

## Investigation of the Inter-molecular Dynamics of Non-dipolar Molecules using the Rotational Velocity Correlation Function

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The rotational velocity correlation function is used to assess the Colpa-Ketelaar and Litovitz models of the intermolecular motions of compressed gaseous and liquid non-dipolar molecules which give rise to their broad band absorptions in the far infra-red (2-200  $\text{cm}^{-1}$ ). The simple Colpa-Ketelaar bimolecular collision model is found to be satisfactory only in the case of  $\text{N}_2(\text{g})$ . The Litovitz model of the liquid state, although approximate in derivation, is rather more successful, but does not show the very short time (*ca.* 0.1-0.5 ps) oscillations observed in the experimental functions up to 2.0 ps.

The far infra-red (2-200  $\text{cm}^{-1}$ ) absorptions of non-dipolar molecules in the compressed gaseous and liquid states have recently been the subject of much experimental study.<sup>1-7</sup> The origin of the absorptions has been uniformly attributed to multibody molecular interactions of a complex nature. Despite this, a much used equation in the description of these spectra is that derived by Colpa and Ketelaar<sup>8</sup> for quadrupolar induced dipole absorptions during bimolecular collisions of linear molecules, which they used successfully with hydrogen.

One of the objectives of this work is to mould the original equation into a form suitable for direct comparison in the relevant time interval of 0-2 ps with a function derived from the experimental data which reflects the evolution with time of the molecular dynamics giving rise to the infra-red absorption. The function used is that which Brot<sup>9</sup> calls the rotational velocity correlation function (RVCF), this being the negative of the second derivative of the usual vectorial correlation function. This has the advantage of detailing the short time behaviour associated with these far infra-red bands, which superficially resemble those of dipolar molecules in the same range.

Rotational velocity correlation functions are derived by Fourier transforming: (i) experimental results on the far infra-red absorption  $\alpha(\bar{\nu})$ , the power coefficient per unit length (neper  $\text{cm}^{-1}$ ) of Lambert's law,  $\bar{\nu}$  being the wavenumber ( $\text{cm}^{-1}$ ); (ii)  $\alpha(\bar{\nu})$  from the theory<sup>8</sup> of Colpa and Ketelaar; (iii)  $\alpha(\bar{\nu})$  from the theory<sup>3</sup> of Litovitz *et al.*

These values of  $\alpha(\bar{\nu})$  are all transformed in the same way so that this particular Fourier transform of the measured absorption spectra can be lucidly compared with these proposed theoretical shapes. The comparison is made for the linear molecules:  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $(\text{CN})_2$  and  $\text{CS}_2$ , and the discrepancies in the use of the Colpa-Ketelaar equation with molecules other than  $\text{H}_2$  or  $\text{N}_2$  are discussed.

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## RESULTS AND DISCUSSION

The Fourier transformation (i) is carried out on the experimentally available<sup>1, 4, 6, 7, 13</sup> data by means of the equation:

$$R''_{\text{exp}}(t) = \langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle = \int_{-\infty}^{\infty} \frac{3h\bar{\nu}c^3 n(\bar{\nu}) \alpha(\bar{\nu}) \cos(2\pi\bar{\nu}ct) d\bar{\nu}}{4\pi^2(1 - \exp(-h\bar{\nu}c/kT))} \quad (1)$$

derived from the very well-known Gordon relations.<sup>3, 10</sup> In eqn (1),  $\mathbf{u}$  is the vector along the linear molecular axis.  $n(\bar{\nu})$  is the frequency dependent refractive index,  $c$  the velocity of light,  $T$  the absolute temperature. Here,  $\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle$  is related to the angular velocity of the molecule by Anderson's expression:

$$\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle \propto \langle \sin \theta(0) \sin \theta(t) \dot{\theta}(0) \dot{\theta}(t) \rangle \quad (2)$$

where  $\theta(0)$ ,  $\theta(t)$  are the angles between the axis of the molecule and the direction of the incident electric field at times 0 and  $t$  respectively. In the limit of small diffusive steps:

$$\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle \propto \langle \dot{\theta}(0) \cdot \dot{\theta}(t) \rangle. \quad (3)$$

The computation of (1) was carried out over real (positive) frequencies using an algorithm which evaluated the integral numerically using Simpson's rule. Two possible sources of distortion in the final correlation functions are those arising from the truncation of the integral limits from  $(-\infty, \infty)$  to  $(0, \bar{\nu}_g(\alpha = 0))$ ; and from the interval  $\Delta\bar{\nu}$  at which values of  $\alpha(\bar{\nu})$  were taken along the experimental curve. The effects of these modifications are discussed in the appendix. It is shown there that the method of computation should produce no distortion in the rotational velocity correlation function provided that: (i) the experimental spectrum is truncated only when  $\alpha(\bar{\nu}) \rightarrow 0$  on the high frequency side; (ii) the sampling interval  $\Delta\bar{\nu}$  is chosen sufficiently small that  $R''_{\text{exp}}(t) = 0$  for  $t > 1/(2\Delta\bar{\nu}c)$ .

