

## $M, J$ Diffusion and Torsional Oscillation in $\text{CHF}_3$ and $\text{N}_2\text{O}$

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It is shown that the molecular dynamical representation appropriate to the far infra-red absorption ( $6\text{--}200\text{ cm}^{-1}$ ) of liquid  $\text{N}_2\text{O}$  and  $\text{CHF}_3$  observed by Baise<sup>1</sup> falls between the extremes of adiabatic collision-interrupted free rotation (the  $M$  and  $J$  diffusion models) and torsional oscillation within a multi-well potential (the Brot-Larkin model). The role of induced dipolar absorption is discussed in relation to models such as these which deal only with the motion of the permanent dipole.

This work aims to compare some selected far infra-red ( $10\text{--}200\text{ cm}^{-1}$ ) experimental data<sup>1</sup> on compressed gaseous and low density liquid  $\text{CHF}_3$  and  $\text{N}_2\text{O}$  with molecular models of the dynamics giving rise to the absorptions encountered. The models used here express two extremes within which the data fall. They were developed by statistical averaging in the time domain in a closely comparable manner. On the one hand, the  $M$  and  $J$  diffusion models originally developed for linear molecules by Gordon,<sup>2</sup> and extended to symmetric tops by McClung,<sup>3, 4</sup> involve averaging over a system with free rotation between instantaneous collisions which randomise the molecular angular momentum in direction in the  $M$  model and in both magnitude and direction in the  $J$  model.

On the other hand, the Brot-Larkin model<sup>5, 6</sup> is based on the classical correlation function of an ensemble of harmonic vibrators subjected to random collisions which are also supposed adiabatic, but the results were extended<sup>7</sup> to torsional oscillators (librators) and later<sup>8</sup> to describe the angular motion of molecules submitted to thermal collisions in a multi-well potential. This model accounts for the finite moment of inertia and, consequently, under the action of a restoring torque (derivative of the potential) the molecules carry out a *librational* motion in the wells.

Recently, analytical expressions have been developed<sup>9</sup> which enable the direct comparison of the rotational velocity correlation function ( $\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle$ , where  $\mathbf{u}$  is a vector along the permanent dipole moment  $\mu$  of a molecule) derived from the Brot-Larkin and Gordon  $M$ -diffusion model with the relevant form of the experimental data. There are at least four ways of presenting the experimental data, any one of which throws light on aspects of the complex molecular interrelations in the liquid state which the other three may inherently distort or suppress.

(1) The vast majority of far infra-red spectra are presented as  $\alpha(\bar{\nu})$  in the frequency ( $\bar{\nu}$ ) domain,  $\alpha$  being the absorption coefficient per unit path length. This method relegates the absorption below *ca.*  $10\text{ cm}^{-1}$  to virtual insignificance—an important consideration since the integrated absorption intensity per molecule:

$$A = \frac{1}{N} \int_0^\infty \alpha(\bar{\nu}) d\bar{\nu}$$

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is often used<sup>10</sup> in the analysis of such data. At the same time, the higher frequency parts of the molecular relaxational processes are unduly emphasized.

(2) The vast majority of microwave data (up to *ca.* 3 cm<sup>-1</sup>) are presented as  $\epsilon''(\bar{\nu})$  in the frequency domain, where  $\epsilon''$ , the loss factor, is very nearly proportional to  $\alpha(\bar{\nu})/\bar{\nu}$ , and thus reduces the absorption above *ca.* 10 cm<sup>-1</sup> to a very small shoulder on the high frequency part of the loss curve.<sup>10</sup>

(3) Both the above methods record, at each frequency point, the resultant absorption due to dipolar fluctuations averaged over all times. A Fourier transform from the frequency to the time domain, giving the function :

$$f_1(t) = \int_{-\infty}^{\infty} \frac{\alpha(\bar{\nu}) \cdot \bar{\nu} \exp(2\pi i \bar{\nu} ct) d\bar{\nu}}{(1 - \exp(-hc\bar{\nu}/kT))}$$

is a way of presenting the absorption data such that at each point in time after an arbitrary initial  $t = 0$  the molecular fluctuations averaged over all frequencies have an instantaneous configuration which can be related to that at  $t = 0$  with a suitable correlation function. Thus this presentation  $f_1(t)$  has the advantage of separating short-time from longer-time behaviour and measures one's decreasing knowledge about the dynamic state of the system as time progresses.

