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Collisional line-broadening in far i.r. induced dipolar absorption

MYRON W. EVANS*
Physical Chemistry Laboratory, South Parks Road, Oxford, OX1 3OZ

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Abstract—The J-diffusion model [10] is used to broaden the set of $J \rightarrow J+2$ line absorptions evolved from bimolecular quadrupole-induced dipolar absorption theory [5, 6] in non-dipolar linear (and symmetric-top) molecules. By progressively decreasing the characteristic time (τ) between pertubing events (assumed to be instantaneous encounters) a broad band absorption is generated from the original far i.r., $J \rightarrow J+2$ delta functions. The model is used to compute theoretical absorption bands for compressed gaseous and liquid nitrogen and for liquid cyanogen ($(CN)_2$). These are compared with the experimental data of BOSOMWORTH and GUSH [1] and of JONES [21] for N_2(g) and N_2(l) respectively. Effective molecular quadrupole moments are derived from each curve fitting. The poor agreement between model and observed absorptions in $(CN)_2$ (l) emphasizes the need, in condensed phases, to account for the intermolecular mean squared torque, which the J-diffusion formalism ignores.

INTRODUCTION

The absorptions of non-dipolar, linear molecules in the compressed gaseous and liquid phases observed [1–4] in the last few years in the far i.r. (2–250 cm^{-1}) have been treated usually in terms of bimolecular collisions [5, 6]. A dipole moment is induced in one molecule by the electrostatic field of the other and is modulated by the latter's rotational motion, the effects being mutual. The field is conveniently expanded in terms of point multipole moments [7], the first and dominant of these being the quadrupole (Q) term. It is a consequence of the tensorial nature [7] of Q that the subsequent theoretical spectrum consists of a series of line absorptions, spaced at intervals of $4B$, corresponding to $J \rightarrow J+2$ transitions. Here B is the linear molecule's rotational constant, and J the rotational quantum number.

However, the *observed* absorptions are broad bands, indicating that the translational, or collisional, widening of the proposed $J \rightarrow J+2$ lines must be taken into account. This paper aims to treat this perturbation simply, in terms analagous to those of GORDON's [8] J-diffusion model. The molecules are therefore considered to undergo periods of free rotation interrupted by instantaneous events ("collisions") which cause the magnitude of the angular momentum vector to be randomized onto a Boltzmann distribution and its orientation to be completely randomized. A collisional event is assumed to occur at an average rate τ^{-1}, where τ is the mean time between events. Since each collisional event destroys all correlation in the angular momentum of the molecule, the angular momentum correlation time is τ. In our case these events naturally cause the induced absorption observable in the far i.r. A disadvantage of assuming instantaneous collisions is that the behaviour of the computed spectrum at short times (high frequency) will not be realistic [9] in the sense that spectral transparency at high frequencies is reached too slowly. This model retains also the disadvantage of point–multipole-induced dipole absorption theory in that:

(i) an eigenstate of the interacting pair is taken as the product of the eigenstates of the isolated molecules. This is adequately correct only for a purely central intermolecular potential U_{AA} (R), which can then be approximated by a Lennard–Jones potential.

(ii) Three body and higher interactions are ignored.

(iii) Short range interactions are not explicitly treated.

The theoretical spectrum $\alpha(\bar{\nu})$ is derived below for both linear and symmetric top molecules. Here, α is the absorption coefficient per unit path length (neper cm^{-1}) and $\bar{\nu}$ (cm^{-1}) is the wavenumber. This is compared with the observed $\alpha(\bar{\nu})$ for liquid nitrogen and liquid cyanogen, $(CN)_2$. The former's geometry is much better suited to a point–multipole field expansion, which may partly explain why this model is more successful in describing the observed absorption in liquid nitrogen.

Theory

These far i.r. absorption bands [1–4] have associated time correlation functions, given in general

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*Present address. Edward Davies Chemistry Laboratories, Aberystwyth, SY23 1WE.

