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Dynamics of non-rigid molecules.**II. — Quasi-Elastic Neutron Scattering study of liquid cyclopentene**

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Résumé. — Le cyclopentène liquide a été étudié par diffusion quasiélastique des neutrons afin d'identifier, dans les profils observés, une éventuelle contribution de la dynamique interne d'inversion.

Pour de faibles valeurs du transfert de moment Q et à très haute résolution, le coefficient de diffusion translationnelle a été extrait. Ses valeurs, mesurées entre 298 et 128 K, sont en parfait accord avec celles mesurées par la technique d'écho de spin en RMN et conduisent à la relation : D ($\text{cm}^2 \cdot \text{s}^{-1}$) = $1,3 \times 10^{-3} \exp(-8653/RT)$ avec $R = 8,314 \text{ J} \cdot \text{degré}^{-1} \cdot \text{mole}^{-1}$. D'autre part, les réorientations d'ensemble de la molécule peuvent être décrites par un modèle de diffusion rotationnelle sphérique ($D_r = 6,2 \times 10^{10} \text{ s}^{-1}$ à 180 K). Enfin, une analyse précise des ailes du spectre permet de mettre en évidence une composante supplémentaire due à la dynamique d'inversion et correspondant à une fréquence moyenne de $1,1 \times 10^{12}$ sauts/s à 180 K. Cependant, le fait que la largeur de cette composante augmente avec Q révèle un processus plus complexe que le simple modèle de sauts instantanés entre deux positions d'équilibre.

Abstract. — Quasi-Elastic Neutron Scattering (Q.E.N.S.) measurements have been performed on liquid cyclopentene in order to detect an eventual contribution of the ring-puckering dynamics to the observed profiles.

For small momentum transfer values Q and at high resolution, the self-diffusion coefficient has been extracted between 298 and 128 K. Its values are in good agreement with those measured using the NMR spin-echo technique D ($\text{cm}^2 \cdot \text{s}^{-1}$) = $1.3 \times 10^{-3} \exp(-8653/RT)$, with $R = 8.314 \text{ J} \cdot \text{degree}^{-1} \cdot \text{mole}^{-1}$. Furthermore, it has been possible to describe reorientations of the whole molecule in terms of spherical rotational diffusion with a D_r value of $6.2 \times 10^{10} \text{ s}^{-1}$ at 180 K. Finally, a precise analysis of the wings of the Q.E.N.S. spectra at higher Q values allows a further component of the motion to be detected. It is due to the internal dynamics and corresponds to a mean jump rate of $1.1 \times 10^{12} \text{ s}^{-1}$ at 180 K. However, the Q -dependence of the width of this component indicates that the ring-puckering process does not occur by instantaneous jumps between two puckered conformations but certainly involves a more complicated diffusive model.

1. Introduction.

The results obtained in the last few years on the dynamics of rigid and rather symmetrical molecules such as cyclopropane [1] or methylene chloride [2] in the liquid state have shown the complementary rôles played by infrared (IR), Raman, NMR and Quasi-Elastic Neutron Scattering (Q.E.N.S.) spectroscopies in understanding translational, rotational and vibrational motion at the microscopic level.

The aim of the present work is to extend these methods to a non-rigid molecule, cyclopentene, which

undergoes a well-known ring-puckering motion in the gas phase [3, 4]. Only the Q.E.N.S. results are presented here, the NMR, IR and Raman studies being reported in separate papers [5, 6].

2. Theory.

The total scattering cross-section of the cyclopentene molecule is 842.5 barns, of which 797.4 come from the incoherent scattering of the protons. Therefore, only the individual dynamics of these protons are considered in the following.

