

## Decrease in Frequency of Maximum Far-Infra-Red Power Absorption of Polar Fluids with Temperature.

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**Summary.** — It is shown how the inherent nonlinearity of the equations of motion of coupled dipoles qualitatively explains a number of features of the observed far-infra-red spectrum of polar fluids. These include the almost linear decrease of the peak position of the FIR power absorption coefficient with increasing temperature and the temperature independence of the band width.

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It has been repeatedly observed<sup>(1-5)</sup> that the position of maximum far-infra-red (FIR) absorption for various polar fluids shows considerable temperature dependence. We cite dichloromethane<sup>(1,3,4)</sup> supercooled halogenobenzene-decalin solutions, methylchloride<sup>(5)</sup> and acetone<sup>(6)</sup>. The frequency  $(f_{\max})_{\alpha} = c\bar{\nu}_{\max}$  of maximum FIR power absorption appears to decrease

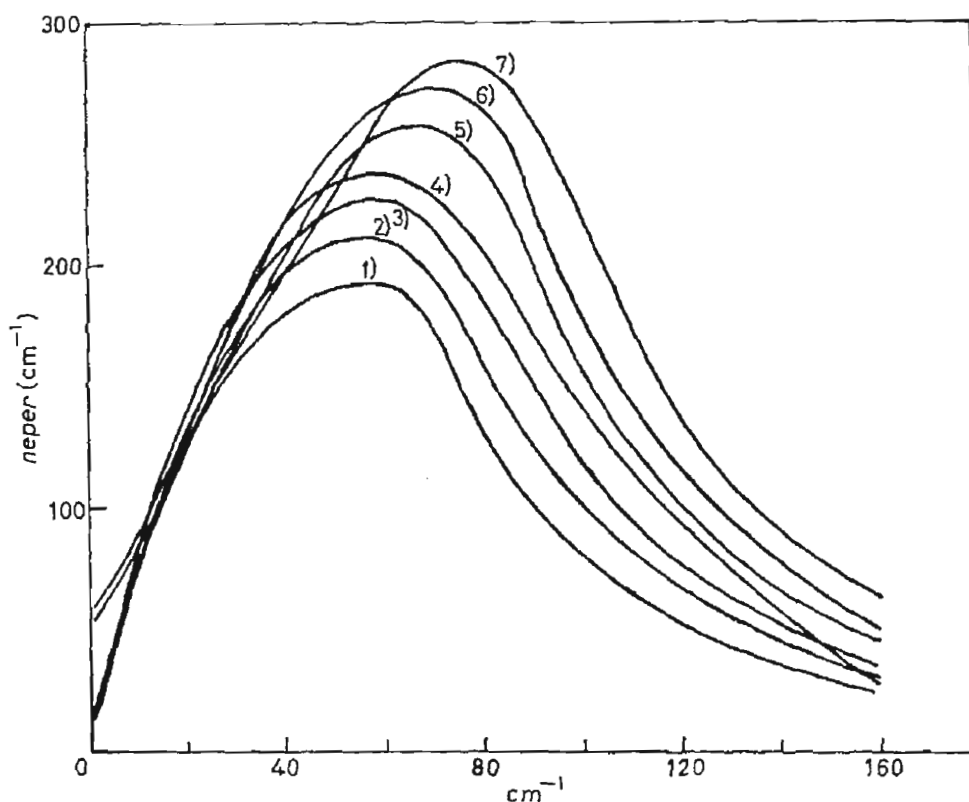


Fig. 1. — Power absorption coefficient  $\alpha$  in neper  $\text{cm}^{-1}$  as a function of wave number for methyl chloride; curves 1)-7) for temperatures of 333, 313, 293, 273, 253, 233 and 213 K, respectively. Results deduced using the Maxwell relationship

$$\alpha(\omega) = \frac{\omega \epsilon''(\omega)}{n(\omega)c}, \text{ where } n(\omega) = \sqrt{\frac{1}{2}[\epsilon'(\omega) + \sqrt{\epsilon'(\omega)^2 + \epsilon''(\omega)^2}]}$$

and  $c$  is the velocity of light *in vacuo* from measurements reported in ref. (5).