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[10] by:

$$C(t)=\int_{-\infty}^{\infty}\exp(i\omega t)\left(\frac{3\hbar c}{4\pi^2}\right)\frac{\sigma(\omega)\,\mathrm{d}\omega}{\omega(1-\exp(-\hbar\omega/kT))} \tag{1}$$

where σ is the absorption cross section per molecule, ω is the angular frequency ($2\pi\bar{\nu}c$), t the time elapsed from an arbitrary initial $t=0$. The absorption cross section $\sigma(\omega)$ is related to the absorption intensity, which for each quantum transition in a bimolecular collision of non-dipolar molecules is given by [5, 6]:

$$I_{\mathrm{AA}}=\frac{4\pi^3\bar{\nu}N^2}{3hc}\rho(\bar{\nu})\int_0^{\infty}4\pi R^2\exp(-U_{\mathrm{AA}}(R)/kT$$
$$\times\sum_{m_i m_f}|\langle im_i|\boldsymbol{\mu}^{\mathrm{AA}}(R)|fm_f\rangle|^2\,\mathrm{d}R \tag{2}$$

Where $\rho(\bar{\nu})$ is a Boltzmann distribution term, R is the intermolecular separation, $|im_i\rangle, |fm_f\rangle$ are rotational-type eigenstates for the pair, $\boldsymbol{\mu}^{\mathrm{AA}}(R)$ is the induced dipole moment, and N the molecular number density.

The classical approximation to $C(t)$ has the general property [11] of being an even function in time, and is also a solution of the integrodifferential equation:

$$\dot{C}(t)=-\int_0^t K_0(t-\tau')C(\tau')\,\mathrm{d}\tau' \tag{3}$$

where the set of kernels $K_0(t),\ldots, K_n(t)$ obey the set of coupled Volterra equations such that:

$$\frac{\partial}{\partial t}K_{n-1}(t)=-\int_0^t K_n(\tau')K_{n-1}(t-\tau')\,\mathrm{d}\tau' \tag{4}$$

with $n=0, 1,\ldots, N$.

The M and J diffusion models of Gordon [8] and McClung [12] have been simply and elegantly rederived by Bliot *et al.* [13–15] by truncating the series of Equations (4) using the hypothesis that the reorientation of the molecular angular momentum is instantaneous, and governed by a Poisson law:

$$K_0(t)=K_{FR}(t)\exp(-|t|/\tau) \tag{5}$$

where $K_{FR}(t)$ is associated via Equation (3) with $C_{FR}(t)$ the correlation function for the contour of the unbroadened line absorptions. Here, the hypothesis (5) is applied to $C_{FR}(t)$ derived from the Equation (2).

The resulting spectrum $\alpha(\bar{\nu})$ is related to an effective quadrupole moment through Buckingham's [16] equation for the total dispersion, ($\varepsilon_0-\varepsilon_\infty$).

For bimolecular, quadrupole-induced dipolar absorption in linear, non-dipolar molecules, the correlation function associated with Equation (2) may be written [17] as:

$$C_{FR}(t)=\frac{1}{A}\int_0^{\infty}f_0(\Omega)\cos\Omega t\,\mathrm{d}\Omega \tag{6}$$

where

$$A=\int_0^{\infty}f_0(\Omega)\,\mathrm{d}\Omega,$$

and

$$f_0(\Omega)=\left(\frac{\Omega}{4\pi Bc}-\frac{4\pi Bc}{\Omega}\right)$$
$$\times\exp\left[-\frac{hcB}{4kT}\left(\frac{\Omega}{4\pi Bc}-3\right)\left(\frac{\Omega}{4\pi Bc}-1\right)\right]$$