The measured quantity, $d^2\sigma/d\Omega d\omega$, which is the number of neutrons scattered per unit solid angle $d\Omega$ and energy transfer $d\omega$ can be related to the incoherent scattering law $S_{\text{inc}}(\bar{Q}, \omega)$ and to the intermediate scattering law $I_s(\bar{Q}, t)$ according to the well-known expressions [7] :

$$d^2\sigma/d\Omega d\omega = Nb_{\text{inc}}^2 \frac{k}{k_0} S_{\text{inc}}(\bar{Q}, \omega) \quad (1)$$

$$S_{\text{inc}}(\bar{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_s(\bar{Q}, t) \exp(-i\omega t) dt \quad (2)$$

$$I_s(\bar{Q}, t) \propto \langle e^{-i\bar{Q}\cdot\mathbf{r}(0)} e^{i\bar{Q}\cdot\mathbf{r}(t)} \rangle. \quad (3)$$

In these expressions, the momentum transfer $\hbar\bar{Q} = \hbar(\bar{k} - \bar{k}_0)$ and energy transfer $\hbar\omega = \frac{\hbar^2}{2m} (k^2 - k_0^2)$ have their usual definition. N is the number of protons in the sample, m the mass of the neutron and b_{inc} the hydrogen incoherent scattering length. The brackets in (3) indicate a statistical average. It is convenient to expand the proton position vector $\bar{r}(t)$ into a sum :

$$\bar{r}(t) = \bar{R}(t) + \bar{d}(t) + \bar{u}(t) \quad (4)$$

where $\bar{R}(t)$ refers to the molecular centre of mass, $\bar{d}(t)$ to the distance between the scatterer and the centre of mass and $\bar{u}(t)$ to the vibrational amplitude vector. In the case of cyclopentene, one of the $3N-6$ internal vibrations contributes in a very special way to $\bar{u}(t)$ since it occurs in a double well potential energy function. In the gas phase the ring-puckering coordinate separation between the two energy minima is 0.23 Å and the energy barrier is of the order of 230 cm^{-1} (29 meV) [3, 4]. A very schematic representation of this motion and of the corresponding scattering law is given in figure 1. As the energy of thermal agitation in the liquid is of the order of magnitude of the ring-puckering barrier, the molecule is expected to perform several more or less damped oscillations around one of its bent conformations before jumping to the other.

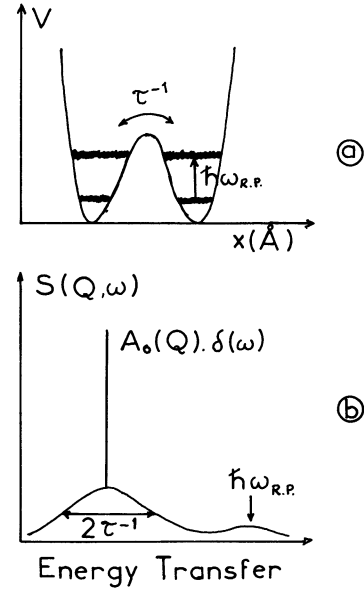


Fig. 1. — Ring-puckering motion in the liquid state. (a) Schematic representation of the potential energy function; (b) Corresponding neutron scattering spectral density. $\hbar\omega_{\text{RP}}$ is the energy transfer corresponding to the mean ring-puckering frequency.

The oscillations give rise to a maximum in the inelastic neutron scattering spectrum as well as in the IR and Raman spectra at about 170 cm^{-1} [8]. The jumps from one well to the other lead to a quasi-elastic broadening if they are faster than the observation time defined by the resolution of the spectrometer. This process is also characterized by a proton jump distance a (Fig. 2). With this qualitative description of the internal motion and as a starting hypothesis which will be discussed below, assuming that the whole molecule reorientations are isotropic, the thermal averages corresponding to the various motions can be performed separately giving :

$$I_s(\bar{Q}, t) = \langle \exp i\bar{Q}(\bar{R}(t) - \bar{R}(0)) \rangle \langle \exp i\bar{Q}(\bar{d}(t) - \bar{d}(0)) \rangle \langle \exp i\bar{Q}(\bar{a}(t) - \bar{a}(0)) \rangle \langle \exp i\bar{Q}(\bar{u}(t) - \bar{u}(0)) \rangle \quad (5)$$

or

$$I_s(\bar{Q}, t) = I_s^{\text{T}}(\bar{Q}, t) \cdot I_s^{\text{R}}(\bar{Q}, t) \cdot I_s^{\text{I}}(\bar{Q}, t) \cdot I_s^{\text{V}}(\bar{Q}, t)$$

where T, R, I and V stand respectively for translation, rotation inversion and vibration.