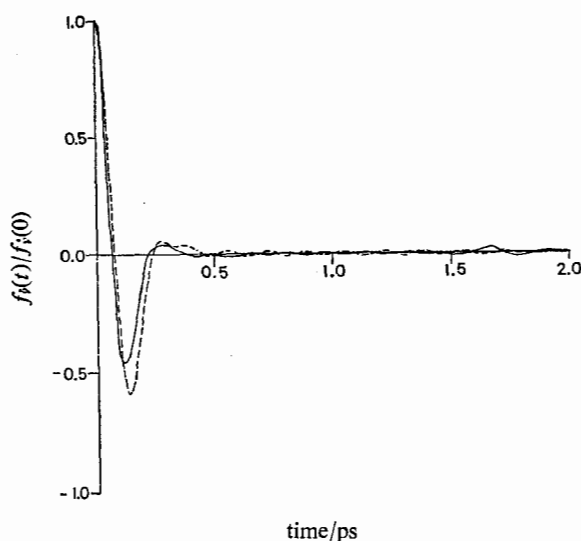


FIG. 1.—Plots of: —, experimental RVCF for nitrogen gas at 300 K; ---, eqn (10).

The greatest sampling interval chosen was that of  $5 \text{ cm}^{-1}$  for  $\text{N}_2$  and  $\text{O}_2$ , so that in these cases the condition that  $R''_{\text{exp}}(t) = 0$  for  $t > 3 \text{ ps}$  must be complied with to prevent aliasing of the correlation function. It can be seen from fig. 1-4 that  $R''_{\text{exp}}(t)$  is damped out at  $< 0.7 \text{ ps}$  in these cases. For  $(\text{CN})_2$ ,  $\text{CS}_2$  and  $\text{CO}_2$ ,  $\Delta\bar{\nu} = 2 \text{ cm}^{-1}$ , so that the upper limit is  $8 \text{ ps}$ . It is emphasized that the experimental functions (fig. 1-8) can only be as accurate and reliable as the original experimental data, which are sometimes uncertain to the extent of  $\pm 10 \%$ , especially on the low frequency (long time) side. The latter point is one reason why the rotational velocity correlation function is preferred to the vectorial one for far infra-red data. In the original data <sup>6</sup> for cyanogen (l), an extrapolation on the high frequency side to avoid the quartz

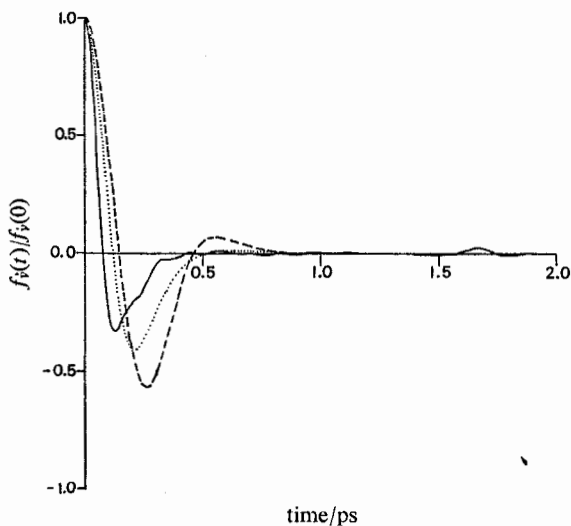


FIG. 2.—Plots of: —, experimental  $^{13}\text{C}$  RVCF for nitrogen liquid at  $76.4 \text{ K}$ ; ---, eqn (10) with  $B = 1.993 \text{ cm}^{-1}$ ; ·····, eqn (11).