(1) M. W. EVANS, G. J. EVANS, W. T. COFFEY and P. GRIGOLINI: *Molecular-Dynamics and Theory of Broad Band Spectroscopy* (Wiley Interscience, New York, N. Y., 1982).

(2) J. K. VIJ, C. J. REID, G. J. EVANS, M. FERRARIO and M. W. EVANS: *Adv. Mol. Relaxation Int. Processes*, **22**, 79 (1982).

(3) C. J. REID and J. K. VIJ: *J. Chem. Phys.*, **79**, 4624 (1983).

(4) C. J. REID, G. J. EVANS, M. W. EVANS and W. T. COFFEY: *Chem. Phys. Lett.*, **56**, 529 (1978).

(5) A. GERSCHEL, T. GROCHULSKI, Z. KISIEL, L. PSICZOLKOWSKI and K. LEIBLER: *Mol. Phys.*, **54**, 97 (1985).

(6) J. K. VIJ and F. HUFNAGEL: in *Dynamical Processes in Condensed Matter*, edited by M. W. EVANS, Vol. **63**: of *Advances in Chemical Physics* (Wiley Interscience, New York, N. Y., 1985).

almost linearly with temperature, while the band width of the FIR spectrum is almost temperature independent (see fig. 1-4). This temperature dependence is in marked contrast to that of the dielectric loss peak in the microwave band. The frequency of maximum dielectric loss ( $f_{\max}$ )<sub>s</sub> increases with increase in temperature as predicted by the Debye theory (6).

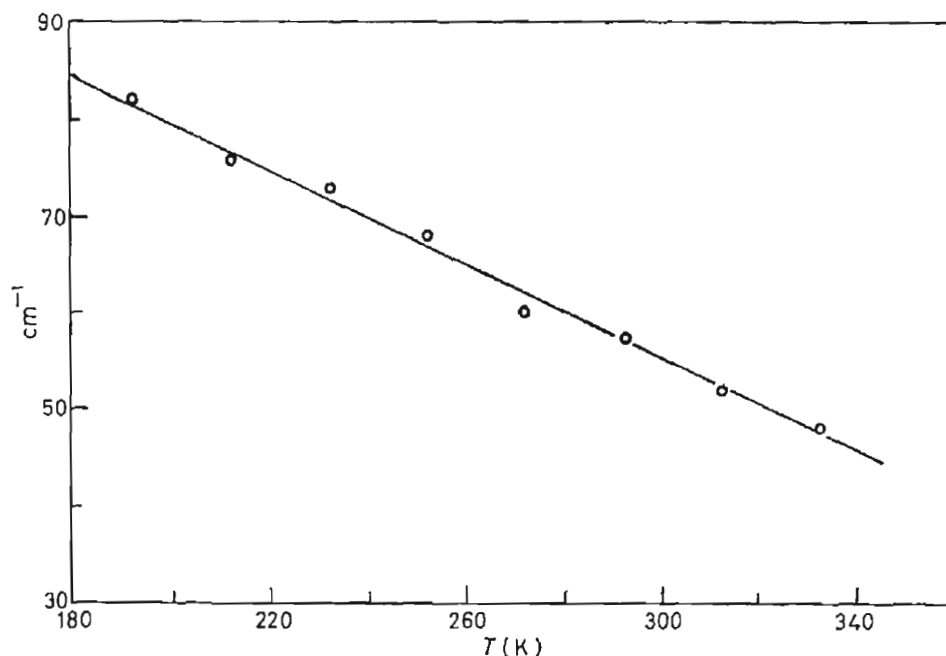


Fig. 2. - Position of the frequency of maximum power absorption coefficient in  $\text{cm}^{-1}$  as a function of temperature in K for methyl chloride.