Neglecting collision induced dipole effects,<sup>1</sup>  $f_1(t)$  is related<sup>11</sup> via a "dynamic internal field factor" to the function  $\langle \dot{\mathbf{u}}(0) \cdot \Sigma_i \dot{\mathbf{u}}_i(t) \rangle$ . If cross correlations are neglected, then no summation is necessary within the bracket  $\langle \rangle$  which denotes the ensemble averaging. The factor  $\bar{\nu}/(1 - \exp(-hc\bar{\nu}/kT))$  is often<sup>11</sup> approximated by  $kT/hc$ , whereupon  $f_1(t)$  becomes merely the Fourier transform of  $\alpha(\bar{\nu})$ , with the result that the short time behaviour of the system is detailed at the expense of the long time stochastic, cooperative process. This is equivalent to saying that data below 10 cm<sup>-1</sup> are unimportant in the evaluation of  $f_1(t)$ .

(4) The function

$$f_2(t) = \int_{-\infty}^{\infty} \frac{\alpha(\bar{\nu}) \exp(2\pi i \bar{\nu} t) d\bar{\nu}}{\bar{\nu}(1 - \exp(-hc\bar{\nu}/kT))}$$

is proportional to the vectorial autocorrelation function  $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$  when cross correlations and collisional induced dipoles are neglected. It has the advantage of representing the data in time, but, being roughly the Fourier transform of  $\epsilon''(\bar{\nu})/\bar{\nu}$ , requires very good data at low frequencies to give accurate values of  $f_2(t)$  at long times, and underemphasises the data above *ca.* 10 cm<sup>-1</sup>. However, in the absence of the former, the decay function at long times is often well approximated by a simple exponential and three appropriately placed  $\epsilon''(\bar{\nu})$  values will define a Fuoss-Kirkwood (or other) function adequately representing the cooperative region. Currently, an uncertainty of *ca.* 1 % at least would be typical for  $\epsilon''(\bar{\nu})$ . Also, for direct frequency domain comparison with light scattering data,<sup>12</sup> the function  $\alpha(\bar{\nu})/(\bar{\nu}(1 - \exp(-hc\bar{\nu}/kT)))$  is convenient.

The functions  $f_1(t)$  and  $f_2(t)$  have the advantage of highlighting band shape discrepancies<sup>13, 14</sup> between experience and prediction, but have the one shortcoming that if normalised to unity at  $t = 0$  do not give an idea of differences between the experimental and predicted values of  $A$ . Such discrepancies appear in this work and arise in part because the classical models of Brot and Gordon have the necessary<sup>2</sup> short time development  $1 - kTt^2/I + \mathcal{O}(t^4)$  for  $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ , thus they conform with Gordon's sum rule<sup>15</sup> and take no account of the movement of dipoles induced by molecular collisions. Baise<sup>1</sup> and Gerschel<sup>16</sup> have shown that in CHF<sub>3</sub> the excess

absorption over that predicted<sup>15</sup> for all rotational modes of the permanent dipole is small even in the liquid state (at most 11 % in the least dense liquid near the critical point). In  $N_2O$ , however,<sup>1</sup> the quadrupole- and dipole-induced dipolar absorption

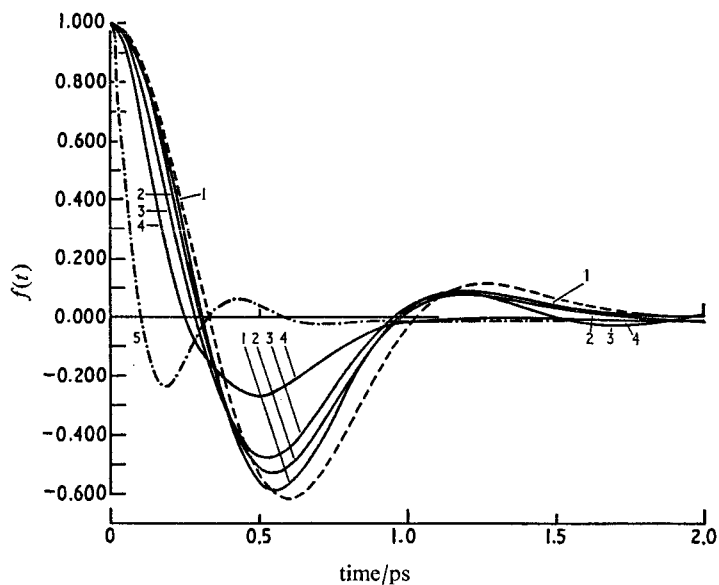


FIG. 1. —, The functions  $f_1(t)$  for  $CHF_3$ . (1) Compressed gas<sup>1</sup> at 10 bar, 296 K; (2) compressed gas at 20 bar, 296 K; (3) compressed gas at 33.4 bar, 296 K; (4) liquid at 296 K. ---, free rotor (Kummer function<sup>11</sup>); -.-.-,  $\langle \dot{u}(0) \cdot \dot{u}(t) \rangle$  calculated from the Brot-Larkin model with the parameters shown in the table, and normalised to 1 at  $t = 0$ .