For non-dipolar symmetric tops [6]:

$$f_1(\Omega)=\sum_{K=-J}^{J}[S(I,\ K)\Gamma_K\exp\left(-\zeta\left(\frac{\bar{\nu}}{4B}-\frac{3}{2}\right)\left(\frac{\bar{\nu}}{4B}-\frac{1}{2}\right)\right)$$
$$\times\left[\frac{18\alpha_0^2}{\bar{\nu}^2}\mathrm{f}(\bar{\nu},\ K)\right], \tag{7}$$

where

$$\Gamma_K=\exp(-(A'-B)K^2hc/kT);$$
$$\zeta=Bhc/kT;$$

and

$$f_1(\bar{\nu},\ K)=\frac{\bar{\nu}(\bar{\nu}-2B(2K-1))(\bar{\nu}-2B(2K+1))\times(\bar{\nu}+2B(2K+1))(\bar{\nu}+2B(2K-1))}{8B(\bar{\nu}-2B)(\bar{\nu}+2B)}$$

with $\Omega=2\pi\bar{\nu}c$. In these equations, $S(I,\ K)$ is a nuclear spin weighting factor [3, 6], A' and B are the rotational constants, and K the projection quantum number in the molecule-fixed axis of the total angular momentum quantum number J, the latter being given [3, 6] by $\bar{\nu}=2B(2J+3)$.

Taking Laplace transforms of Equations (3) and (5) yields:

$$C(p)=1/(p+K_{FR}(p+1/\tau)) \tag{8}$$

where p is the Laplace variable and $\tilde{C}(\omega)$, the inverse transform of $C(p)$, is a function related to $\alpha(\omega)$. We also have

$$C_{FR}(p+1/\tau)=1/[K_{FR}(p+1/\tau)+(p+1/\tau)] \tag{9}$$

and thus:

$$C(p)=\frac{C_{FR}(p+1/\tau)}{1-\tau^{-1}C_{FR}(p+1/\tau)} \tag{10}$$

$$=\sum_{n=0}^{\infty}\frac{1}{\tau^n}C_{FR}^{n+1}(p+1/\tau) \tag{11}$$

from MacLaurin's theorem. The inverse Laplace transform of this series gives the perturbed correlation function $C_p(t)$ directly as:

$$\begin{aligned}C_p(t) = \mathrm{e}^{-t/\tau}\Bigg[C_{FR}(t) + \frac{1}{\tau} & \\ & \times \int_0^t C_{FR}(t-t_1) C_{FR}(t_1)\,\mathrm{d}t \\ & + \frac{1}{\tau^2}\int_0^t C_{FR}(t-t_1)\,\mathrm{d}t_1 \\ & \times \int_0^{t_1} C_{FR}(t-t_2) C_{FR}(t_2)\,\mathrm{d}t_2 \\ + \ldots\ldots\ldots & + \frac{1}{\tau^n}\int_0^t C_{FR}(t-t_1)\,\mathrm{d}t_1 \\ & \times \int_0^{t_1} C_{FR}(t_1-t_2)\,\mathrm{d}t_2 \ldots \\ & \times \int_0^{t_{n-1}} C_{FR}(t_{n-1}-t_n) C_{FR}(t_n)\,\mathrm{d}t_n \Bigg] \qquad (12)\end{aligned}$$

which can be computed conveniently on a fast machine.

The perturbed spectral profile is proportional to $\tilde{C}(\omega)$, which is the Fourier transform of $C_p(t)$. Its calculation is greatly simplified because the kernel $K_0(t)$ has an exponential factor $\exp(-|t|/\tau)$—the fraction of molecules not having undergone collision at time t from an arbitrary initial $t=0$. The interval τ is real, positive, number such that the poles of $C(p)$ have a real, negative part, and:

$$\tilde{C}(\omega) = \mathrm{Real}\,[C(p)]_{p=i\omega} \qquad (13)$$

$$= \mathrm{Real}\,[C(i\omega)] \qquad (14)$$

Therefore, in Equation (11):

$$C(i\omega) = \frac{C_{FR}(i\omega+\tau^{-1})}{1-\tau^{-1}C_{FR}(i\omega+\tau^{-1})} \qquad (15)$$