It follows that the total scattering law is the convolution product (symbol \otimes) of four contributions :

$$S_{\text{inc}}(\bar{Q}, \omega) = S^{\text{T}}(\bar{Q}, \omega) \otimes S^{\text{R}}(\bar{Q}, \omega) \otimes S^{\text{I}}(\bar{Q}, \omega) \otimes S^{\text{V}}(\bar{Q}, \omega). \quad (6)$$

The first term, derived from Fick's law, can be represented by the well-known Lorentzian form [7] :

$$S^{\text{T}}(\bar{Q}, \omega) = \frac{1}{\pi} \frac{D_{\text{T}} Q^2}{\omega^2 + (D_{\text{T}} Q^2)^2} \quad (7)$$

where D_{T} is the centre of mass diffusion coefficient. The second term is given by Sears' theory for spherical rota-

tional diffusion [9]

$$S^R(Q, \omega) = j_0^2(Qd) \delta(\omega) + \sum_{l=1}^{\infty} \frac{1}{\pi} (2l+1) j_l^2(Qd) \frac{l(l+1) D_r}{\omega^2 + [l(l+1) D_r]^2} \quad (8)$$

Where d is the mean radius of gyration of the different protons of the molecule (Fig. 2), D_r the rotational diffusion coefficient and $j_l(Qd)$ the spherical Bessel functions of order l .

The third term can be approximated by a jump model between two equivalent positions [7] :

$$S^T(Q, \omega) = A_0(Q) \delta(\omega) + [1 - A_0(Q)] \frac{1}{\pi} \frac{\tau^{-1}}{\omega^2 + \tau^{-2}} \quad (9)$$

Where τ^{-1} is the jump rate and $A_0(Q)$ the incoherent structure factor for the ring-puckering motion. As there are three types of proton jumps in cyclopentene, as represented in figure 2, after powder averaging, $A_0(Q)$ takes the following form :

$$A_0(Q) = \frac{1}{2} \left[\frac{1}{4} \left(1 + \frac{\sin Qa_1}{Qa_1} \right) + \frac{1}{2} \left(1 + \frac{\sin Qa_2}{Qa_2} \right) + \frac{1}{4} \left(1 + \frac{\sin Qa_3}{Qa_3} \right) \right] \quad (10)$$

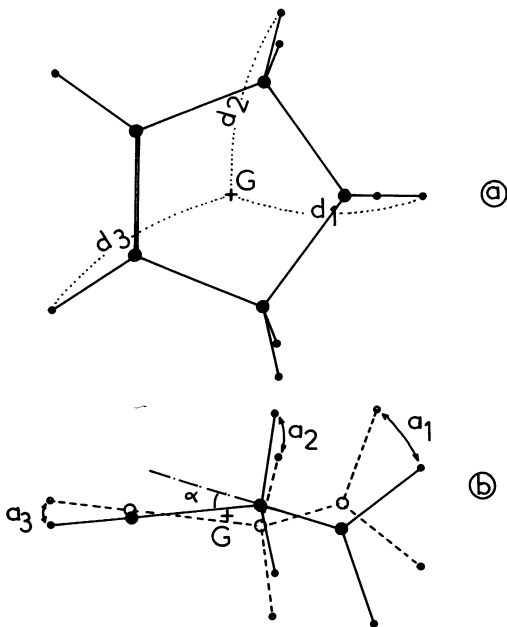


Fig. 2. — Geometry of the cyclopentene molecule in the gas state ($\alpha = 26^\circ$). (a) Definition of the mean radius of gyration $d = 2.16 \text{ \AA}$ from the three kinds of distances of the protons to the centre of mass : $d_1 = 2.105 \text{ \AA}$, $d_2 = 2.10 \text{ \AA}$ and $d_3 = 2.34 \text{ \AA}$; (b) In the jump process between the two puckered structures, three different jump distances for protons are also involved.

A bent conformation with a dihedral angle α of about $26 \pm 4^\circ$ has been deduced from several NMR studies [10, 12] yielding respectively $a_3 = 0.315 \pm 0.045 \text{ \AA}$, $a_2 = 0.73 \pm 0.10 \text{ \AA}$ and $a_1 = 0.95 \pm 0.14 \text{ \AA}$.

