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MOLECULAR REORIENTATION OF COMPRESSED GASEOUS $CHCl_3$

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Infrared measurements of the chloroform fundamental vibration $\nu_1(A_1)$ band in mixtures with He, Ar, N_2 as the function of foreign gas pressure have been carried out. The correlation functions, the second moments and the orientational correlation times have been determinated from the band profile at pressure 60, 100, 150, 250, 500, 1000 and 1500 10^5 N/m^2. The J-diffusion model was used to describe the experimental angular position correlation function. Very accurate fittings were obtained at low densities. At high densities the band shape is predominantly determined by vibrational relaxation.

1. *Introduction*

Molecular reorientation in liquids and gases has been investigated by various techniques, such as NMR, IR absorption, Raman and Rayleigh scattering, neutron diffraction etc. To obtain detailed information about the time dependence of molecular motion and establish an experimental basis for testing theoretical models, it is necessary to use pressure, temperature and concentration as variables. There are numerous experimental studies in this field, but still there are many questions to be answered.

Chloroform is a standard substance for examination due to its simplicity. (*i*) It is a symmetric top molecule, and for this kind of molecules there exist reorientation relaxation models [1, 2]. Therefore, it is possible to compare experimental results with theoretical predictions. (*ii*) C—H oscillation appears especially convenient for investigation in IR and Raman spectroscopy. Chabbal and Barchewitz [11] have shown that the vibrational energy of chloroform at 3020 cm^{-1} ($\nu_1(A_1)$) mode is nearly entirely localized in the discussed oscillations. (*iii*) According to Brodbeck et al. [3] rotation-vibration coupling in this oscillation as well as interoscillator coupling are negligible. Hence, it appears possible to eliminate the vibrational relaxation contribution to the Raman line shape by the standard method [4]. The last advantage, valid for Raman spectroscopy only, caused many studies on molecular motion in haloforms to be performed by Raman band-shape analysis using the correlation

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function approach [3, 5–10]. In those measurements IR spectroscopy plays a subsidiary part. A review of former experimental results together with a discussion of possible models for orientational motion are assembled in Ref. [9].

Despite numerous investigations the problem of the reorientational relaxation in $CHCl_3$ is still unresolved. In dense liquids molecular motion is quite complicated, whereas in gases it can be rather simply described. As the collisional frequency between molecules in the gas phase increases their motion approaches the motion in the liquid phase. Such a process can be achieved by changing the total pressure. When the pressure increases the gaseous spectrum changes and at a large enough pressure it looks like a liquid phase spectrum. A comparison of an experimentally obtained spectrum (or correlation function) with a spectrum (or correlation function) predicted by the extended diffusion model, enables us to determine the character of the rotational relaxation process.

In the gaseous phase we can neglect the vibrational relaxation process [12–14] and we can assume that the infrared band contour provides information on rotational motion only. Moreover, high pressure infrared measurements are less complicated than Raman ones. That is why we have decided to investigate the C—H vibration absorption band of $CHCl_3$ in the vapour phase as a function of pressure.

2. *Data reduction and results*

A. Introduction

The shape of the absorption band of a molecule gives the Fourier transform of the appropriate correlation function of the transition dipole moment $\vec{\mu}$:

$$\phi(t) = \frac{\langle \vec{\mu}(t) \cdot \vec{\mu}(0) \rangle}{\langle \mu^2(0) \rangle} = \frac{\int I(\omega) \exp [i(\omega - \omega_0)t] d\omega}{\int I(\omega) d\omega} . \tag{1}$$

$I(\omega)$ is the absorption intensity at frequency ω and ω_0 is the frequency of the band center. In the infrared region $I(\omega)$ is defined as:

$$I(\omega) \sim n(\omega) \cdot k(\omega) \cdot \coth \left(\frac{\hbar\omega}{2kT} \right),$$

where $n(\omega)$ and $k(\omega)$ are the real and imaginary parts of the complex refractive index. For the band studied the term $\coth \left(\frac{\hbar\omega}{kT} \right)$ equals 1 and in the gaseous phase $n(\omega)$ is constant in the observed frequency range. Thus $I(\omega) \sim k(\omega) = \frac{\varepsilon(\omega)}{\omega}$, where $\varepsilon(\omega)$ is the absorption coefficient defined as:

$$\varepsilon(\omega) = \frac{1}{p \cdot l} \ln \frac{J_0(\omega)}{J(\omega)} .$$

$J_0(\omega)$ and $J(\omega)$ are the transmittances at the frequency ω of the baseline and of the band, p is the density of the absorbing molecules and l is the absorption length.