Taking the Laplace transform of Equation (6) gives:

$$C(p) = \frac{1}{A}\int_0^\infty \frac{f(\Omega)p}{p^2+\Omega^2}\,\mathrm{d}\Omega \qquad (16)$$

so that

$$C_{FR}(i\omega+\tau^{-1}) = \Gamma + i\Lambda \qquad (17)$$

with

$$\Gamma(\omega,\Omega) = \frac{1}{A}\int_0^\infty f(\Omega)\left[\frac{\tau^{-1}(\Omega^2+\omega^2+\tau^{-2})}{(\Omega^2-\omega^2+\tau^{-2})^2+4\omega^2\tau^{-2}}\right]\mathrm{d}\Omega$$

$$\Lambda(\omega,\Omega) = \frac{1}{A}\int_0^\infty f(\Omega)\left[\frac{\omega(\Omega^2-\omega^2-\tau^{-2})}{(\Omega^2-\omega^2+\tau^{-2})^2+4\omega^2\tau^{-2}}\right]\mathrm{d}\Omega$$

Taking the real part of Equation (15) gives:

$$\tilde{C}(\omega) = \frac{\Gamma(1-\tau^{-1}\Gamma)-\tau^{-1}\Lambda^2}{(1-\tau^{-1}\Gamma)^2+\tau^{-2}\Lambda^2} \qquad (18)$$

The absorption coefficient is then given [16] by:

$$\alpha(\omega) = \frac{(\varepsilon_0-\varepsilon_\infty)\omega^2}{n(\omega)c}\,\tilde{C}(\omega) \qquad (19)$$

where $n(\omega)$ is the frequency dependent refractive index, and c the velocity of light. For quadrupole-induced dipole absorption in pair collisions [16]:

$$(\varepsilon_0-\varepsilon_\infty) = \frac{16\pi^2}{kT}N^2\bar{\alpha}_p^2Q^2 \times \int_0^\infty R^{-6}\exp(-U_{AA}(R)/kT)\,\mathrm{d}R \qquad (20)$$

with $\bar{\alpha}_p$ as the mean molecular polarizability and Q the quadrupole moment. The integrals Γ and Λ can be evaluated numerically and both vanish as $\omega\to\infty$. The quadrupole in Equation (20) is regarded as the apparent value needed to fit the observed integrated intensity.

DISCUSSION

The broadening of the individual $J\to J+2$ absorptions is an important effect in the description of these spectra, since the individual features have been resolved only for H_2 [1] and for HCl and HBr [18] in the compressed gaseous phase. Figure 1 shows how Equation (19) produces a function $\alpha(\bar{v})$

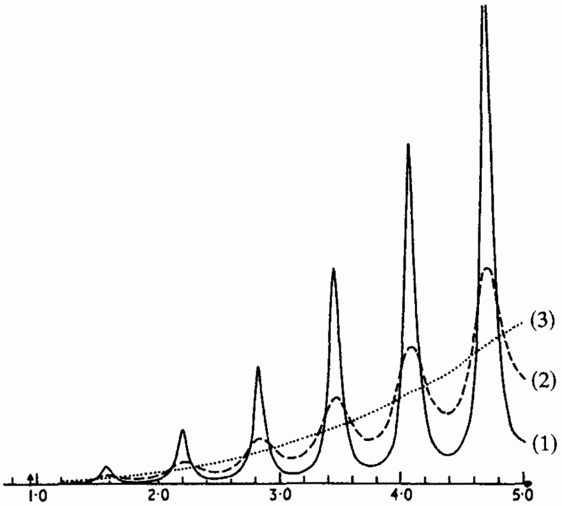

Fig. 1. The first few $J\to J+2$ transitions broadened by Equation (19) for cyanogen ($B=0.1571\,\mathrm{cm}^{-1}$) at 350 K. (1) $\tau=100$ ps; (2) $\tau=35$ ps; (3) $\tau=10$ ps. *Ordinate* Intensity (arbitrary units). *Abscissa* $\bar{v}$/cm^{-1}.