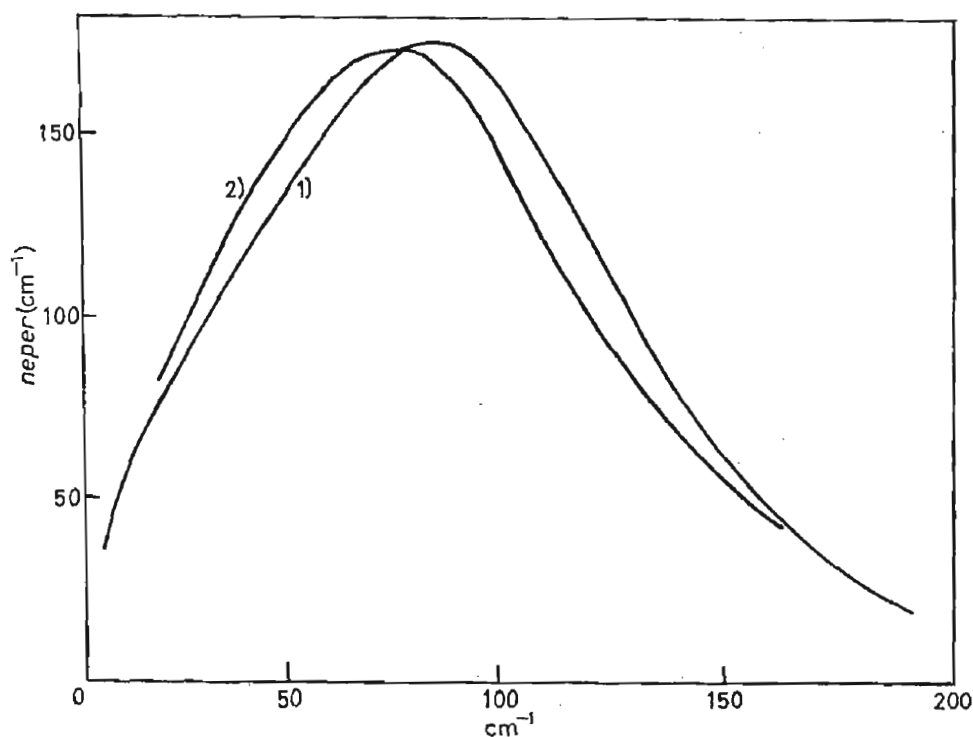


Fig. 3. - Power absorption coefficient for dichloromethane at two temperatures: i) 308 K, ii) 312 K.

Here we wish to demonstrate how the variation of  $(f_{\max})_{\alpha}$  may be predicted by extending the Debye theory <sup>(8)</sup> to include both inertial effects and dipole-dipole coupling.

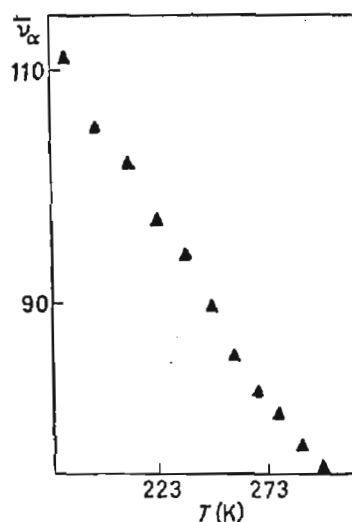


Fig. 4. — Position of the frequency of maximum power absorption in  $\text{cm}^{-1}$  as a function of temperature for dichloromethane. (Curve reproduced from ref. <sup>(7)</sup>).