The fourth term concerns the vibrational degrees of freedom of the molecule which occur at higher frequency.

They contribute to the Q.E.N.S. intensity by a Debye-Waller factor $\exp(-\langle u^2 \rangle Q^2)$ where $\langle u^2 \rangle$ is the mean-square vibrational amplitude. This factor,

close to unity, can be neglected in so far as we are dealing with relative intensities.

Finally, the total scattering law is characterized by the convolution products of the translational Lorentzian component (7) with two other profiles having elastic components superimposed on a quasi-elastic profile. The individual incoherent structure factors for rotation $j_0^2(Qd)$, and for inversion, $A_0(Q)$, are represented in figure 3a.

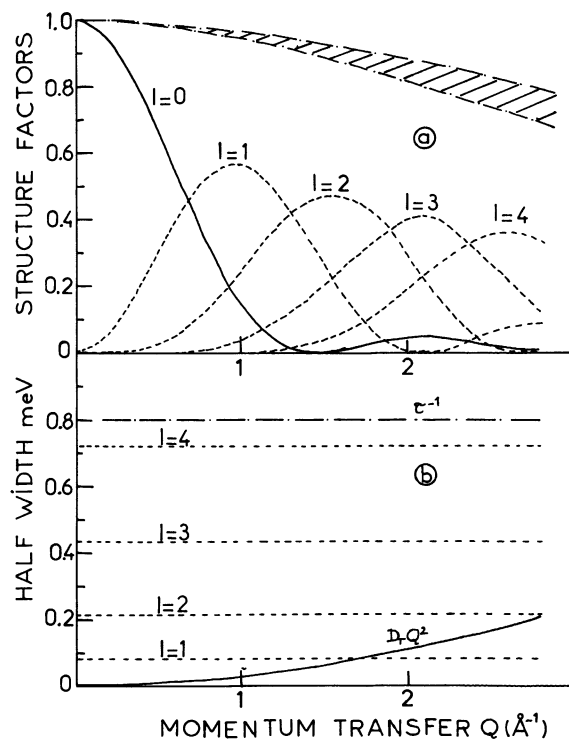


Fig. 3. — (a) Theoretical structure factors : $A_0(Q)$ associated with the internal motion between two conformations characterized by $\alpha = 26 \pm 4^\circ$ (dashed area), $j_l^2(Qd)$: terms of Sears' model; (b) Comparison of the quasi-elastic widths associated with the translational (solid line), rotational (dots) and internal (dashes, dots) motions.

Even if the ring-puckering motion is fast enough to give detectable broadening, it is clear from figure 3a that the relatively slow decrease of its structure factor $A_0(Q)$ will make its quasi-elastic contribution very weak.

One of the aims of the present work is to see whether this contribution can be detected among all the other dynamical contributions (and within the framework of this simplified dynamical model).

We have chosen to investigate mainly the liquid at low temperature for two reasons. First, on the basis of our other studies [5, 6], the activation energy of the internal motion is expected to be lower than those of the translational and rotational motions, in such a way that a better differentiation of the internal and external quasi-elastic components will be obtained at low temperature. Secondly, the population of the ring-puckering levels will be larger below the barrier, making the system closer to the jump model described in figure 1.

3. Experimental part.

The Q.E.N.S. experiments were performed at the Laue-Langevin Institute, Grenoble with the back-scattering machine IN 10 [13] and the multichopper time-of-flight spectrometer IN 5 [14] under the experimental conditions summarized in table I. The cyclopentene sample was carefully distilled before its introduction into a thin-walled circular aluminium cell.

The data reduction was performed with the standard programs available at Grenoble [15]. No correction was made for multiple-scattering because the transmission was always kept at about 90 %. NMR spin-echo measurements were also performed on the proton resonance line at 60 MHz according to the method described previously [16].

4. Results.

4.1 CENTRE OF MASS TRANSLATIONAL DIFFUSION. — The self-diffusion coefficient D_T was evaluated from several different sources : NMR spin-echo data taken between 296 and 182 K, high-resolution Q.E.N.S. spectra (IN 10) obtained in the same temperature range, and finally medium resolution Q.E.N.S. spectra (IN 5) analysed at small Q values. The NMR spin-

echo data were obtained with reference to water or to pentane according to the temperature range investigated [16].