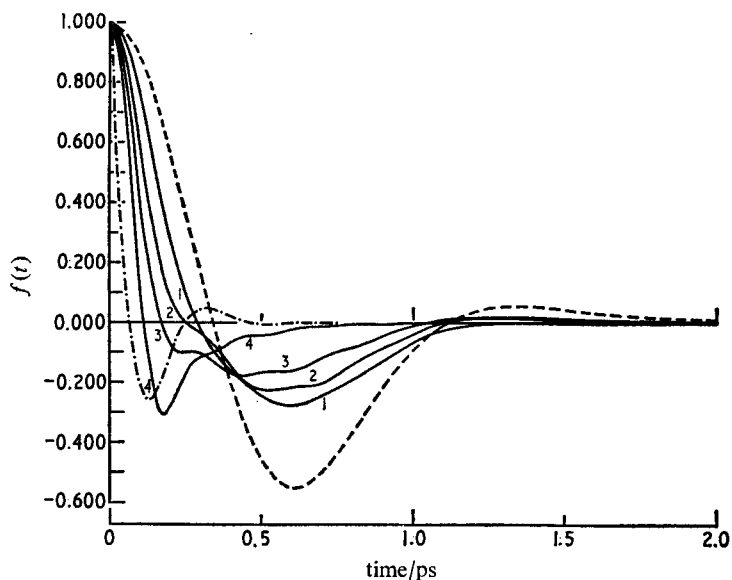


FIG. 2. —, The functions  $f_1(t)$  for  $N_2O$ . (1) Gas at 34.5 bar, 296 K; (2) gas at 41.4 bar, 296 K; (3) gas at 56.5 bar, 298 K; (4) liquid at 298 K; ---, free rotor (Kummer function); -.-.-,  $\langle \dot{u}(0) \cdot \dot{u}(t) \rangle$  from the Brot-Larkin model (parameters in text).

accounts for more than 50 % of that observed in the dense gas and liquid phase. Colpa and Ketelaar<sup>17</sup> have produced a theory of bimolecular collision induced absorption in linear molecules, and lately the potential of the molecular field at its neighbour has been expanded<sup>13</sup> to the hexadecapole term in linear molecules, and to the octupole term in symmetric tops.<sup>18</sup> However, this bimolecular "gas-phase" model becomes inadequate at near-liquid densities, and becomes wholly so in the dense liquid.<sup>19, 20</sup> Part of this work, therefore, emphasizes the effect on the far infra-red bandshape of compressed gaseous and liquid dipolar molecules of collisional induced dipoles. Their neglect not only results in the predicted values of  $A$  being too small (sometimes by nearly an order of magnitude<sup>21</sup>) but also in considerable bandshape discrepancies which are demonstrated here by comparing the  $M$  diffusion predictions with the compressed gaseous and liquid  $N_2O$  data using  $f_1(t)$ , there being no absorption data for  $N_2O(l)$  below  $6\text{ cm}^{-1}$ .

The derived, experimental  $f_1(t)$  curves are also compared with the  $\langle \dot{u}(0) \cdot \dot{u}(t) \rangle$  functions calculated<sup>9</sup> from the Brot-Larkin model,<sup>5</sup> the resulting discrepancies quite clearly showing that in the relatively low density  $N_2O$  and  $CHF_3$  liquids, the molecular motion is still predominantly quasi-free rotation (barriers to such of  $\lesssim kT$ ), but with "clusters" occasionally being formed, a central molecule within which being temporarily constrained to a torsional oscillatory motion against barriers of up to about  $(2.5-4.0) kT$ . A study of the long time (up to 5 ps) behaviour of liquid  $CHF_3$  by comparing  $f_2(t)$  with the equivalent function  $\langle u(0) \cdot u(t) \rangle$  derived from the  $J$  diffusion model supports this conclusion.