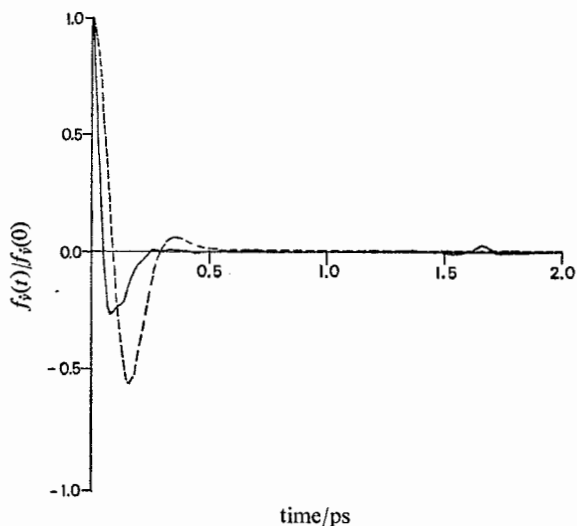


FIG. 3.—Plots of: —, experimental  $^{16}\text{O}$  RVCF for oxygen gas at  $300 \text{ K}$ ; ---, eqn (10) with  $B = 1.4345 \text{ cm}^{-1}$ .

absorption has been made. However, it is improbable that the pronounced oscillation in the corresponding  $R''_{\text{exp}}(t)$  (fig. 7) is due to the uncertainties in this extrapolation, since the former also occurs in the compressed gaseous function (fig. 6), where no extrapolation of the original data<sup>6</sup> was necessary, the absorption being over by  $\bar{\nu} = 100 \text{ cm}^{-1}$ .

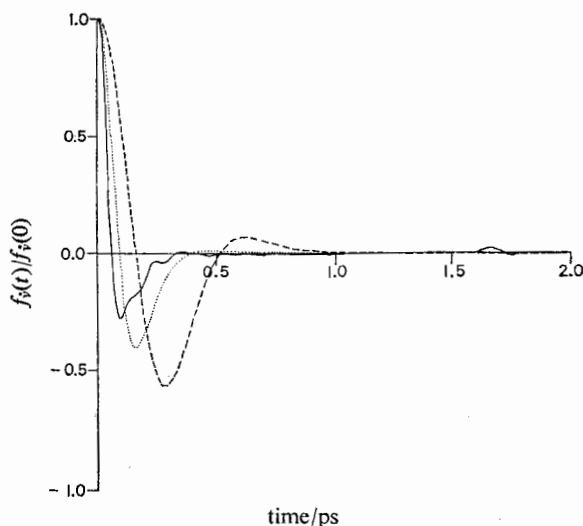


FIG. 4.—Plots of: —, experimental<sup>13</sup> RVCf for oxygen liquid at 88.1 K; ---, eqn (10); ·····, eqn (11).

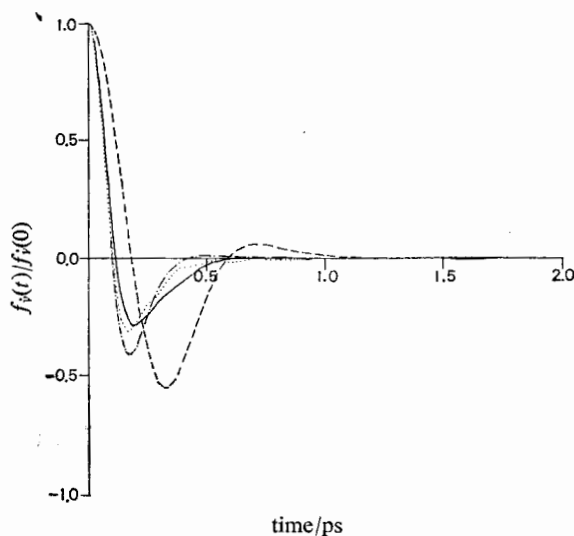


FIG. 5.—Plots of: —, experimental<sup>7</sup> RVCf for  $\text{CO}_2(\text{g})$  at 273 K; ·····, experimental<sup>7</sup> RVCf for  $\text{CO}_2(\text{l})$  at 273 K; ---, eqn (10) with  $B = 0.393 \text{ cm}^{-1}$ ; - · - · -, eqn (11).

#### MODEL TRANSFORMS

(1) Following Baise,<sup>12</sup> an expression for  $\langle \dot{\mathbf{u}}(0) \cdot \dot{\mathbf{u}}(t) \rangle$  can be obtained from the Colpa-Ketelaar treatment of non-dipolar linear molecules undergoing collision with resulting quadrupole induced dipolar far infra-red absorption, by using the eqn (4),

(5), and (6) below, where eqn (4) is the Gordon<sup>12</sup> relation, and eqn (6) that of Colpa and Ketelaar in its quantised form.  $J$  is the pure rotational quantum number,  $B$  the rotational constant (in  $\text{cm}^{-1}$ ),  $\epsilon''(\bar{\nu})$  the frequency dependent dielectric loss,  $\nu$  the frequency ( $\text{s}^{-1}$ ) and  $I(\nu)$  the frequency dependent spectral intensity.