Since the change of the dipole moment $\vec{\mu}$ results from the variation in its orientation $\hat{\mu}$ and in its magnitude m, Eq. (1) can be written as follows

$$\phi(t) = \langle \vec{\mu}(t) \cdot \vec{\mu}(0) \rangle = \langle \hat{\mu}(t) \cdot \hat{\mu}(0) \rangle \cdot \langle m(t) \cdot m(0) \rangle = G_{\mathrm{rot}}(t) \cdot G_{\mathrm{vib}}(t). \tag{2}$$

$G_{\mathrm{rot}}(t)$ and $G_{\mathrm{vib}}(t)$ denote the rotational correlation function and vibration correlation function respectively. Such separation of both relaxation functions is possible only if the vibration-rotation coupling can be neglected. Brodbeck et al. [3] found that the coupling in haloform C—H oscillations are negligible. In many respect papers [12–14] both phenomena (G_{rot}, G_{vib}) were attracting a good deal of attention and a conclusion that for dilute gases in the picosecond time region $G_{\mathrm{vib}}(t) = 1$ is drawn. This means that $\tau_{\mathrm{vib}} \gg \tau_{\mathrm{rot}}$ ($\tau_{\mathrm{vib}} = \int_0^\infty G_{\mathrm{vib}}(t)dt$; $\tau_{\mathrm{rot}} = \int_0^\infty G_{\mathrm{rot}}(t)dt$).

Thus the correlation function (1) describes rotational relaxation process only and consequently:

$$\phi(t) = G_{\mathrm{rot}}(t).$$

In nature chloride appears mainly in the form of two isotopes ^{35}Cl and ^{37}Cl. Chloroform has four isotopes species $CH^{35}Cl_3$ — 42.9%, $CH^{35}Cl_2{}^{37}$ Cl — 42.0%, $CH^{35}Cl^{37}Cl_2$— 13.7%, $CH^{37}Cl_3$ — 1.4%.

Isotopes splitting of ν_1 is insignificant and is less than 0.1 cm^{-1} [16, 17]. Therefore no isotopes correction was applied.

The ν_1 band is disturbed by three hot bands [18], but due to their small intensities we are able to assume that the Fourier transform of the ν_1 band shape represents rotational relaxation unperturbed by the hot bands.

B. Pressure measurements

The IR bands were obtained using a UR-20 spectrophotometer. The high pressure optical cell with sapphire windows was described in a previous publication [19]. The working pressure was up to 3×10^8 N/m^2 (3 kbar). Pressure measurements were determined with two independent Bourdon type gauses and with one resistance manometer built from a manganin coil with a 1×10^5 N/m^2 accurancy up to 5×10^7 N/m^2 and 1×10^6 N/m^2 above 5×10^7 N/m^2. Vapour of spectroscopically pure chloroform at a pressure of $0.3 \times \times 10^5$ N/m^2 was compressed by He, Ar, N_2 up to 1.5×10^8 N/m^2. The cell was termostated at the temperature 30°C. He, Ar, N_2 were commercial products without further purification. The spectra of the pure broadener gases were taken and were found to give a straight horizontal baseline in the investigated frequency region.

The spectra were recovered in digital form on paper tape. For each set of physical conditions 15 runs were numerically averaged. The spectral resolution in our measurements was 5 cm^{-1}. The correlation functions have been deconvoluted with a slit function by means of the Fourier transform method, but in Fig. 1 the band shapes have been reproduced without any correction.

From the measured spectra apart from the correlation functions, integrated intensities A

$$A = \int_{\text{band contour}} \varepsilon(\nu)d\nu, \tag{3a}$$

second moments

$$M(2) = \frac{\int \varepsilon(\nu)\cdot(\nu-\nu_0)^2 d\nu}{\int \varepsilon(\nu)d\nu}, \tag{3b}$$

and correlation times

$$\tau_{\text{exp}} = \int_0^\infty \phi(t)dt \tag{3c}$$

were determined.