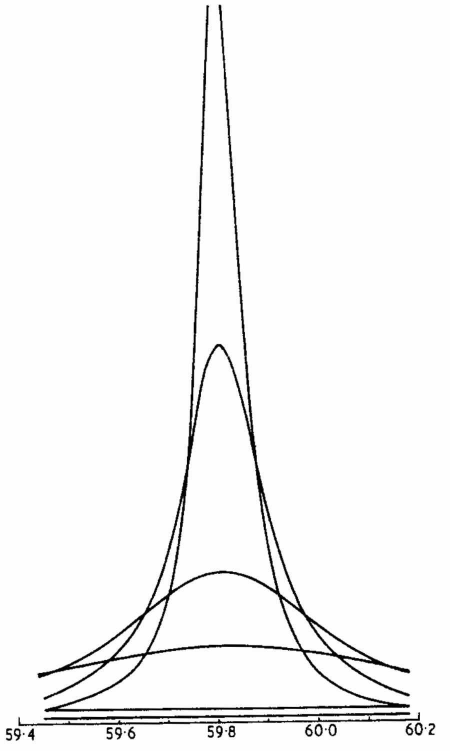

Fig. 2. An individual $J \rightarrow J+2$ peak's behaviour with varying τ for nitrogen at 76.4 K. From top to bottom: $\tau = 100$ ps; 50 ps; 20 ps; 10 ps; 1 ps; and 0.1 ps. *Ordinate* Intensity (arbitrary units). *Abscissa* $\bar{\nu}$/cm^{-1}.

which simulates the broadening and eventual fusing of the proposed $J \rightarrow J+2$ lines in, for example, cyanogen ($B = 0.1570$ cm^{-1}). A broad continuum is reached at $\tau \doteq 10$ ps, which, according to simple kinetic theory, corresponds to a mean free path of about 38 Å. Thus, according to this model, a continuum absorption is reached before triple collisions become significant. As τ decreases from 100 ps to 10 ps the overall integrated intensity, given by:

$$A_0 = \int_{\text{band}} \alpha(\bar{\nu})\, \mathrm{d}\bar{\nu}$$

is conserved. Figure 2 illustrates the broadening of a single $J \rightarrow J+2$ transition in nitrogen ($B = 1.993$ cm^{-1}) at 76.4 K.

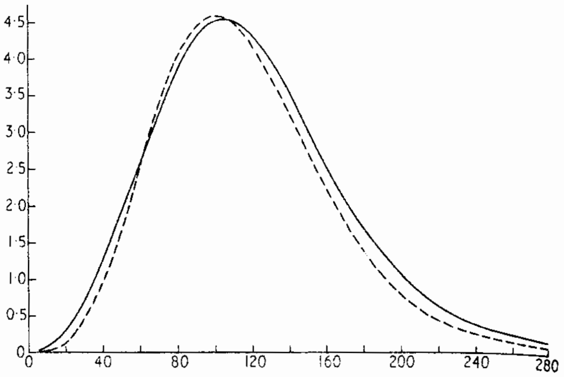

Fig. 3. ——— Absorption [1] of compressed gaseous nitrogen in the far i.r. at 300 K. ---- Equation (19) with $\tau = 0.4$ ps, $|Q| = 5 \times 10^{-40}$ C m^2. *Ordinate* Intensity (10^6 cm^{-1} amagat^{-2}). *Abscissa* $\bar{\nu}$/cm^{-1}.

The calculated $\alpha(\bar{\nu})$ of Equation (19) is matched with experimental data for nitrogen in Figs. 3 and 4. Figure 3 illustrates the far i.r. band observed in compressed gaseous nitrogen at 300 K by BOSOMWORTH and GUSH [1], and superimposed is $\alpha(\bar{\nu})$ from Equation (19) with an angular momentum correlation time of 0.4 ps [19]. An effective quadrupole moment of $|Q| = 5 \times 10^{-40}$ C m^2 was extracted from this curve fitting procedure using Equation (20) for the effective total dispersion $\varepsilon_0 - \varepsilon_\infty$. Despite the neglect of effects such as three body collisions, higher multipole-induced dipolar absorptions (involving $J \rightarrow J+4$ absorptions), translational, and electronic overlap absorption [20], this estimate of $|Q|$ compares favourably with KIELICH'S [7] collection of $|Q| = 4.5$–6.9×10^{-40} C m^2 taken from the results of techniques unrelated to far i.r. pressure-induced absorption. Therefore this model is capable of giving a reasonably effective quantitative account of the absorption intensity and bandshape in N_2(g). Previous descriptions [1–5, 17, 18, 20] have not included a mechanism of broadening for the assumed quantized absorptions, which have been left as a set of $J \rightarrow J+n$ ($n = 1, 2$) lines.