$$I(\nu) = \frac{3h\epsilon''(\nu)}{8\pi^2(1 - \exp(-h\nu/kT))} \quad (4)$$

$$\alpha(\bar{\nu}) = \frac{2\pi\epsilon''(\nu) \cdot \nu}{n(\nu)c} \quad (5)$$

$$\alpha(J \rightarrow J+2) \propto \frac{\bar{\nu} \cdot (J+1)(J+2)}{(2J+3)} \exp(-E(J)/kT)(1 - \exp(-hc\bar{\nu}(J)/kT)) \quad (6)$$

with  $\bar{\nu}(J) = 2B(2J+3)$ ,  $E(J) = hcBJ(J+1)$ ,  $\bar{\nu} = \nu/c$ . From (4), (5) and (6)

$$I(\nu) \propto \left( \frac{\nu}{2Bc} - \frac{2Bc}{\nu} \right) \exp \left( -\frac{hcB}{4kT} \left( \frac{\nu}{2Bc} - 3 \right) \left( \frac{\nu}{2Bc} - 1 \right) \right). \quad (7)$$

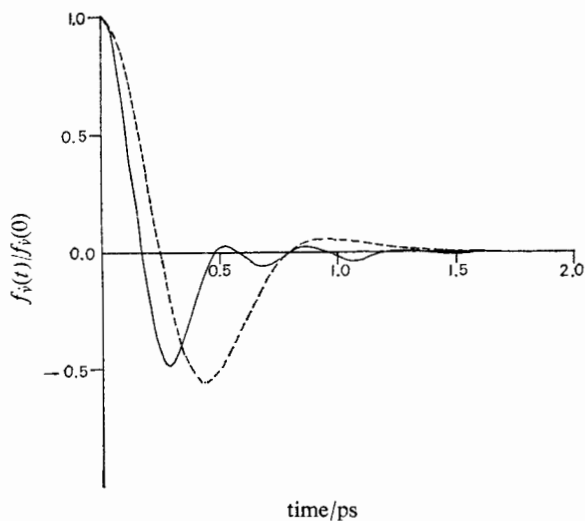


FIG. 6.—Plots of: —, experimental<sup>6</sup> RVCF for  $(\text{CN})_2$  (g) at 383 K; - - -, eqn (10) with  $B = 0.1571 \text{ cm}^{-1}$ .

The vectorial correlation function  $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$  is related to the real part of the Fourier transform  $C^*(t)$  of  $I(\nu)$ :

$$\begin{aligned} C^*(t) &= R(t) + iI(t) \\ &= \int_{-\infty}^{\infty} I(\bar{\nu}) \exp(2\pi i \nu t) d\nu \end{aligned} \quad (8)$$

giving:

$$\begin{aligned} R''_{\text{CK}}(t) &= -d^2(R(t))/dt^2 \\ &\propto \int_0^{\infty} 8\pi^2 \left( \frac{\nu^3}{2Bc} - 2Bc\nu \right) \exp \left( -\frac{hcB}{4kT} \left( \frac{\nu}{2Bc} - 3 \right) \left( \frac{\nu}{2Bc} - 1 \right) \right) \times \cos 2\pi\nu t \cdot d\nu. \end{aligned} \quad (9)$$

(2) For the band shapes in question, Litovitz *et al.*<sup>3</sup> have recently proposed the equation:

$$\alpha(\omega) \propto \omega^{26/7} \exp(-\omega/\omega_0) \quad (10)$$

$$\omega_0^{-1} \doteq \frac{\pi r_0}{6} \left( \frac{\mu}{kT} \right)^{\frac{1}{2}} \left( 1 - \frac{2}{\pi} \tan^{-1} \left( \frac{2\varepsilon}{kT} \right)^{\frac{1}{2}} \right) \quad (11)$$

where  $r_0$  and  $\varepsilon$  are Lennard-Jones parameters,  $\mu$  is the reduced mass of the colliding molecules, and  $k$  the Boltzmann constant. This is a semi-empirical expression for  $\alpha(\omega)$  in terms of the angular velocity  $\omega$  (radians  $s^{-1}$ ) derived from a consideration of deformation of the molecular polarisability during a collision.

Eqn (10) can be transformed to the corresponding rotational velocity correlation function using:

$$R_L''(t) \propto \int_{-\infty}^{\infty} \frac{\omega^{33/7} \exp(-\omega/\omega_0) \cos \omega t \, d\omega}{(1 - \exp(-h\omega/2\pi kT))} \quad (12)$$

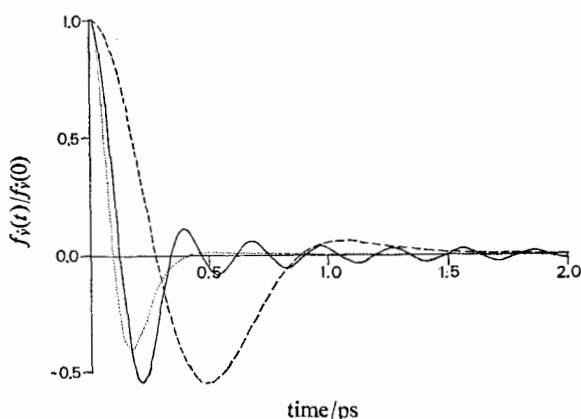


FIG. 7.—Plots of: —, experimental<sup>6</sup> RVCF for  $(CN)_2(l)$  at 301 K; ---, eqn (10); ....., eqn (11).