In his theory of dielectric relaxation, DEBYE <sup>(8)</sup> considered an assembly of molecules, each having a permanent dipole moment  $\mu$ . He supposed that the dipole-dipole coupling between each dipole and the inertia of a dipole may be ignored. Thus the problem of dielectric relaxation is reduced to the rotational Brownian motion without inertial effects of a rigid rotator subjected to a weak external unidirectional electric field  $E$ . The relaxation is studied by assuming that  $E$  is suddenly switched off at a time  $t = 0$ . Thus, if  $\varphi(t)$  is the angle which  $\mu$  makes with the direction that  $E$  had, for  $t > 0$  the equation of motion of  $\mu$  is

$$(1) \quad \zeta \dot{\varphi}(t) = \lambda(t),$$

$\zeta \dot{\varphi}$  is the viscous drag torque acting on  $\mu$  due to Brownian motion;  $\lambda$  is a white-noise driving torque.

The effect of inertia alone may be fully incorporated into the Debye theory <sup>(8,9)</sup>. Severe computational difficulties arise, however, when dipole-dipole coupling is included. One is then faced with the many-body problem.

<sup>(7)</sup> F. MARCHESONI, J. K. VIJ and W. T. COFFEY: *Z. Phys. B*, **61**, 357 (1985).

<sup>(8)</sup> J. R. McCONNELL: *Rotational Brownian Motion and Dielectric Theory* (Academic Press, New York, N. Y., 1980).

<sup>(9)</sup> B. K. P. SCAIFE: *Complex Permittivity* (The English Universities Press, London, 1971).

Due to that problem, it is really only possible to take into account in detail the effects of its nearest neighbour on the dynamics of a particular dipole. Thus, following a suggestion of Scaife<sup>(10)</sup>, we modify eq. (1) to read

$$(2) \quad I_1 \ddot{\varphi}_1(t) + \zeta_1 \dot{\varphi}_1(t) + b \sin(\varphi_1 - \varphi_2) = \lambda_1(t),$$

$$(3) \quad I_2 \ddot{\varphi}_2(t) + \zeta_2 \dot{\varphi}_2(t) - b \sin(\varphi_1 - \varphi_2) = \lambda_2(t).$$

These equations incorporate fully the effect of a nearest-neighbour dipole  $\mu_2$  which rotates about the same axis as the dipole  $\mu_1$ ,  $I_1$  is the moment of inertia of  $\mu_1$ ,  $\zeta_1 \dot{\varphi}_1$  and  $\lambda_1$  are the Brownian torques acting on  $\mu_1$ ;  $I_2$ ,  $\zeta_2 \dot{\varphi}_2$ ,  $\lambda_2$ , likewise for  $\mu_2$ ;  $\varphi_1$  and  $\varphi_2$  are the angles  $\mu_1$  and  $\mu_2$  make with a reference direction taken as the direction which a d.c. field switched off at  $t = 0$  had.  $b \sin(\varphi_1 - \varphi_2)$  is due to dipole-dipole coupling. Equations similar to (2) and (3), but with  $I_1 = I_2 = 0$ , were discussed by BUDÓ<sup>(11)</sup>. He reduces the solution to a Sturm-Liouville problem.

In the case in which inertial effects are included, the complex polarizability may be calculated by writing down the Kramers equation<sup>(12,13)</sup>. This leads to a set of differential-difference equations<sup>(13)</sup> (the Brinkman equations). These govern the exact time dependence of the polarization, etc. They can only be solved numerically. This requires extensive computing time<sup>(14)</sup>.

A major simplification can be made if the stochastic torques are supposed very weak in comparison to the deterministic ones. Then

$$(4) \quad I_1 \ddot{\varphi}_1(t) + b \sin(\varphi_1 - \varphi_2) = 0,$$

$$(5) \quad I_2 \ddot{\varphi}_2(t) - b \sin(\varphi_1 - \varphi_2) = 0.$$

These possess a first integral, namely the Hamiltonian. For maximum simplicity, let  $I_1 = I_2$ . Then, with

$$(6) \quad \chi = \frac{\varphi_1 + \varphi_2}{2}, \quad \eta = \frac{\varphi_1 - \varphi_2}{2},$$

$$(7) \quad I \ddot{\chi} = 0,$$

$$(8) \quad 2\ddot{\eta} + \omega_0^2 \sin 2\eta = 0,$$

$$(9) \quad \omega_0 = \sqrt{\frac{2b}{I}}.$$

<sup>(10)</sup> B. K. P. SCAIFE: private communication.