The high resolution Q.E.N.S. experiment is limited by its narrow energy window. Therefore, reliable data could only be obtained at low temperature and for small scattering angles. The experimental points were fitted by a Lorentzian folded with the instrumental resolution given by a standard vanadium plate. The temperature of 128 K corresponds in principle to the plastic phase of cyclopentene since fusion occurs at 138 K [17]. However, a supercooled liquid phase is easily obtained by cooling and such is the case in this experiment, as checked by subsequent temperature cycles : when cyclopentene was really in its plastic phase, only elastic scattering was observed. This does not exclude the presence of a broad rotational component giving a flat background but indicates that with the available resolution, no translational motion can be detected in the plastic phase.

Finally, with the IN 5 time-of-flight spectrometer working at $\lambda_0 = 10 \text{ \AA}$, the profiles of the small-angle spectra are also quite nicely fitted by a simple Lorentzian.

The results of these fits at 182 K are reported in figure 4 in the form of a ΔE versus Q^2 plot. The half-width of the Lorentzian ΔE follows a straight line up to Q values of $\sim 0.5 \text{ \AA}^{-1}$ but above this value there is a positive deviation from the linear relationship. This indicates the progressive appearance of another quasi-elastic component of rotational and/or conformational origin.

As is usual, the D_T value is extracted from the initial slope of the line. A comparison of the three series of measurements is reported in figure 5 yielding the relation :

$$D (\text{cm}^2 \cdot \text{s}^{-1}) = 1.3 \times 10^{-3} \exp\left(\frac{-8653}{RT}\right) \quad (11)$$

where R is the gas constant = $8.314 \text{ J} \cdot \text{degree}^{-1} \times \text{mole}^{-1}$.

The D_T values found for cyclopentene are quite consistent with those obtained for other similar liquids as already explained in reference [16].

Table I. — *Experimental conditions for the Q.E.N.S. experiments.*

Instrument	λ_0 (Å)	Investigated $\hbar\omega$ range (meV)	Investigated $\hbar Q$ range (Å ⁻¹)	Resolution FWHH (μeV)	Transmission of sample (*)	Investigated temperatures (K)
IN 10	6.28	$\pm 1.2 \times 10^{-3}$	0.315, 0.740	1.29, 1.08	0.85	182, 124
IN 5	10.03	- 0.23 to 2.5	0.13 to 1.1	18	0.87	182
IN 5	5.015	- 2.2 to 3.8	0.218 to 2.27	188	0.89	179

(*) Measured experimentally from the monitor counts and by comparison with the transmission of the standard vanadium plate.

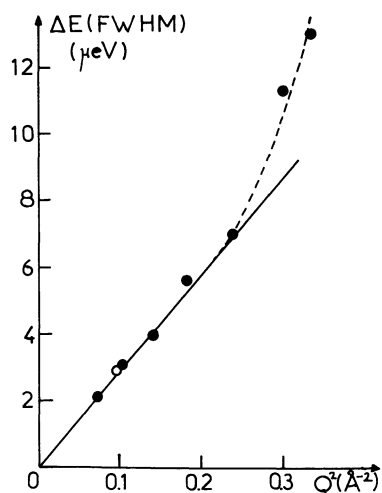


Fig. 4. — Halfwidth ΔE of a single Lorentzian fit (convoluted with the resolution) plotted versus Q^2 at 182 K for the back-scattering experiment (○) and for the time-of-flight experiment (●).

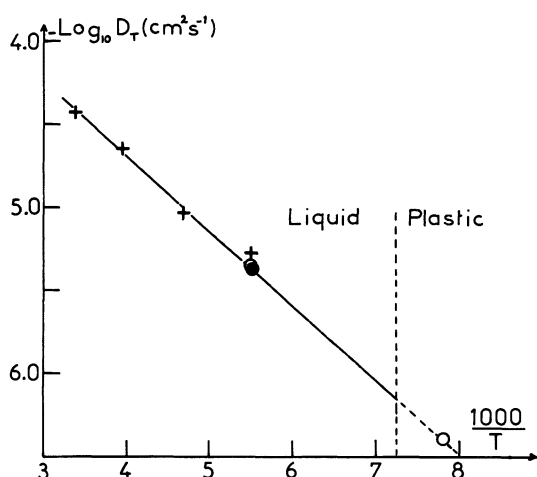


Fig. 5. — Comparison of the NMR (+), high resolution Q.E.N.S. (○) and good resolution Q.E.N.S. (●) determination of D_T . The vertical dotted line indicates the temperature of fusion. The point obtained below this temperature corresponds to the supercooled liquid.

