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Far infrared power absorption in the low friction limit
The effect of static electric fields

by M. W. EVANS
Department of Physics, UCNW,
Bangor, Gwynedd LL57 2UW, Wales

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A theory of molecular diffusion in liquids that takes into account the shape of intermolecular potential wells with a cosine potential produces fine spectral detail in the far infrared. The effect of a static external electric field is to shift this panoply of peaks to higher frequency, increase the number of peaks, and shift their individual relative frequencies and intensities.

1. INTRODUCTION AND THEORY

The recent reports [1–3] of ultra-fine structure in the far infrared power absorption of structured and/or associated liquids such as acetonitrile and aniline, and in liquid crystals such as n heptyl n′ cyano biphenyl (7CB) have prompted the reexamination of the Kramers theory of molecular diffusion with the purpose of producing the effect qualitatively.

Reid [4] and Dianoux *et al.* [5] have recently provided solutions for the Kramers equation [6]:

$$\frac{\partial \rho}{\partial t} + \dot{\theta}\frac{\partial \rho}{\partial \theta} - \frac{V'}{I}\frac{\partial \rho}{\partial \dot{\theta}} = \beta \frac{\partial}{\partial \dot{\theta}}\left(\dot{\theta}\rho + \frac{kT}{I}\frac{\partial \rho}{\partial \dot{\theta}}\right), \tag{1}$$

$$V = -V_0 \cos N\theta. \tag{2}$$

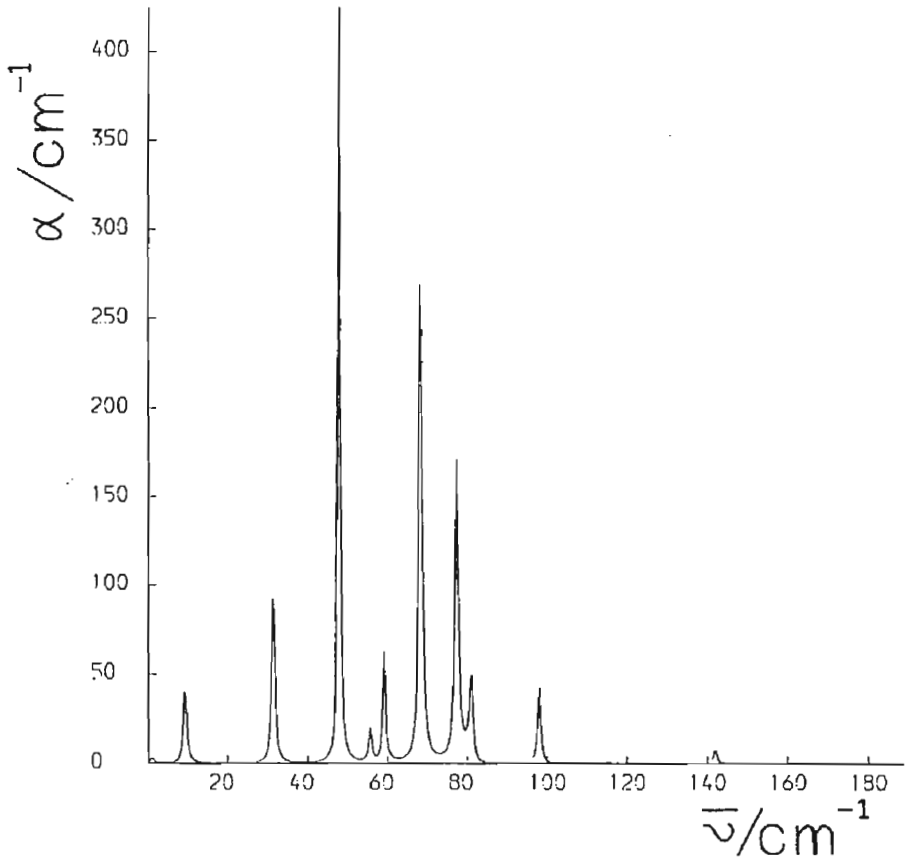
This is the partial differential equation governing circular diffusion [5] in potential wells of type (2) where N is the well multiplicity, and v_0 the barrier height. In equation (1) $\rho(\theta, \dot{\theta}, t|\theta_0, \dot{\theta}_0, 0)$ is the conditional probability density function in the phase space of θ and $\dot{\theta}$, the angular coordinate [4], I the moment of inertia of the diffusing molecule, and β the friction coefficient. Dianoux *et al.* considered the equivalent Smoluchowski equation in the context of neutron scattering [5], and pointed out that the case $N = 2$ is relevant to molecular diffusion in the smectic E or VI phase of TBBA. They also mentioned that equation (2) can be generalized for circular diffusion in wells of arbitrary shape using

$$V_A = -\sum_{N=1}^{\infty} \frac{V_N}{2} \cos N\theta. \tag{3}$$

Equation (1) is equivalent to the rotational Langevin equation:

$$I\ddot{\theta}(t) + I\beta\dot{\theta}(t) + V'(\theta) = \dot{W}(t), \tag{4}$$

where $W(t)$ is a Wiener process [6].