<sup>(11)</sup> A. BUDÓ: *J. Chem. Phys.*, **17**, 686 (1949).

<sup>(12)</sup> S. CHANDRASEKHAR: *Rev. Mod. Phys.*, **15**, 1 (1943).

<sup>(13)</sup> W. T. COFFEY, M. W. EVANS and P. GRIGOLINI: *Molecular Diffusion and Spectra*, (Wiley Interscience, New York, N. Y., 1984).

<sup>(14)</sup> M. W. EVANS, M. FERRARIO and W. T. COFFEY: *Adv. Mol. Relaxation Int. Processes*, **20**, 10 (1980).

The equation  $\eta$  is the pendulum equation with a  $\cos 2\eta$  potential. We note that these equations do not contain any stochastic torques. There can be no net absorption of energy and the question will arise as to what one means by the complex polarizability, etc. We state that we regard such equations as giving the behaviour when the stochastic forces are still present, but are weak compared to the deterministic ones.

With  $2\eta = \delta$  we can recast eq. (8) as <sup>(15)</sup>

$$(10) \quad \ddot{\delta} + \frac{2b}{I} \sin \delta = 0.$$

The Hamiltonian is

$$(11) \quad E = \frac{1}{2} I \dot{\delta}^2 - 2b \cos \delta.$$

We now suppose that the motion is oscillatory so that  $\dot{\delta} = 0$  for  $\delta = \pm \delta_0$ . Thus

$$(12) \quad E = -2b \cos \delta_0,$$

so that

$$(13) \quad \cos \delta_0 = \frac{-E}{2b}.$$

Now the periodic time <sup>(16)</sup> is

$$(14) \quad \tau(\delta_0) = 2\pi \sqrt{\frac{I}{2b}} \left[ 1 + \left(\frac{1}{2}\right)^2 K^2 + \left(\frac{1.2}{3.4}\right) K^4 + \dots \right],$$

where

$$(15) \quad K^2 = \sin^2 \frac{1}{2} \delta_0 = \frac{1}{2} \left( 1 + \frac{E}{2b} \right).$$

The angular frequency is then

$$(16) \quad \omega(\delta_0) = \omega_0 \left[ 1 - \frac{1}{8} \left( 1 + \frac{E}{2b} \right) + O(K^4) \dots \right]$$

in agreement with ref. <sup>(16)</sup>.

If  $E \simeq kT$ , where  $2b > kT$ , we have

$$(17) \quad \omega(\delta_0) = \omega_0 \left[ 1 - \frac{1}{8} \left( 1 + \frac{kT}{2b} \right) + O(K^4) \dots \right].$$

<sup>(15)</sup> J. L. SYNGE and B. A. GRIFFITH: *Principles of Mechanics* (D. Van Nostrand Co., New York, N. Y., 1950).

<sup>(16)</sup> H. RISKEN and H. D. VOLLMEER: *Mol. Phys.*, **46**, 555 (1982).

Thus the natural frequency of oscillation appears to *decrease* with increasing temperature in accordance with experiment <sup>(14)</sup>.

The temperature dependence of the *Q*-factor and the band width may also be roughly predicted.

For the equation

$$(18) \quad \ddot{\delta} + \beta\dot{\delta} + \omega_0^2\delta = A(t),$$

the *Q* factor is <sup>(17)</sup>

$$(19) \quad Q_0 = \frac{\omega_0}{\beta}.$$

If we consider small nonlinearities, *Q* becomes

$$(20) \quad Q_0 \left[ 1 - \frac{1}{8} \left( 1 + \frac{kT}{2b} \right) + O(K^4) \dots \right].$$

Thus the resonant peak will become less sharp as *T* increases. The band width should not be greatly affected by *T* because

$$(21) \quad B \simeq \frac{f(\delta_0)}{Q},$$

so the nonlinear effects will tend to cancel each other out in accord with experimental observations <sup>(16)</sup>.