4.2 REORIENTATIONAL MOTIONS. — Several arguments are in favour of a model of spherical rotational diffusion (8) for cyclopentene.

From IR and Raman band-shape analysis, it has been shown that the three rotational diffusion constants have very close values [6]. The same conclusion has been reached from a ^{13}C T_1 NMR study [5]. It must be also pointed out that quasi-isotropic molecular rotations have been found for the rather similar molecules of furan and thiophene [18].

Further, our previous experience with cyclopropane [1] and the detailed work of Brier and Perry on methylene chloride [2] indicate that Q.E.N.S. is even less sensitive than the previous spectroscopic

techniques to a small anisotropy of reorientation. Therefore the spherical rotational diffusion model has been adopted. It involves only one parameter, D_r , since the radius of gyration is rather well known (Fig. 2).

Q.E.N.S. analysis has first been performed on the time-of-flight experiment obtained at 182 K with the best resolution (18 μeV) and up to moderate Q values. Indeed, in this case the influence of the ring puckering motion must be negligible since $A_0(Q)$ is close to 1 (Fig. 3) and we are left with a convolution product of the translational and rotational scattering laws.

Every individual spectrum is fitted separately and very good agreement is obtained between the calculated and experimental spectra at all Q values. Furthermore, the fitted D_r values lie in a narrow range : $D_r = (5.5 \pm 0.8) \cdot 10^{10} \text{ s}^{-1}$, justifying *a posteriori* the validity of the model.

It must be pointed out that if the D_T value of $4.4 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ is varied by more than 5% in the above fitting procedure, the agreement is noticeably less good even with small compensating variations of D_r . Hence, the values of D_T and D_r seem to be rather precisely determined.

4.3 RING-PUCKERING MOTION. — It is then interesting to analyse the data obtained at nearly the same temperature, 179 K, but with an intermediate resolution (188 μeV) and in a larger Q range.

In this case, the fitted D_r values are systematically higher ($D_r \approx 6.4 \times 10^{10} \text{ s}^{-1}$) and the presence of an additional component can be inferred.

The jump model [7] between two positions has been introduced to take account of this extra-broadening in terms of the internal dynamics of the molecule.

A great number of simulations of the experimental profiles have been performed according to whether the parameters D_r , τ^{-1} or $A_0(Q)$ are varied altogether or separately. A systematic result has been obtained for τ^{-1} in any situation. This quantity, which is the halfwidth of the Lorentzian in the jump model, is found to increase from about 0.4 ± 0.2 to $1.1 \pm 0.2 \text{ meV}$ when Q increases from 0.6 to 2.2 \AA^{-1} (Fig. 6).

5. Discussion.

In earlier work on the rigid molecule of cyclopropane [1, 16] we have shown that the Q.E.N.S. results obtained on the long time translational dynamics are fully consistent with those deduced from the macroscopic NMR measurements, provided a certain number of conditions are fulfilled :

(I) $Qd < 1$ so that the translational component can be analysed when $j_0^2(Qd)$ is the dominant term in the Bessel expansion (8). For cyclopentene which has a radius of gyration of 2.16 \AA , this means that the value of D_T determined for $Q \leq 0.5 \text{ \AA}^{-1}$ makes not only the $j_0^2(Qd)$ term predominant but ensures an $A_0(Q)$ value close to 1 (Fig. 3a).

