lm}^*(0) (\omega(0) \cdot J)^2 a_{lm}(0) \rangle . \quad (A.4)$$

which leads for a symmetric top to:

$$M_{lm} = - \frac{\ddot{G}_{lm}(0)}{G_{lm}(0)} = m^2 \frac{kT}{I_\parallel} + [l(l + 1) - m^2] \frac{kT}{I_\perp} . \quad (A.5)$$

where $I_\parallel$ and $I_\perp$ are respectively the inertial moments around and about the molecular axis. Furthermore, if one assumes that the angular velocity correlation time is less than the orientational correlation time (fast modulation), one can separate the averages in the relationship (A.3). For a symmetric top, if one assumes that the principal axes of inertia are the principal axes of the tensor

$$\int_0^t \langle \omega(\tau) \otimes \omega(0) \rangle d\tau$$

where $\otimes$ symbolizes the direct product, one has

$$\dot{G}_{lm}(t) = - \int_0^t dt \langle \omega(t) - \tau \rangle G_{lm}(\tau) \quad (A.6)$$

with the following memory function

$$K(t) = m^2 \langle \omega_x(t) \omega_x(0) \rangle + [l(l + 1) - m^2] \langle \omega_x(t) \omega_x(0) \rangle . \quad (A.7)$$

Using the Laplace transform properties, it is easy to compute the profile corresponding to $G_{lm}(t)$ which is, according to the hypothesis made, lorentzian in a large frequency domain.

The correlation time is

$$\tau_{lm} = \frac{\int_0^\infty G_{lm}(t) dt}{G_{lm}(0)} \quad \frac{1}{\int_0^\infty K(t) dt} \quad (A.8)$$

and defining:

$$\tau_{\omega lm} = \frac{\int_0^\infty K(t) dt}{m^2 \frac{kT}{I_\parallel} + [l(l + 1) - m^2] \frac{kT}{I_\perp}} \quad (A.9)$$

one finds the generalized Hubbard's relation

$$\tau_{lm} \tau_{\omega lm} = \frac{1}{m^2 \frac{kT}{I_\parallel} + [l(l + 1) - m^2] \frac{kT}{I_\perp}} \quad (A.10)$$

The condition of validity of these relations, according to the previous hypothesis:

$$\tau_{\omega lm} \ll \tau_{lm}$$

can be written by specifying the diffusion constants:

$$D_{\parallel} = \int_0^\infty \langle \omega_x(0) \omega_x(t) \rangle dt \quad (A.11)$$

$$D_{\perp} = \int_0^\infty \langle \omega_x(0) \omega_x(t) \rangle dt \quad (A.12)$$

$$m^2 D_{\parallel} + [l(l + 1) - m^2] D_{\perp} < \left[ m^2 \frac{kT}{I_\parallel} + [l(l + 1) - m^2] \frac{kT}{I_\perp} \right]^{1/2} . \quad (A.13)$$

This is the condition of fast modulation. The half width at half height of the rotational profile must be smaller than the square root of its second moment.
References

[34] BUTCHER, R. J., JONES, W. J., J. Mol. Spectrosc. 47 (1973) 64.