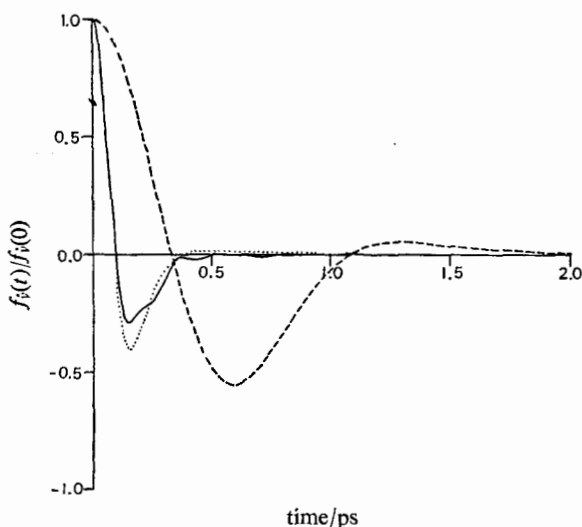


FIG. 8.—Plots of: —, experimental<sup>5, 14</sup> RVCF for  $CS_2(l)$  at 297 K; ---, eqn (10) with  $B = 0.1082 \text{ cm}^{-1}$ ; ....., eqn (11).

and this function is illustrated for  $N_2(l)$ ,  $O_2(l)$ ,  $CO_2(l)$ ,  $(CN)_2(l)$ , and  $CS_2(l)$  in fig. 2, 4, 5, 7, and 8 respectively. The parameters<sup>15</sup> used in Litovitz's eqn (11), together with  $\omega_{\max}$  (the calculated frequency of maximum absorption) are shown in table 1.

Direct comparison of the experimental  $\alpha(\bar{\nu})$  data with the  $J \rightarrow J+2$  line spectra calculated from Colpa and Ketelaar's original equation is available in the literature<sup>1, 2, 4-7</sup> for all the cases described here, and direct comparison of the observed  $(\omega)_{\max}^{\text{obs.}}$  and Litovitz predicted ( $\omega_{\max}$ ) values of the angular frequency of maximum absorption is given in table 1 for all the liquids studied here. It may be briefly indicated that in the cases of  $O_2$  and  $(CN)_2$  the  $J \rightarrow J+2$  quadrupole-induced transitions reach a peak<sup>1, 6</sup> at a lower frequency than the experimental band, the high frequency absorptions being attributed to overlap or hexadecapole-induced dipolar ( $J \rightarrow J+4$ ) absorptions.

TABLE 1.—PARAMETERS USED IN EQN (11)

liquid	$(\epsilon/k)/K$	$r_0/\text{\AA}$	$T/K$	$\omega_0/\text{cm}^{-1}$	$\omega_{\max}/\text{cm}^{-1}$	$\omega_{\max}^{\text{obs.}}/\text{cm}^{-1}$
$N_2$	71.4	3.80	76.4	14.1	52.3	66 <sup>13</sup>
$O_2$	106.7	3.47	88.1	17.2	63.7	82 <sup>13</sup>
$CO_2$	195.2	3.94	273	18.6	69.0	70 <sup>1</sup>
$(CN)_2$	348.6	4.36	301	19.4	72.1	78 <sup>6</sup>
$CS_2$	467	4.48	298	19.8	73.5	75 <sup>5</sup>

Two general points are noticeable from the comparison of these correlation functions, derived from wholly collision-induced absorptions, with eqn (9). The first is that the mean time between collisions  $\tau_{bc}$ , defined by Litovitz,<sup>3</sup> as that necessary for the angular velocity to go to zero, is shorter, even in the small diatomics  $N_2$  and  $O_2$ , than that obtained from the cutting of the time axis by eqn (9). It is known<sup>6, 7</sup> that in the larger molecules such as  $CO_2$  and  $(CN)_2$ , the quadrupole-quadrupole interaction potential ought not to be neglected in collisional theory and the consequences of its neglect are apparent in fig. 5 to 8: in the fairly dilute gas, where collisions of no greater than two-bodies are probable the apparent  $\tau_{bc}$  is up to 50 % less than predicted. At higher pressures in nitrogen and oxygen gas, three-body and higher collisions are likely to be the cause of the respective discrepancies in  $\tau_{bc}$ .