#### COMPUTATIONAL DETAILS

The curves  $f_1(t)$  and  $f_2(t)$  were computed<sup>14</sup> from the experimental<sup>1</sup>  $\alpha(\bar{\nu})$  data using a fast Fourier transform (FFT) as implemented in Algol by Singleton<sup>22</sup> and previously used by Baise.<sup>23</sup> The functions  $f_1(t)$  for compressed gaseous and liquid  $CHF_3$  and  $N_2O$  are shown in fig. 1 and 2 respectively, and  $f_2(t)$ , evaluated for liquid  $CHF_3$  with the aid of Gerschel's low frequency data, is given in fig. 4.

The rotational velocity correlation function  $\langle \dot{u}(0) \cdot \dot{u}(t) \rangle$  has been evaluated for  $N_2O$  using the relevant analytical form<sup>9</sup> of Gordon's  $M$  diffusion model, and is shown in fig. 3 for various values of  $\tau$ , the mean time between adiabatic collisions. Vectorial autocorrelation functions  $\langle u(0) \cdot u(t) \rangle$  evaluated for  $CHF_3$  using McClung's memory function method on a CDC 7600 computer, are displayed in fig. 4. The far infra-red frequency domain band shapes predicted by the Brot-Larkin model are compared with the experimental\*  $\alpha(\bar{\nu})$  data in fig. 5 and 6. For  $CHF_3(l)$ , the lower frequency (microwave) values of  $\alpha(\bar{\nu})$  have been estimated from Gerschel's data,<sup>16</sup> which predict a critical relaxation time of 2.9 ps, this being taken to define the Brot-Larkin parameter  $\tau_r$ , the mean time of residence within a potential well.<sup>5, 6</sup> For  $N_2O$ , no such low frequency data are available, but the value of  $\tau_r$  predicted by the model (11 ps) is appropriate. In applying the Brot-Larkin model, estimates of  $\zeta$ ,  $V$  and  $\tau_i$ , respectively the mean half angular aperture of a particular well (whose simple, functional form  $U(\theta)$  is arbitrary<sup>5</sup>), the barrier height to libration and the inverse bandwidth, are used to generate a theoretical bandshape, together with the functionally related parameters  $\tau_r$ ,  $\tau_a$  (the characteristic time of the correlation function of a molecule in a state of jump from one well into another<sup>8</sup>), and  $\tau_j$ , the mean time of jump from one

\* The quoted<sup>1</sup> uncertainty ( $\pm 2\%$ ) in these data is not such that several models may be accommodated within the spread. By reference to fig. 2 and 3, it may be seen that the Brot-Larkin and  $M$  diffusion models give theoretical  $f_1$  functions which would Fourier transform into bandshapes  $\alpha(\bar{\nu})$  that substantially differ. This difference is much bigger than the spread in the absolute values of the experimental  $\alpha(\bar{\nu})$ .

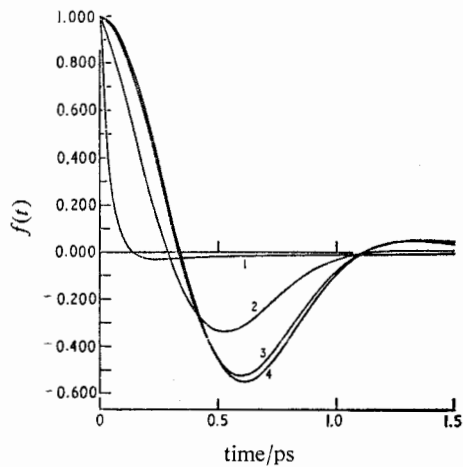


FIG. 3.— $\langle \dot{u}(0) \cdot \dot{u}(t) \rangle$  (normalised) calculated<sup>9</sup> for  $\text{N}_2\text{O}$  at 298 K from Gordon's  $M$ -diffusion model<sup>2</sup> for various  $\tau$  (mean time between collisions). (1)  $\tau = 0.1$  ps; (2)  $\tau = 1.0$  ps; (3)  $\tau = 10.0$  ps; (4)  $\tau \rightarrow \infty$  (free rotor).