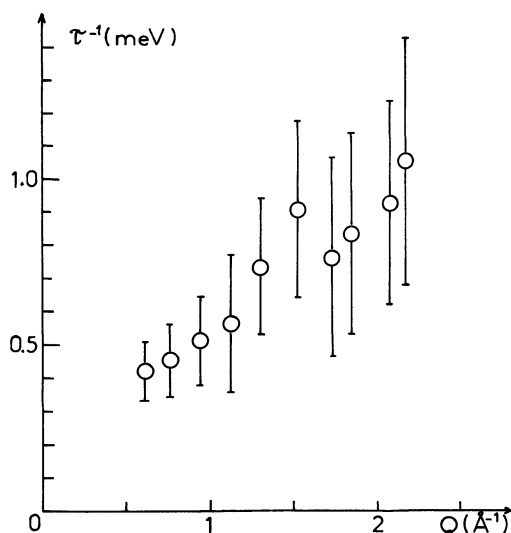


Fig. 6. — Momentum transfer dependence of the half-width τ^{-1} of the Lorentzian associated with the jump process. The error bars correspond to the range of τ^{-1} values found by varying the parameters $A_0(Q)$, d , D_T and D_r inside their own error bars.

(II) $D_T Q^2 < D_r$ for a clear separation of the translational and rotational quasi-elastic components. Figure 3b indicates that this condition is fulfilled for an even larger Q range ($\leq 1 \text{ \AA}^{-1}$) and that we have also $D_T Q^2 \ll \tau^{-1}$.

(III) $D_T Q^2 \geq 1/5$ of the instrument resolution for an accurate measurement of the broadening. This condition was well satisfied for the two Q.E.N.S. experiments at high ($1 \mu\text{eV}$) and good ($18 \mu\text{eV}$) resolution (Fig. 3b).

Therefore, it is not surprising that good agreement has been found between the Q.E.N.S. D_T values and the NMR macroscopic ones. Nevertheless a strong hypothesis is made in the following analysis, namely that the $D_T Q^2$ law holds up to Q values of about 2.2 \AA^{-1} .

Once D_T has been accurately determined, it is important to consider the validity of the D_r measurements within the frame of the simplified isotropic reorientation hypothesis. Apart from the good simulation of the experimental spectra by the calculated ones, it can be noted that the D_r value which is deduced ($(5.5 \pm 0.8) \cdot 10^{10} \text{ s}^{-1}$ at 180 K) is in very good agreement with the values found at the same temperature not only from the IR and Raman band-shape analysis ($(5.6 \pm 0.4) \cdot 10^{10} \text{ s}^{-1}$ [6] but also from the $^{13}\text{C } T_1$ NMR data [5].

This agreement, already noted for cyclopropane [1], cannot be fortuitous. It can also be pointed out that for cyclopentene it occurs at lower Q values ($< 1.1 \text{ \AA}^{-1}$) and at good resolution.

As soon as the Q.E.N.S. profiles are considered in larger energy and momentum transfer ranges, the specific non-rigidity of cyclopentene manifests itself

by the presence of a new quasi-elastic component associated with the ring-puckering motion. This component has a relatively weak intensity. Nevertheless, the best proof of its existence is given by the fact that variations of the various parameters $A_0(Q)$, d , D_T and D_r inside their error limits cannot reproduce the entire profiles satisfactorily.

An illustration of the different contributions is given in figure 7 for the particular momentum transfer value of 1.5 \AA^{-1} . The small differences which exist between the profiles with or without the ring-puckering contribution illustrate the difficulty of the analysis.

The real situation is represented in figure 8 where the fitted scattering law including the ring-puckering contribution and the convolution by the resolution function is compared with the experimental points for two characteristic scattering angles of the time-of-flight experiment at 179 K.

A clearer separation could possibly be achieved in two different ways :

— either by freezing some internal degrees of freedom in the plastic phases which exist for all these non-rigid small cyclic molecules [17],

— or, by choosing molecules having slower external dynamics and larger amplitudes for the internal motion. Such is the case for cyclic molecules of larger size but the conformational dynamics then become much more complex [19].