Secondly, the negative peak of the rotational velocity correlation function (which reflects a tendency of the molecule to reverse its rotational direction on collision) is related<sup>3</sup> to the maximum in  $\alpha(\omega)$  of the frequency spectrum. This negative peak is always greater, according to eqn (9) than that in either the observed compressed gaseous or the liquid rotational velocity correlation functions. This may reflect the fact that the symmetry of interactions involving more than two molecules leads to an incomplete cancellation of the forces inducing the central dipole. The collisional damping<sup>9</sup> of the rotational velocity correlation function is more effective than the Colpa-Ketelaar equation would allow.

Future models for these dynamical aspects should, therefore, include: (i) a consideration of many body collision effects and their symmetry; (ii) wider use of an anisotropic intermolecular potential.

Some more detailed comments can be made about the shape of the experimental correlation functions, and in particular about the oscillation superimposed on the overall shapes.

Nitrogen gas at 300 K can be accepted as a reference case: the degree of agreement between the simple theory and experiment is maximal and, at this stage, probably little comment is justified on the deviations in fig. 1. Clearly, liquid  $N_2$  departs seriously from the gas collisional state, and, again, it seems reasonable to suggest that

the experimental curve will typify that for a simpler non-dipolar liquid of slightly anisotropic molecules. The significance of these remarks becomes apparent when the data for oxygen gas and liquid are considered. The  $O_2$  gas spectrum is itself immediately seen to differ markedly from that of  $N_2$ —but no analysis of this difference<sup>2</sup> appears to have been made. The striking indication is that the rotational velocity correlation function for the collisionally induced dipole in  $O_2$  shows a distinct resemblance in pattern to that in the liquid  $N_2$ : for the latter there are “minima” or shoulders at 0.12; 0.25; 0.36 ps; in  $O_2$  gas similar features appear at 0.08; 0.13; and 0.20 ps. Thus the former repeat at intervals of *ca.* 0.12 ps the latter *ca.* 0.07 ps.

The former  $\Delta t \doteq 0.12$  ps corresponds to a frequency of  $8 \times 10^{12} \text{ s}^{-1}$ , which is some three times the Mic<sup>15</sup> estimated “collision frequency” in liquid  $N_2$ ; in gaseous  $O_2$  no collision frequency can match 0.07 ps ( $\nu \doteq 14 \times 10^{12} \text{ s}^{-1}$ ). These frequencies (if they are related to real molecular processes) are conceivably those of weakly bonded molecular pairs ( $N_2$ ) . . . ( $N_2$ ) or ( $O_2$ ) . . . ( $O_2$ ).

In cyanogen,<sup>6</sup> the “oscillation” in  $R''_{\text{exp}}(t)$  is very pronounced, in the gas, the minima appear at 0.28; 0.68; 1.06; and 1.5 ps, intervals of about 0.4 ps: in the liquid the pattern is 0.21; 0.53; 0.83; 1.12; 1.41; and 1.71 ps with a repeat interval of 0.30 ps. There is clearly some unrecognized feature of the molecular collisional process shown by these details. Whilst cyanogen is molecularly very anisotropic, it is some detail in the dynamics of the collisional interaction which is revealed by  $R''_{\text{exp}}(t)$ .

It can be seen in fig. 2, 4, 5, 7 and 8 that Litovitz's rotational velocity correlation function shows no superimposed oscillations, the difference between this prediction and the experimental being especially marked in cyanogen (fig. 7). The Litovitz equation is one based solely on collision-induced anisotropy, but with correlation between successive collisions not taken into account. Therefore, although this semi-empirical equation gives a good estimate of the observed  $\omega_{\text{max}}$  and has the required temperature dependence, it does not, as might be expected, adequately describe the very short time reversals in the direction of motion of the angular momentum vector observed here in nearly all of these linear molecules, and which may tentatively be ascribed to libration of the molecules equivalent to that in the well-known Brot and Willie models for far infra-red absorptions of dipolar molecules.<sup>16</sup>