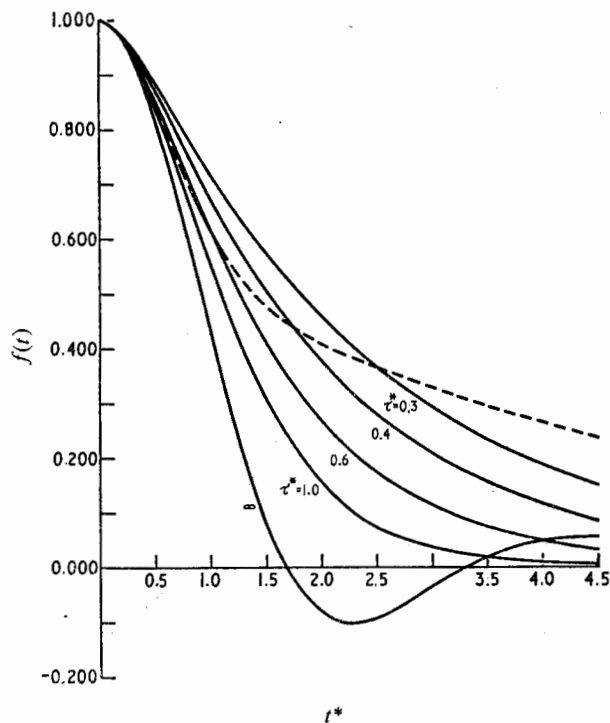


FIG. 4. —,  $\langle u(0) \cdot u(t) \rangle$  (normalised) calculated for  $\text{CHF}_3$  at 298 K from McClung's  $J$ -diffusion model for symmetric tops. From the top downwards:  $\tau^* = 0.3$  ps, 0.4 ps, 0.6 ps, 1.0 ps, and the free rotor, where  $\tau^* = \tau(kT/I_x)^{1/2}$ ,  $\tau$  being the mean time between collisions and  $I_x$  the moment of inertia about an axis perpendicular to that of the permanent molecular dipole. ---, The function  $f_2(t)$  for  $\text{CHF}_3$  liquid at 298 K. Computed with Lassier's program CHINT assuming Debye behaviour at low frequencies with a critical relaxation time<sup>16</sup> of 2.9 ps.

well into another. Therefore, the model uses two adjustable parameters  $V$  and  $\tau_1$  (three if the molecular "coordination number" is unknown experimentally), compared with one (the mean time between collisions) in the  $M$  and  $J$  diffusion models. The quality of fit to the experimental curve of  $\alpha(\bar{\nu})$  against  $\bar{\nu}$  is usually judged by comparison of  $\tau_r$  with the observed Debye relaxation time, of the predicted and observed  $\bar{\nu}_{\max}$ , of the overall bandshape, and of the predicted and observed values of  $A$ .

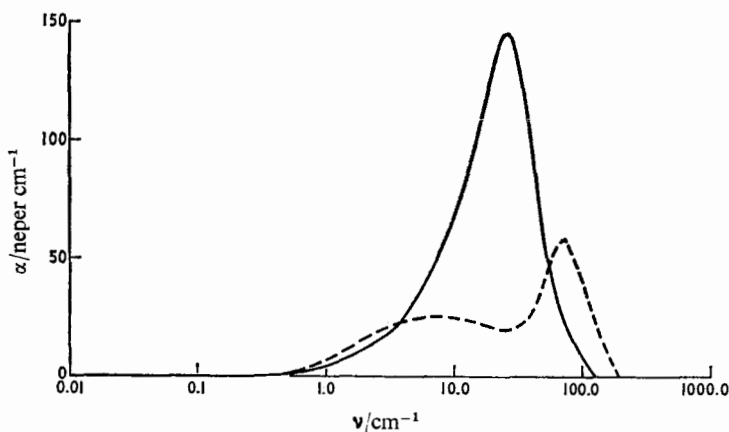


FIG. 5. —, Experimental<sup>1, 16</sup>  $\alpha(\bar{\nu})$  plotted against  $\bar{\nu}$  for  $\text{CHF}_3$  liquid at 298 K. ---, Brot-Larkin lineshapes with parameters listed in the text.