From a theoretical point of view, we are aware that the jump model may only be a very crude description of the internal motion of a molecule in the liquid state. This model was taken as a working hypothesis which had the advantage of involving only one parameter : the jump rate τ^{-1} . Actually, the experimental results seem to indicate that τ^{-1} has a momentum transfer dependence : it increases with Q as

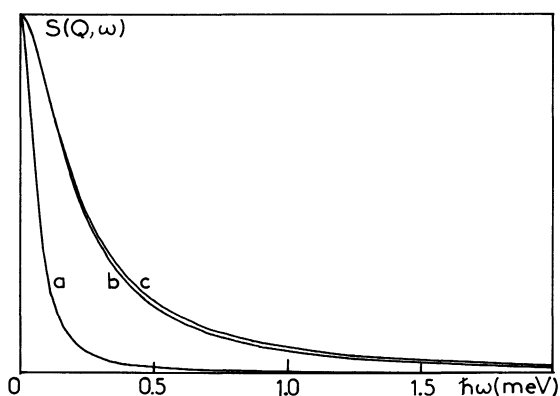


Fig. 7. — Simulation of the Q.E.N.S. profiles at $Q = 1.5 \text{ \AA}^{-1}$ and $T = 182 \text{ K}$ corresponding to : (a) the translational component alone; (b) the translational component folded with the rotational one; (c) the convolution product of the three contributions; translational, rotational and internal. Only the positive half of the incoherent symmetrized scattering law is shown and all the profiles are scaled to the same maximum.

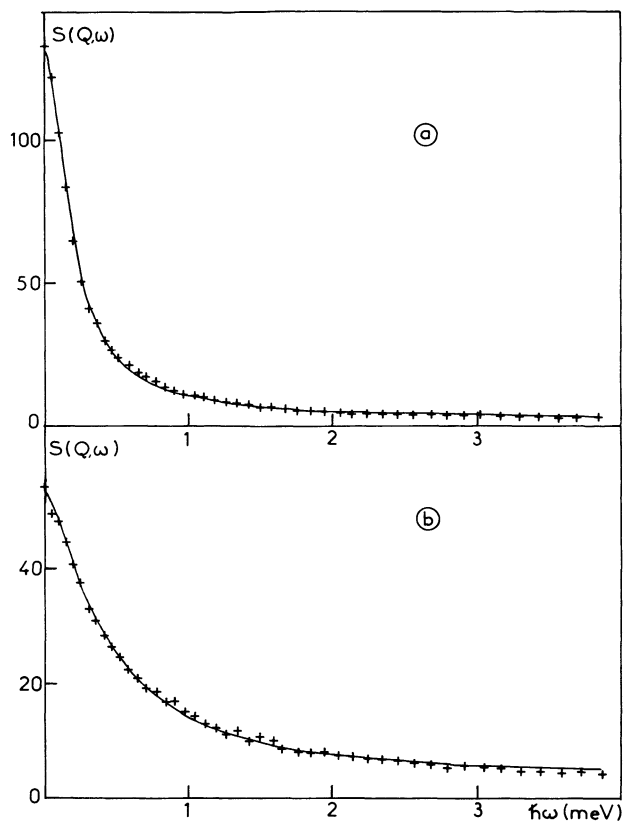


Fig. 8. — Fit of the experimental scattering law (crosses) by the complete model (solid line) for two scattering angles : (a) $2\theta = 63^\circ$, $Q = 1.31 \text{ \AA}^{-1}$ at $\hbar\omega = 0$; (b) $2\theta = 112^\circ$, $Q = 2.08 \text{ \AA}^{-1}$ at $\hbar\omega = 0$.

expected for any bounded diffusive motion. Some kind of diffusion of the protons on an arc of a circle could for example be invoked. However, the accuracy of the present experiments makes the usefulness of such theoretical refinements questionable.

The main conclusion remains that an extrabroadening due to the internal ring-puckering motion has been detected and that a mean jump rate of $(1.1 \pm 0.5) \cdot 10^{12} \text{ s}^{-1}$ is deduced at 180 K. This order of magnitude is in good agreement with an independent evaluation made in the previous paper from ^{13}C T_1 NMR relaxation time measurements [5]. It would be, however, interesting to repeat Q.E.N.S. measurements in a larger Q range and at several temperatures to take advantage of the unique ability of this technique to unravel the mechanism of the internal motion.

A more detailed discussions of the complementarity of the various techniques, NMR, Q.E.N.S., IR and Raman, will be given in the following papers [6, 20] with special emphasis on the method of selective deuteration [21] to study the dynamics of non-rigid molecules in the condensed state.

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