## APPENDIX

### TRUNCATION

In practice, the limits of integration in (1) are restricted to  $0 \leq \bar{\nu} \leq 2\bar{\nu}_m$  (where  $\bar{\nu}_g = 2\bar{\nu}_m$ ) This truncation can be expressed by multiplying the function

$$P(\bar{\nu}) = \frac{3h\bar{\nu}c^3n(\bar{\nu})\alpha(\bar{\nu})}{4\pi^2(1 - \exp(-h\bar{\nu}c/kT))}$$

by a “window function”  $G(\bar{\nu})$ . Therefore taking:

$$\hat{R}''_{\text{exp}}(t) = \int_{-\infty}^{\infty} P(\bar{\nu}) \exp(2\pi i\bar{\nu}ct) d\bar{\nu}$$

then:

$$\int_{-\infty}^{\infty} G(\bar{\nu})P(\bar{\nu}) \exp(2\pi i\bar{\nu}ct) d\bar{\nu} = \hat{R}''_{\text{exp}}(t) \otimes \hat{T}(t),$$

where  $\hat{T}(t)$  is the Fourier transform of  $G(\bar{\nu})$ , and is convoluted with  $R''_{\text{exp}}(t)$ , i.e.,

$$\hat{R}''_{\text{exp}}(t) \otimes \hat{T}(t) = \int_{-\infty}^{\infty} \hat{R}''_{\text{exp}}(u)\hat{T}(t-u) du$$

which is a function of  $t$ .



The function  $G(\bar{\nu})$  used in the algorithm was :

$$G(\bar{\nu}) = \begin{cases} 1 & \text{for } 0 \leq \bar{\nu} \leq 2\bar{\nu}_m \\ 0 & \text{otherwise} \end{cases}$$

the Fourier transform of which is :

$$\hat{T}^*(t) = 2\bar{\nu}_m \left[ \frac{\sin(2\bar{\nu}_m t)}{2\bar{\nu}_m t} + \frac{i \cos(2\bar{\nu}_m t)}{2\bar{\nu}_m t} \right].$$

Taking  $\hat{T}(t)$  as the real part of  $\hat{T}^*(t)$ , and defining  $\text{sinc}(y) = (\sin y)/y$ , then :

$$\begin{aligned} \hat{R}_{\text{exp}}''(t) \otimes \hat{T}(t) &= \int_{-\infty}^{\infty} \hat{R}_{\text{exp}}''(u) \cdot 2\bar{\nu}_m \text{sinc}(2\bar{\nu}_m(t-u)) du \\ &= \int_{-\infty}^{\infty} P(\bar{\nu}) G(\bar{\nu}) \exp(2\pi i \bar{\nu} ct) d\bar{\nu} \\ &= \int_0^{2\bar{\nu}_m} P(\bar{\nu}) \exp(2\pi i \bar{\nu} ct) d\bar{\nu} \\ &= \int_{-\infty}^{\infty} \hat{R}_{\text{exp}}''(u) \cdot 2\bar{\nu}_m \text{sinc}(2\bar{\nu}_m(t-u)) du. \end{aligned} \quad (\text{A.1})$$

To illustrate the effect on  $\hat{R}_{\text{exp}}''(t)$  of its convolution with  $\hat{T}(t)$ , consider the delta function  $\delta(\bar{\nu}_0)$  representing a line absorption at the frequency  $\bar{\nu}_0 < \bar{\nu}_g$ . The corresponding correlation function is :

$$R_{\text{exp}}''(t) = P(\bar{\nu}_0) \cos(2\pi \bar{\nu}_0 ct).$$

Substituting this in (A.1), then :

$$\begin{aligned} R_{\text{exp}}''(t) \otimes \hat{T}(t) &= \int_{-\infty}^{\infty} P(\bar{\nu}_0) \cos(2\pi \bar{\nu}_0 ct) 2\bar{\nu}_m \text{sinc}[2\bar{\nu}_m(t-u)] du \\ &= \pi P(\bar{\nu}_0) \cos(2\pi \bar{\nu}_0 ct) \quad \text{if } n\bar{\nu}_m > \bar{\nu}_0 \\ &= 0 \quad \text{if } \bar{\nu}_0 > \bar{\nu}_m \end{aligned}$$

where  $n$  is a positive integer.

Therefore, the only effect of the truncation on the transformation of the function  $\delta(\bar{\nu}_0)$  is to multiply the final result by  $\pi$ . As the experimental band spectrum can be considered for digital computation as a sum of such delta functions  $\delta(\bar{\nu}_i)$ ,  $i = 1, 2, \dots, m$ , and as the Fourier transform of a sum is itself a sum, then the normalisation of  $R_{\text{exp}}''(t)$  to unity at  $t = 0$  cancels out the truncation effect provided the condition  $n\bar{\nu}_m > \bar{\nu}_0$  holds, i.e., the experimental spectrum must be truncated at the point where  $\alpha(\bar{\nu}) = 0$  on the high frequency side so that  $\bar{\nu}_i$  never exceeds  $\bar{\nu}_g$ .