With its flexibility, it is a temptation when applying this model, to fit  $\bar{\nu}_{\max}$  first, and then to satisfy as far as possible the other criteria, introducing more adjustable parameters, such as a well narrowing factor<sup>21, 24</sup> where necessary. However, in cases where the induced dipole contribution is greater than the permanent one, such as in  $\text{N}_2\text{O}(l)$ , there is no reason why this model should reproduce the experimental  $\bar{\nu}_{\max}$  since it deals with the motion of the permanent dipole alone. On trying to "force fit" the theoretical and experimental  $\bar{\nu}_{\max}$  in  $\text{N}_2\text{O}(l)$  and  $\text{CHF}_3(l)$ , it was found that

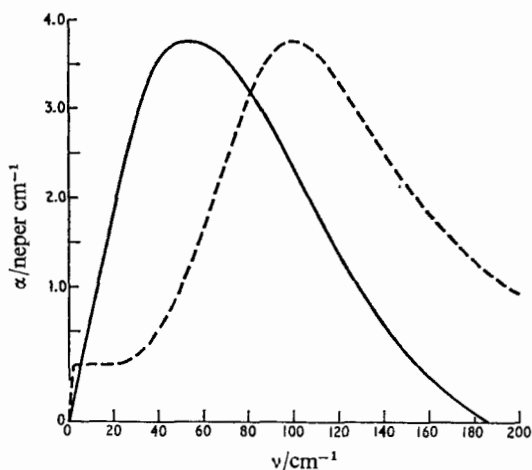


FIG. 6. —, Experimental<sup>1</sup>  $\alpha(\nu)$  plotted against  $\bar{\nu}$  for  $\text{N}_2\text{O}$  liquid at 296 K. ---, Brot-Larkin lineshape, the maximum absorption of which has been normalised<sup>5, 6</sup> to  $\alpha(\nu)_{\max}$  of the experimental curve.

barriers ( $V$ ) of about  $kT$  only were needed, the resulting computed bandshapes being distorted at *ca.*  $10\text{ cm}^{-1}$  by a sharp, intense, spurious, and physically meaningless peak in  $\alpha(\bar{\nu})$  (computed). In order to suppress this peak, a minimum value of  $V = 4kT$  ( $10\text{ kJ mol}^{-1}$ ) was needed for  $\text{N}_2\text{O}$ , and  $2.6kT$  ( $6\text{ kJ mol}^{-1}$ ) for  $\text{CHF}_3$ ; which shifted the predicted  $\bar{\nu}_{\text{max}}$  up to  $100\text{ cm}^{-1}$  and  $72\text{ cm}^{-1}$  respectively. These compare with the observed  $\bar{\nu}_{\text{max}}$  of  $54\text{ cm}^{-1}$  and  $26\text{ cm}^{-1}$  for the liquids at room temperature in equilibrium with the respective vapours. The parameters used in calculating the curves together with the functionally related  $\tau_a$ ,  $\tau_j$ , and  $\tau_r$ , are given in table 1.

TABLE 1.—BROT-LARKIN PARAMETERS FOR  $\text{N}_2\text{O}(\text{l})$  AND  $\text{CHF}_3(\text{l})$  AT ROOM TEMPERATURE

liquid	$\bar{\nu}_{\text{max}}(\text{obs})/\text{cm}^{-1}$	$\bar{\nu}_{\text{max}}(\text{calc})/\text{cm}^{-1}$	$\tau_D(\text{obs})/\text{ps}$	$\tau_r/\text{ps}$	$V/\text{kJ mol}^{-1}$	$\xi/\text{rad}$	$\tau_a/\text{ps}$	$\tau_j/\text{ps}$
$\text{CHF}_3$	26	72	2.9	2.9	6	0.59	0.1	0.25
$\text{N}_2\text{O}$	54	100	—	11.0	10	0.59	0.1	0.2

#### INTERPRETATION

Any interpretation of the differences between the predicted and observed spectra must first adequately take into account the extent to which induced dipolar absorption affects the overall bandshape and thus the functions  $f_1(t)$  and  $f_2(t)$ . This aspect is very different for  $\text{CHF}_3$  and  $\text{N}_2\text{O}$ .

There are now available data on  $\text{CHF}_3(\text{l})$  from the low density liquid studied by Baise<sup>1</sup> to the liquid at low temperatures near the freezing point (Gerschel). It is significant that throughout the whole liquid range, the excess absorption over Gordon's sum is of the order of only 5-8 %, suggesting a cancellation of inducing fields,<sup>19, 20</sup> or small multipole moments, or both. Therefore, to a large extent, the bandshape may be attributed to the motion of the permanent dipole alone. The absorption band of  $\text{CHF}_3(\text{l})$  at room temperature in equilibrium with the vapour is a broadened version of the theoretical  $J \rightarrow J+1$  bar spectrum<sup>1</sup> for free rotation in the dilute gas, peaking at  $\bar{\nu}_{\text{max}} = 26\text{ cm}^{-1}$  but with a small high frequency shoulder. The latter becomes predominant<sup>16</sup> in the dense liquid near the freezing point, where the  $\bar{\nu}_{\text{max}}$  is now at  $60\text{ cm}^{-1}$ . The Brot-Larkin model predicts a room temperature peak at  $72\text{ cm}^{-1}$  with a barrier to whole molecule libration of *ca.*  $6\text{ kJ mol}^{-1}$ , suggesting that the absorption process in the dense liquid is more consistent with torsional oscillation of fairly close packed molecules within the cages formed by their neighbours.