Equation (19) is less successful with N_2(1) at 76.4 K (Fig. 4). The calculated curve is for $\tau = 0.1$ ps and normalized to the $\alpha_{\max}$ of the observed [21] band. The $|Q|$ estimated from this normalization is 3×10^{-40} C m^2, a value significantly less than that deduced from the gas phase curve fitting. This

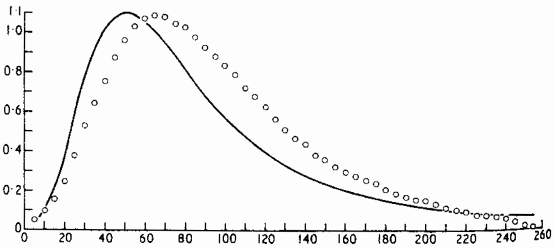

Fig. 4. -○- Absorption [21] of liquid nitrogen at 76.4 K —— Equation (19) with $\tau = 0.1$ ps, $|Q| = 3 \times 10^{-40}$ C m^2 *Ordinate* α/neper cm^{-1}. *Abscissa* $\bar{\nu}$/cm^{-1}.

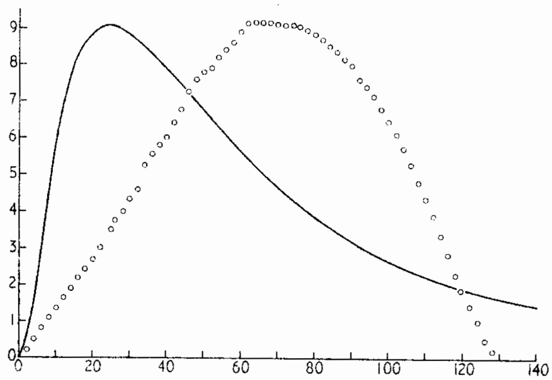

Fig. 5.-○- Absorption of $(CN)_2(1)$ at [4] 301 K. —— Equation (19) with $\tau = 0.1$ ps; $|Q| = 9.7\times10^{-26}$ e.s.u. *Ordinate* $\alpha(\bar{\nu})$/neper cm^{-1}. *Abscissa* $\bar{\nu}/cm^{-1}$.

apparent decrease in Q on going from compressed gas to liquid is characteristic [2–4, 6] when a bimolecular model of induced absorption such as this is used in a condensed phase. Therefore neglect of line broadening in the previous studies is not the cause of an effect which would be physically meaningless if a pair of molecules were considered in isolation. An explanation which has been offered [3, 4] is the reduced efficacy of multi-molecular collisions in generating dipoles since the effective electrostatic field on a central molecule would be the resultant of the coordination number of surrounding ones, and not just the one as in the bimolecular model. In liquid CO_2 [2] that part of the induced dipole moment due to quadrupolar induction is effectively cancelled in the liquid, leaving essentially the contribution from shorter-range interactions.

Equation (19) is least successful with $(CN)_2(l)$ at 301 K (Fig. 5) [4]. There is a considerable discrepancy in the observed and calculated frequencies of the maximum absorption ($\bar{\nu}_{max}$). This shift in the observed $\bar{\nu}_{max}$ can reasonably be interpreted in terms of the increased amount of shorter range interactions in the liquid phase, where the torque forces on a rod-like molecule such as $(CN)_2$ will, a priori, be substantially greater than those on $N_2(1)$. This is merely saying that collision interrupted free rotation is not the case in the liquid phase of the great majority of both non-dipolar and dipolar molecules. Thus shifts between the gaseous and liquid $\bar{\nu}_{max}$ (of rotational type far i.r. absorptions) have been observed of 25 cm^{-1} in [2] CO_2, 30 cm^{-1} in [3] N_2O, and 60 cm^{-1} in [22] propyne. The present J-diffusion type model cannot move the position of $\bar{\nu}_{max}$ vecause the reorientation of the molecular angular momentum is assumed to take place during an infinitely short time, and it is thus impossible to get any information about, or to take any account of, the intermolecular mean square torque $\langle N^2\rangle$.