A more refined demonstration <sup>(7)</sup> of the above effects may be given, by utilizing the concept of the equivalent linear system <sup>(18)</sup> (ELS), as adapted for stochastic systems <sup>(17)</sup>. The method <sup>(17,18)</sup> is the replacement of the non-linear equation

$$(22) \quad \ddot{\delta} + \beta\dot{\delta} + \omega_0^2 \sin \delta = A(t),$$

that is

$$(23) \quad \ddot{\delta} + \beta\dot{\delta} + \omega_0^2\delta + G(\delta) = A(t),$$

$$(24) \quad G(\delta) = \omega_0^2(\sin \delta - \delta)$$

by

$$(25) \quad \ddot{\delta} + \beta\dot{\delta} + \omega_{\text{eq}}^2\delta = A(t).$$

<sup>(17)</sup> T. K. CAUGHEY: *J. Acoust. Soc. Am.*, **35**, 1706 (1963).

<sup>(18)</sup> N. W. McLACHLAN: *Ordinary Nonlinear Differential Equations* (Oxford University Press, London, 1956).

note that  $\alpha$  in this reference denotes polarizability)

$$(31) \quad \alpha(\omega) \simeq \frac{2\mu^2 N}{v\epsilon_0} \frac{\gamma_1^2 \omega_0^2 \beta}{kTc} \left\{ \frac{\omega^2 + 4(\beta^2 + \omega_0^2)}{[(4\omega_0^2 - \omega^2)^2 + 4\omega^2 \beta^2]} \right\}.$$

$N$  is the number of dipoles inside a macroscopic sphere of volume  $v$ ,  $c$  is the velocity of light,

$$(32) \quad \gamma_1 = \frac{kT}{2I\omega_0^2},$$

$\omega_M$  is then (17)

$$\omega_M \simeq 2\omega_0 \sqrt{1 - \frac{\beta^2}{2\omega_0^2}} \simeq 2\omega_0 \left(1 - \frac{\beta^2}{4\omega_0^2}\right),$$

which, for the ELS, becomes

$$\omega_{M\text{els}} \simeq 2\omega_0 \left(1 - \frac{kT}{4b} - \frac{\beta^2}{4\omega_0^2}\right),$$

which decreases linearly with temperature.

Figures 1-4 give the experimental results. They show, as predicted by the theory when nonlinear effects are included,

- i) an almost linear decrease of peak position of the power absorption coefficient with an increase of temperature;
- ii) a decrease in the maximum value of absorption coefficient with increase of temperature;
- iii) the band width of the absorption curve is almost independent of temperature;
- iv) an increase in the sharpness of the absorption curve with a reduction in temperature.

The next step is the inclusion of many-body effects. A method of doing this is suggested by the lattice model considered by ZWANZIG<sup>(24)</sup> as a generalization to the frequency-dependent case of some earlier work of Rosenberg and Lax<sup>(25)</sup>.

\* \* \*

We thank Prof. B. K. P. SCALFE for continuing encouragement.

(24) R. ZWANZIG: *J. Chem. Phys.*, **38**, 2766 (1963).

(25) G. R. ROSENBERG and M. B. LAX: *J. Chem. Phys.*, **21**, 424 (1953).



## ● RIASSUNTO (\*)

Si mostra come l'inerte non linearità delle equazioni di moto di dipoli accoppiati spiega qualitativamente un numero di comportamenti dello spettro osservato nel lontano infrarosso di fluidi polari. Questi includono il decremento quasi lineare della posizione del picco del coefficiente di assorbimento di potenza FIR con l'aumento della temperatura e l'indipendenza della temperatura dell'ampiezza di banda.

(\*) *Traduzione a cura della Redazione.*

Резюме не получено.