At the same time, the molecular rotation on the low density liquid is not merely collision-interrupted free rotation. This is clearly shown in fig. 4, where the experimental data for the  $\text{CHF}_3(\text{l})$  are plotted as  $f_2(t)$  with various autocorrelation functions derived from McClung's  $J$ -diffusion model. The experimental curve follows the predicted behaviour with  $\tau^* = 0.6$  (corresponding, via simple kinetic theory, to a mean distance between collisions of roughly  $0.8\text{ \AA}$ , less than the van der Waals radius) for a time up to 1.0 ps, but there is a pronounced increase in correlation over that predicted at longer times than this. The  $J$  diffusion concept is valid only as long as a molecule translates over a distance greater than its van der Waals radius, when rotational motion then produces no collisions inherently. When a molecule translates between collisions by less than the van der Waals radius, then the rotational motion also produces "collisions". This would lead to the persistence of local organisation all along the liquid domain observed by Gerschel<sup>16</sup> as pronounced short time oscillations in the experimental  $f_1(t)$ , and in fact it is only in the approaches to the critical region that a rapid change to an isotopic distribution of orientations was observed. In  $\text{CHF}_3$ , the effect of long range dipole forces is significant, this being relatively

unimportant in liquids where repulsive, short-range forces predominate. The experimental excess over Gordon's sum may therefore originate from a strong organisation of dipolar origin, whereby the hyperpolarisabilities developed under the effect of the intense field of neighbouring dipoles contribute an increment in the apparent total dipole.

The divergence of  $f_2(t)$  from the curve predicted by the  $J$ -diffusion model at times longer than 1 ps may thus be explained in terms of these attractive dipolar forces keeping the molecules together for a relatively long time after an initial "soft collision" until the chance of an encounter with a third or fourth molecule is significantly high. Therefore, such clusters of molecules would be formed within which the local ordering is enhanced compared with the molecules in the liquid. Torsional oscillation would take place inside the cluster, producing a kind of motion which periodically restores the *local* ordering as it was at the arbitrary initial time  $t = 0$ . In the comparatively low density liquid  $\text{CHF}_3$  at 298 K in equilibrium with the vapour, the "clusters of local ordering" are probably not populous enough to produce pronounced short time oscillations in  $f_1(t)$  (fig. 1), but produce more ordering, and correlation with an initial geometry at  $t = 0$  than the  $J$ -diffusion model foresees. The Brot-Larkin model allows for a much greater degree of ordering (akin to that in rotator phases<sup>6</sup>) than is present in the  $\text{CHF}_3(\text{l})$ , where the molecules are probably involved in collision-interrupted free rotation (with translation of little more than the van der Waals radius), being occasionally constrained to temporary torsional oscillation within transient clusters. The liquid density ( $0.744 \text{ g cm}^{-3}$ ) is such that rotation alone will not cause a collision (i.e., the hypothetical "stationary molecule" of the Brot-Larkin model would have a "barrier to libration" of  $\lesssim kT$ ). The translational motions of a pair of molecules probably results in a finite event approximating the assumed "instantaneous collision" of the  $J$ -diffusion model, but is then liable to be trapped in a temporary cage of neighbours, when its translational movement would be constrained. The vectorial autocorrelation function would still closely resemble that of a free rotor at very short times ( $< \sim 0.5 \text{ ps}$ ) but would be affected by the increased structuring at long times.

In  $\text{N}_2\text{O}(\text{l})$  it is immediately clear from fig. 2 and 3 that the  $M$ -diffusion representation of the molecular dynamics in compressed gaseous and liquid  $\text{N}_2\text{O}$  does not in general produce a function  $\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle$  which agrees with the experimental  $f_1(t)$ . The possible exceptions are the data at 34.5 bar and 296 K, where the induced dipolar component is not yet significant. Analogously with  $\text{CHF}_3(\text{l})$ , the Brot-Larkin model suggests that a process of constrained torsional oscillation of the permanent dipole would produce an absorption peaking at roughly  $100 \text{ cm}^{-1}$ , with a barrier of approximately  $10 \text{ kJ mol}^{-1}$ . The dynamical picture is therefore similar to  $\text{CHF}_3(\text{l})$ , but the far infra-red absorption is not simply a consequence of the permanent dipolar fluctuation, multipole induced dipole absorption becoming *predominant* at the higher gas densities. This is reflected in the  $f_1(t)$  curve as an increasingly important short time minimum (fig. 2) corresponding to the high frequency induced dipolar absorption.