C. Band contours

Fig. 1 and 2 contain examples of the measured absorption band shapes of chloroform at different pressures. The first presents band contours in mixtures with helium, the next in mixtures with nitrogen. The number of absorbing molecules in the cell during measurements was in every case the same. It means that the band shape is sensitive to changes in foreign gas pressure only. The modifications of the band shape indicate that helium is a weaker perturber than nitrogen, and the analysis of the values of total band intensity and second moment (Table I) indicates that argon is stronger than nitrogen. The same

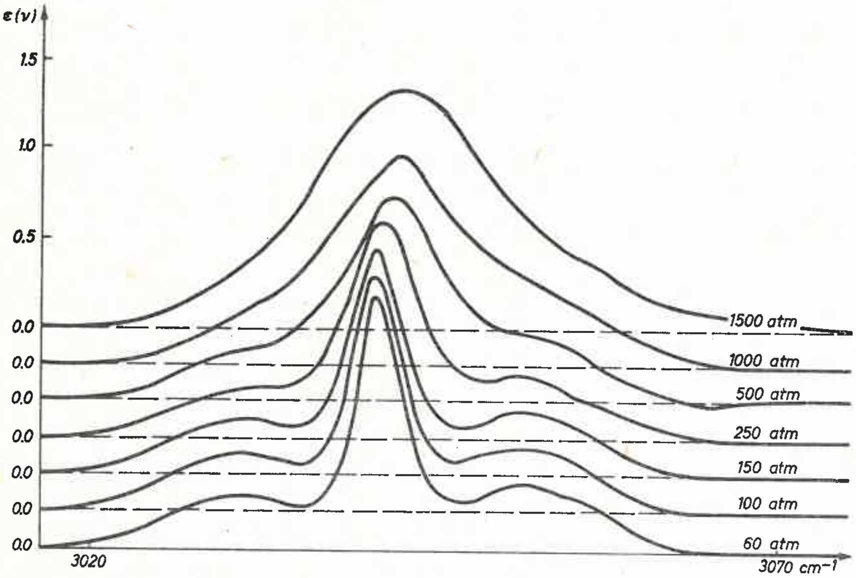

Fig. 1. Band contours of C—H vibrations for $CHCl_3$ perturbed by He

result was confirmed for OCS by Clermontel et al. [12], for CH_3D by Levi and Chalaye [14] and for CS_2 by Żerda et al. [19].

At low pressures we can distinctly observe the *P*, *Q*, *R* branches. Then as the pressure of the foreign gas increases the *Q* branch broadens and its intensity grows and at large enough pressures no distinct structure can be observed. The total intensity also increases and in the case of $CHCl_3+N_2$ at 1.5×10^8 N/m² it is nearly 8 times larger than without any broadener (see Table I). This process is accompanied by increasing the band's asymmetry which in mixtures with helium is small even at 1.5×10^8 N/m², but in argon and nitrogen it is significant already at 1.5×10^6 N/m². Judging from the band shapes one can suppose that a new band appears at 3090 cm⁻¹. This is especially clear at 1.5×10^8 N/m² (Fig. 3a). The same asymmetry can be seen in the spectrum of liquid chloroform dissolved in CCl_4 (Fig. 3b and Fig. 3 in the Ref. [5]). In bromoform and deutero-chloroform the discussed asymmetry is also observable but it is not so strong as in chloroform. It is worth noting that the Raman spectrum of C—H vibrations are nearly completely symmetric [9, 10]. We have tried to explain the nature of the hypothetical band utilizing the molecular constants for $CHCl_3$ [18, 25] but without success. Also, the possibility that the hydrogen bonded C—H vibration produces this additional absorption is hardly admissible [9].