#### SAMPLING

In order to consider the effect of sampling the experimental band at discrete intervals  $\Delta\bar{\nu}$ , the infinite Dirac comb function  $W(\bar{\nu}/\Delta\bar{\nu})$  is used. This has the property that :

$$\begin{aligned} W(\bar{\nu}/\Delta\bar{\nu}) &= \sum_{n=-\infty}^{\infty} \delta(\bar{\nu}/\Delta\bar{\nu} - n) \\ &= \Delta\bar{\nu} \sum_{n=-\infty}^{\infty} \delta(\bar{\nu} - n\Delta\bar{\nu}) \end{aligned}$$

where  $\delta$  represents the Dirac delta function. The Fourier transform of  $W(\bar{\nu}/\Delta\bar{\nu})$  is :

$$1/F \cdot W(t/F)$$

which is another sequence of impulses, but spaced at intervals of  $F = 1/\Delta\bar{\nu}$ .

If we multiply  $P(\bar{\nu})$  by  $W(\bar{\nu}/\Delta\bar{\nu})$  we obtain the sampled function. The transform of this product is the convolution of the individual transforms :

$$\begin{aligned} & \int_{-\infty}^{\infty} P(\bar{\nu})W(\bar{\nu}/\Delta\bar{\nu}) \exp(i2\pi t\bar{\nu}c) d\bar{\nu} \\ &= 1/F \int_{-\infty}^{\infty} W(u/F)P(t-u) du \\ &= \int_{-\infty}^{\infty} \sum_n \delta(u-nF)P(t-u) du \\ &= \sum_{n=-\infty}^{\infty} P(t-nF) \equiv \sum_{n=-\infty}^{\infty} P(t+nF) = P_p(t). \end{aligned}$$

This proves that transformation of a function sampled at intervals leads to a *periodic* function  $P_p(t)$  with period  $F = 1/\Delta\bar{\nu}$ .

If the condition  $R''_{\text{exp}}(t) = 0$  for  $t > F/2$  or  $t > 1/(2\Delta\bar{\nu}c)$  is not fulfilled, then the replication of  $P(t)$  may lead to overlapping, or aliasing of the functions  $R''_{\text{exp}}(t) \otimes W(t/F)$ . Therefore we must choose  $\Delta\bar{\nu}$  sufficiently small for  $R''_{\text{exp}}(t) = 0$  for  $|t| > 1/(2\Delta\bar{\nu}c)$ .

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<sup>1</sup> D. R. Bosomworth and H. P. Gush, *Canad. J. Phys.*, 1965, **43**, 751.

<sup>2</sup> K. D. Möller and W. G. Rothschild, *Far-Infra-Red Spectroscopy* (Wiley Interscience, New York, 1970), chap. 10.

<sup>3</sup> H. Dardy, V. Voltera and T. A. Litovitz, *Chem. Soc. Symp. on Light Scattering and Infra-red Absorption*, Manchester, 1972, Paper 6.

<sup>4</sup> G. J. Davies and J. Chamberlain, *J.C.S. Faraday II*, 1973, **69**, 1739.

<sup>5</sup> G. J. Davies, J. Chamberlain and M. Davies, *J.C.S. Faraday II*, 1973, **69**, 1223.

<sup>6</sup> M. Evans, *J.C.S. Faraday II*, 1973, **69**, 763.

<sup>7</sup> W. Ho, G. Birnbaum and A. Rosenburg, *J. Chem. Phys.*, 1971, **55**, 1028.

<sup>8</sup> J. P. Colpa and J. A. A. Ketelaar, *Mol. Phys.*, 1958, **1**, 343.

<sup>9</sup> A. Gerschel, I. Darmon and C. Brot, *Mol. Phys.*, 1972, **23**, 317.

<sup>10</sup> R. G. Gordon, *J. Chem. Phys.*, 1965, **43**, 1307; 1964, **41**, 1819.

<sup>11</sup> J. E. Anderson and R. Uhlmann, *J. Chem. Phys.*, 1971, **55**, 4406.

<sup>12</sup> A. I. Baise, *J. Chem. Phys.*, 1974, **60**, 2936.

<sup>13</sup> M. C. Jones, N.B.S. Technical Note 390, April 1970, pp. 25-26, (U.S. Dept. of Commerce, Washington, D.C.).

<sup>14</sup> G. J. Davies, *Thesis* (University of Wales, 1971).

<sup>15</sup> R. A. Svehla, *Estimated Viscosities and Thermal Conductivities of Gases at High Temperature*, N.A.S.A. Technical Report No. R 132 (1962).

<sup>16</sup> I. W. Larkin, *J.C.S. Faraday II*, 1973, **69**, 1278.