It is possible that libration of the permanent dipole of the anisotropic  $\text{N}_2\text{O}$  molecule would produce a peak at a higher frequency than absorption by the quadrupole-induced dipole absorption, and as the liquid becomes denser, libration will become the dominant process. This, combined with the effect of cancellation by symmetry of the fields of surrounding molecules upon a central one, will cause a shift of the peak to higher frequencies as the liquid density increases.

Dynamical models such as these, although mathematically complex, still represent a much over-simplified picture of the low density liquid state. There is also the additional problem of induced dipolar absorption (with the associated one of the



tional form of the intermolecular potential) which can be treated fairly satisfactorily only in the cases of two body collisions between linear or symmetric top molecules.<sup>1, 18-20</sup> A different approach to the problem might be via computer dynamics on "ideal" systems to see if these reproduce any features similar to those in  $f_1(t)$  and  $f_2(t)$  of real liquids. Any such simulation would, however, have to take into account the effect of the motion of induced dipoles when generating functions such as  $f_1(t)$  or  $f_2(t)$  which are experimentally derived from the far infra-red.

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- <sup>1</sup> A. I. Baise, *J.C.S. Faraday II*, 1972, **68**, 1904.
- <sup>2</sup> R. G. Gordon, *J. Chem. Phys.*, 1966, **44**, 1830.
- <sup>3</sup> R. E. D. McClung, *J. Chem. Phys.*, 1972, **57**, 5478.
- <sup>4</sup> R. E. D. McClung, *Chem. Phys. Letters*, 1973, **19**, 304.
- <sup>5</sup> I. Larkin, *J.C.S. Faraday II*, 1973, **69**, 1278.
- <sup>6</sup> R. Haffmans and I. W. Larkin, *J.C.S. Faraday II*, 1972, **68**, 1729.
- <sup>7</sup> C. Brot, *J. Physique*, 1967, **28**, 789.
- <sup>8</sup> B. Lassier and C. Brot, *Chem. Phys. Letters*, 1968, **1**, 581.
- <sup>9</sup> M. Evans, *J.C.S. Faraday II*, 1974, **70**, 1620.
- <sup>10</sup> M. Evans, *Spectrochim. Acta*, 1975, in press.
- <sup>11</sup> A. Gerschel, I. Darmon and C. Brot, *Mol. Phys.*, 1972, **23**, 317.
- <sup>12</sup> T. A. Litovitz, personal communication.
- <sup>13</sup> M. Evans, *Mol. Phys.*, 1975, in press.
- <sup>14</sup> M. Evans, *J.C.S. Faraday II*, in press.
- <sup>15</sup> R. G. Gordon, *J. Chem. Phys.*, 1963, **38**, 1724.
- <sup>16</sup> A. Gerschel, *Conf. Molecular Motion in Fluids*, Nancy, 1974.
- <sup>17</sup> J. P. Colpa and J. A. A. Ketelaar, *Mol. Phys.*, 1958, **1**, 343.
- <sup>18</sup> G. J. Davies and M. Evans, *J.C.S. Faraday II*, in press.
- <sup>19</sup> G. Birnbaum, W. Ho and A. Rosenberg, *J. Chem. Phys.*, 1971, **55**, 1028.
- <sup>20</sup> M. Evans, *J.C.S. Faraday II*, 1973, **69**, 763; *Spectrochim. Acta*, 1974, **30A**, 79.
- <sup>21</sup> M. Evans, M. Davies and I. Larkin, *J.C.S. Faraday II*, 1973, **69**, 1011.
- <sup>22</sup> R. C. Singleton, *Comm. A.C.M.*, 1968, **11**, 773; 1969, **12**, 187.
- <sup>23</sup> A. I. Baise, *J. Chem. Phys.*, 1974, **60**, 2936.
- <sup>24</sup> I. Larkin and M. Evans, *J.C.S. Faraday II*, 1974, **70**, 477.