However, the continued fraction representation of Equation (3) produces a hierarchy which implicitly contains equilibrium averages, directly related to $\langle N^2\rangle$ and its time derivatives. Therefore, assuming [23] that in this representation the nth order random force of the molecular interaction process is governed by a Poisson distribution, a new expression for $C(t)$ and thus for $\alpha(\bar{\nu})$ can, in principle, be obtained which takes account of $\langle N^2\rangle$ in these non-dipolar liquids.

The problem of the resultant absorption intensity would still remain, since there seems to be no easy way of predicting the resultant field on the central molecule. Hopefully the problem of bandshape can be separated from that of the overall absolute intensity of absorption, as in the theory above.

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REFERENCES

[1] D. R. Bosomworth and H.P. Gush, *Can. J. Phys.*, **43,** 751 (1965).
[2] W. Ho, G. Birnbaum and A. Rosenberg, *J. Chem. Phys.*, **55(3),** 1028, 1039 (1971).
[3] A. I. Baise, *J. Chem. Soc. Faraday II,* **68,** 1904 (1972).
[4] M. Evans, *J. Chem. Soc. Faraday II,* **69,** 763 (1973).
[5] J. P. Colpa and J. A. A. Ketelaar, *Molec. Phys.*, **1,** 343 (1958).
[6] B. S. Frost, *J. Chem. Soc. Faraday II,* **69,** 1142 (1973); G. J. Davies and M. Evans, *J. Chem. Soc. Faraday II,* **71,** 1275 (1975); **72,** 40 (1976).
[7] S. Kielich, *Dielectric and Related Molecular Processes, Vol. I, Chemical Society Specialist Periodic Reports,* (Ed. Mansel Davies), 1972.
[8] R. G. Gordon, *J. Chem. Phys.*, **44,** 1830 (1965).
[9] I. W. Larkin, *J. Chem. Soc. Faraday II,* **70,** 1457 (1974).
[10] R. G. Gordon, *J. Chem. Phys.*, **43,** 1307 (1965).
[11] B. J. Berne and G. D. Harp, *Adv. Chem. Phys.*, **17,** 63 (1970).
[12] R. E. D. McClung, *J. Chem. Phys.*, **57,** 5478 (1972).
[13] F. Bliot, Thèse d'État, Univ. of Lille, 1973.
[14] F. Bliot and E. Constant, *Chem. Phys. Lett.*, **18,** 253 (1973).
[15] F. Bliot, C. Abbar and E. Constant, *Molec. Phys.*, **24,** 241 (1972).
[16] G. J. Davies, J. Chamberlain, and Mansel Davies, *J. Chem. Soc. Faraday II,* **69,** 1223 (1973).
[17] M. Evans, *J. Chem. Soc. Faraday II,* **71,** 71 (1975).

[18] S. Weiss and R. H. Cole, *J. Chem. Phys.*, **46,** 644 (1967).
[19] T. E. Eagles and R. E. D. McClung, *J. Chem. Phys.*, **59,** 435 (1973).
[20] J. H. van Kranendonk and Z. J. Kiss, *Can. J. Phys.*, **37,** 1187 (1959); J. D. Poll and J. H. van Kranendonk, *Can. J. Phys.*, **39,** 189 (1961).
[21] M. C. Jones, N.B.S. Technical Note 390, April 1970, pp., 25–26, (U.S. Dept. of Commerce, Washington, D.C.).
[22] M. W. Evans, *Spectrochim. Acta*, **30A,** 79 (1974).
[23] F. Bliot And E. Constant, *Chem. Phys. Lett.*, **29** 618 (1974).