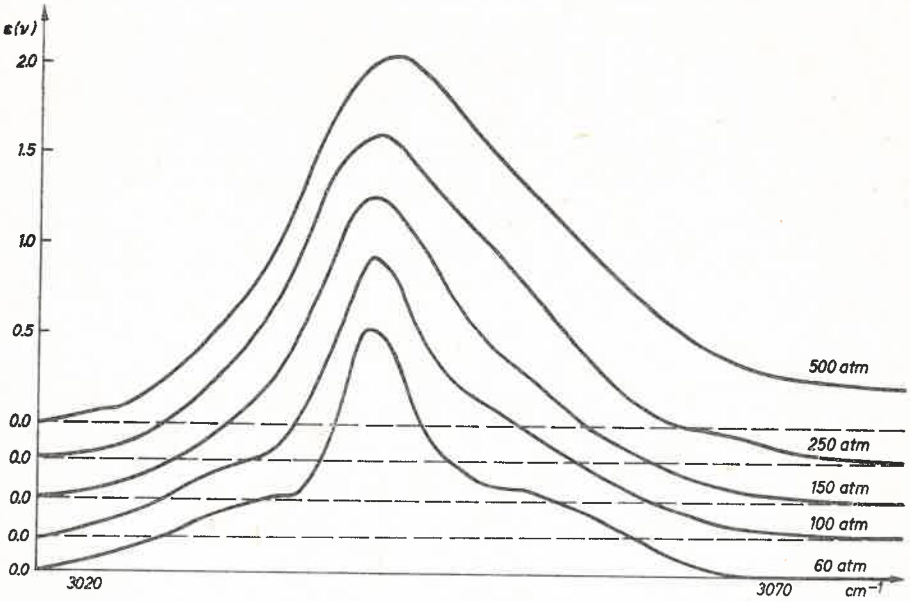

Fig. 2. C—H band contours for $CHCl_3$ perturbed by N_2

In liquid chloroform the C—H band is centered at 3020 cm⁻¹, in the gaseous phase at 3033 cm⁻¹, but when the total pressure increases the center shifts toward the high frequency side. This shift cannot be explained by increasing asymmetry. To our knowledge "blue" shifts caused by pressure are seldom observed.

TABLE I

Pressure dependence of C—H band intensites, moments and correlation times of $CHCl_3$ perturbed by He, Ar, N_2

Gas	Total pressure p [bar]	Band center ν_0 [cm^{-1}]	Total intensity A[a]	Second moment $M(2)$ [cm^{-2}]	Correlation time τ_{exp} [psec]	Angular momentum correlation time τ_J	
						[psec]	$\left[\left(\frac{I_\perp}{kT}\right)^{\frac{1}{2}}\right]$
$CHCl_3$	0.3	3033	14.2	75.5	b	c	c
$CHCl_3+He$	60	3033	14.1	66.4	1.52	5.6	7±2
	100	3033	13.1	65.5	1.56	4.8	6±1
	150	3033.5	13.2	68.3	1.47	3.6	4.5±0.5
	250	3034.5	15.1	53.3	1.46	3.2	4±0.3
	500	3034	19.3	66.4	0.99	2.8	2.5±1
	1000	3034	25.9	73.3	0.94	unfitable	unfitable
	1500	3034.5	33.7	97.6	0.74	unfitable	unfitable
$CHCl_3+N_2$	60	3033	16.0	75,8	1.41	3.6	4.5±0.5
	100	3033	16.7	72,2	1.01	2.6	3.3±0.5
	150	3034	23.3	75.9	0.87	unfitable	unfitable
	250	3035	39.0	233.0	0.66	unfitable	unfitable
	500	3035	68.2	340.0	0.57	unfitable	unfitable
	1000	3036	93.4	866.0	0.38	unfitable	unfitable
	1500	3036	137.7	1400.0	0.30	unfitable	unfitable
$CHCl_3+Ar$	60	3033	14.2	72.5	1.11	3.04	3.8±1
	100	3033.5	15.2	88.1	0.87	unfitable	unfitable
	150	3034	18.3	86.9	0.87	unfitable	unfitable
	250	3034.5	27.8	315.0	0.52	unfitable	unfitable
	500	3035	49.8	1805.0	0.30	unfitable	unfitable
	1000	3035	68.7	1730,0	0.28	unfitable	unfitable
	1500	3036	118.8	1820.0	0.22	unfitable	unfitable

[a] Total intensities A are not absolute values. We were not able to determine precisely the pressure of chloroform vapour. [b] It is impossible to calculate τ_{exp} precisely, $\phi(t)$ does not tend towards the time axis. [c] In this case the correlation function can be compared with the theoretical function of a freely rotating molecule ($\tau_J = \infty$).

As has been already mentioned the total intensity increases above some pressure. This can be interpreted as the creating of the vibrational relaxation process in $CHCl_3$ when the intermolecular distances are small enough. The Fourier transform of Eq. (2) gives the following expression:

$$\mathscr{F}[\phi(t)] = \mathscr{F}[G_{\mathrm{vib}}(t) \cdot G_{\mathrm{rot}}(t)] = (I_{\mathrm{vib}} * I_{\mathrm{rot}})(\omega),$$

where $\mathscr{F}$ denotes the Fourier transform, asterisk denotes convolution, I_{vib} and I_{rot} are intensities connected with the vibrational and rotational relaxation processes. Now it is clear that the assumption $G_{\mathrm{vib}}(t) \approx 1$ is true in the pressure region where the total intensity (Eq. (3a)) is constant. From the intensities data (Table I) we can see that in the helium environment up to 5×10^7 N/m², and in the argon and nitrogen only up to 1×10^7 N/m², experimentally obtained correlation functions can be regarded as exclusively rotational correlation functions.

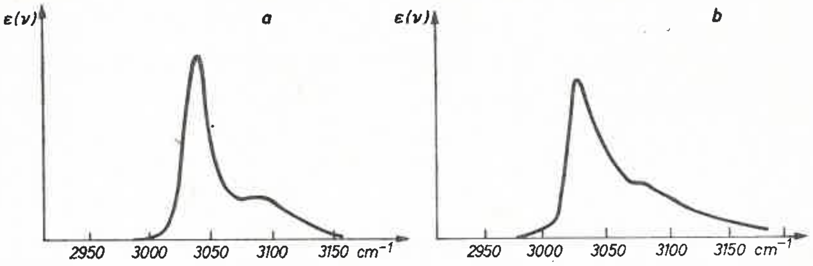

Fig. 3. C—H band contours for $CHCl_3$: a — perturbed by N_2 at 1.5×10^8 N/m²; b — dissolved in CCl_4

D. Correlation functions

As the nature of the C—H band asymmetry is still unknown the total band shape has been taken into computations. Correlation functions of $CHCl_3$ with He and N_2 calculated according to Eq. (1) are shown in Fig. 4a and 4b. The character of the remaining functions are similar to these plots and are not presented here.

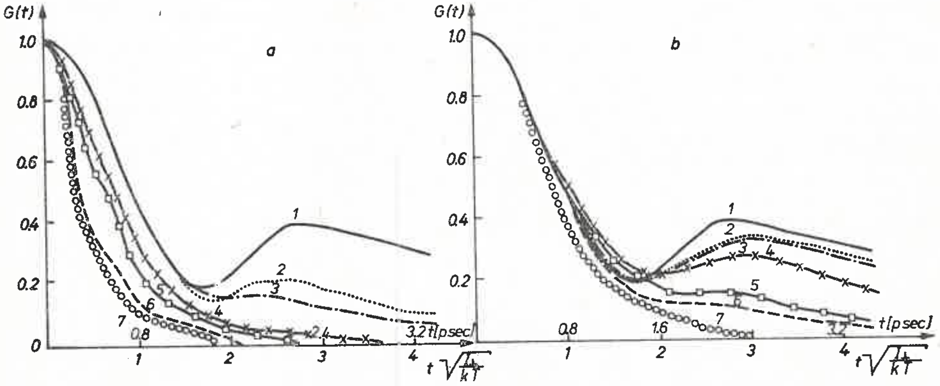

Fig. 4. The correlation functions for $CHCl_3$—N_2 (part a) and $CHCl_3$—He (part b); *1* — pure chloroform, 0.3×10^5 N/m²; *2* — 6×10^6 N/m²; *3* — 1×10^7 N/m²; *4* — 2.5×10^7 N/m²; *5* — 5×10^7 N/m²; *6* — 1×10^8 N/m²; *7* — 1.5×10^8 N/m² total pressure

E. Extended diffusion model

The extended diffusion model [1, 2] may be a very useful approach for molecular reorientation in gases at moderate pressures. In this picture molecules undergo binary collisions only and between collisions they rotate freely. After each collision the molecular angular momentum direction is randomized, whereas the angular momentum magnitude remains constant (M-diffusion) or changes (J-diffusion). It is worth noticing that the M-diffusion model exhibits some unphysical properties [21]. So we have concentrated on the J model only.

Correlation functions obtained in the frame of the J model depend on the τ_J parameter which represents the average time between two consecutive collisions. They were numerically calculated from the relation given by Mc Clung [2]. Then they were compared to the experimental functions to find the best fits. Fig. 5 illustrates an example of the best fit.

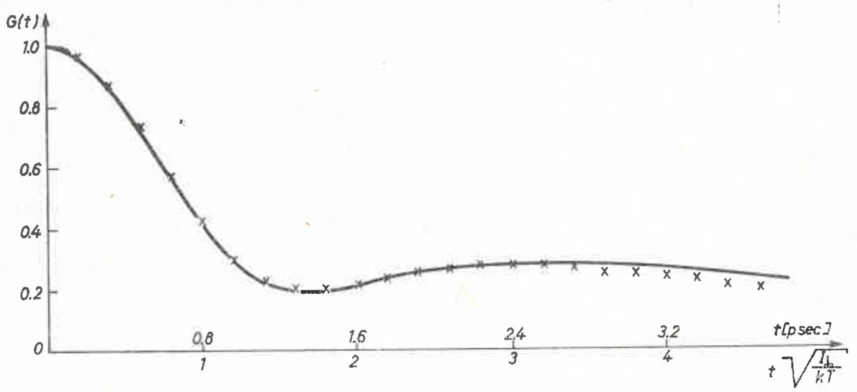

Fig. 5. Comparison of the theoretical correlation function $\tau_J = 5$ with the experimental function for $CHCl_3$—He system at 1.5×10^7 N/m^2

In the low pressure region (up to 1×10^7 N/m^2) it was possible to find good compatibility between the model and the experiment in every case. In the high pressure region ($p > 5\times10^7$ N/m^2) it was impossible to find any compatibility between theoretical and experimental curves. In the intermediate region we were able to compare the theoretically expected functions with the correlation functions obtained from the $CHCl_3$—He system. The values of parameter τ_J (also called angular momentum correlation time) for $CHCl_3$ perturbed by foreign gases at different pressures are assembled in Table I. Note that the fitting procedure could be applied only if A (Eq. (3a)) did not change appreciably. This is in good agreement with our predictions on the processes of appearing vibrational relaxation at high pressures.

F. Vibrational relaxation time

Considerably growth of the vibrational relaxation ought to be accompanied by decreasing τ_{vib}. Litovitz has shown [20] that τ_{vib} can be estimated as follows

$$\tau_{vib} = \frac{1}{P_{1\to0}(T)}\cdot\tau_{BC}, \tag{4}$$

where $P_{1\to 0}$ is the thermal deexcitation probability and τ_{BC} is the mean time between collisions. For $CHBr_3$, at the temperature 300°K $P_{1\to 0}$ equals 320 [22], the same value we adopted for $CHCl_3$. τ_{BC} was calculated from the movable wall cell model [23]

$$\tau_{BC} = \frac{1}{\left(\sqrt{\frac{8kT}{\pi m_1}} + \sqrt{\frac{8kT}{\pi m_2}}\right)} \cdot \left[\left(\frac{1}{\varrho}\right)^{1/3} - \tfrac{1}{2}(\sigma_1+\sigma_2)\right], \tag{5}$$

TABLE II

The observed and calculated relaxation times of $CHCl_3$—N_2 mixtures

p [bar]	τ_{vib} [psec]	τ_{exp} [psec]
60	3.43	1.41
100	2.17	1.01
150	1.56	0.87
250	1.15	0.66
500	0.62	0.57
1000	0.31	0.38
1500	0.27	0.30

m_1, m_2 are molecular weights of both gases, σ_1 and σ_2 their diameters and T — temperature. The density ϱ was calculated from Benedict's equation [24] but it also might be obtained directly from the pressure data given in the amagat units. The τ_{vib} values for $CHCl_3$—N_2 mixtures are given in Table II. As we have expected τ_{vib} decreases with increasing pressure. In Table II τ_{exp} values (calculated according to Eq. (3c)) are also assembled for convenient examination of inequality $\tau_{vib} \gg \tau_{exp}$. In the low pressure region the inequality is performed. At high pressures vibrational relaxation is much faster than rotational and that is why comparisons of experimental correlation functions with the extended diffusion theory are impossible.

3. *Conclusions*

In this work we have shown that the extended diffusion model (J-version) gives a rather good simulation of the reorientational process for $CHCl_3$ molecules compressed by simple gases, but only at low pressures. As gas density increases the vibrational relaxation can no longer be neglected and nothing can be said on the reorientational motion on the basis of the IR band study only. Raman pressure experiments ought to be done to give more precise experimental data on G_{rot} time dependence. They are now being prepared in our laboratory.

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