α /cm^{-1}
400
350
300
250
200
150
100
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80
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120
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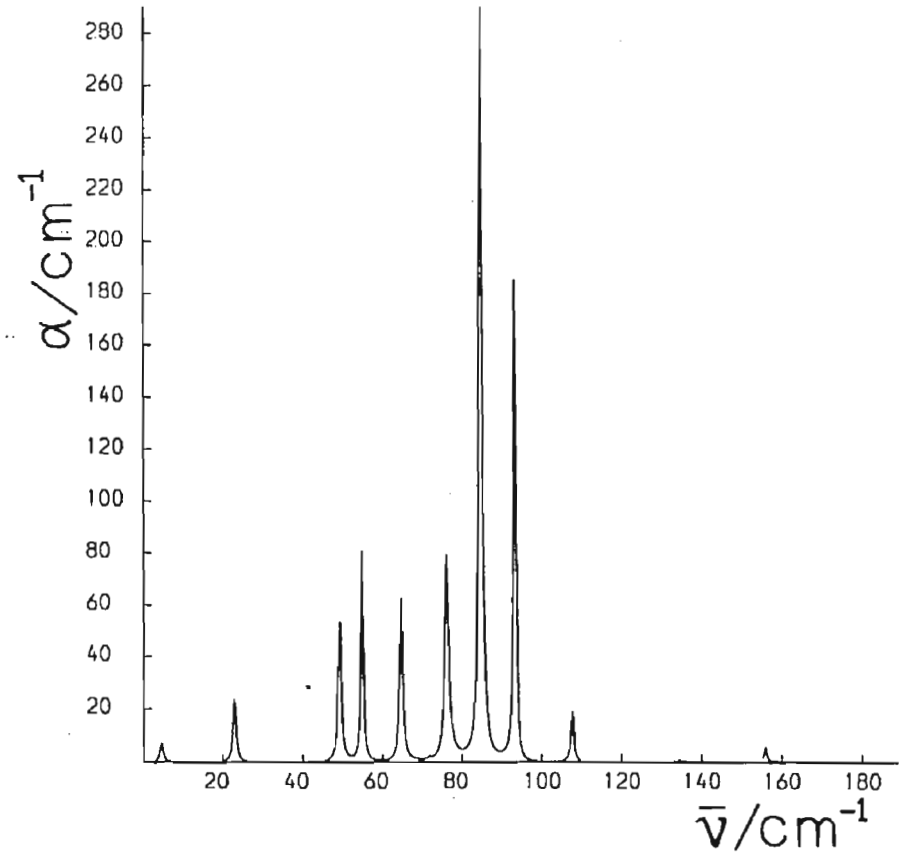
$\bar{\nu}$/cm^{-1}

(*a*)


α/cm^{-1}
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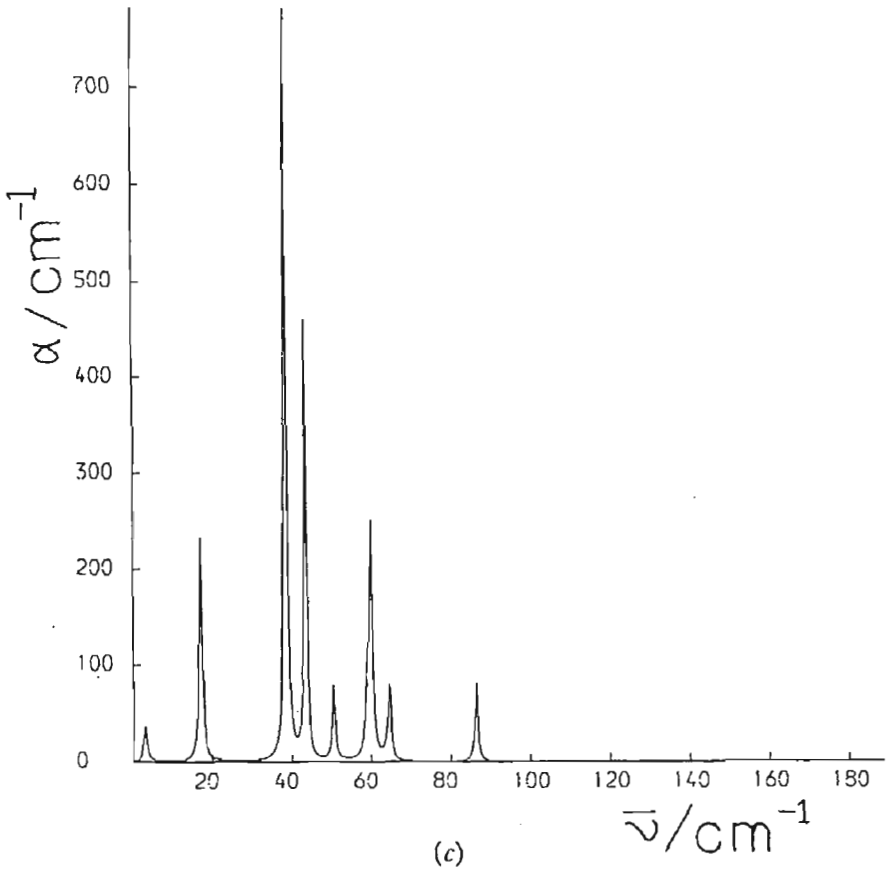
(*b*)



Effect of increasing γ factor on the far infrared power absorption coefficient from equation (1). (*a*) $\alpha = 15$; $\beta = 0{\cdot}1$; $\gamma = 15$; $N = 2$. (*b*) $\alpha = 15$; $\beta = 0{\cdot}1$; $\gamma = 20$; $N = 2$. (*c*) $\alpha = 15$; $\beta = 0{\cdot}1$; $\gamma = 10$; $N = 2$. The abscissa scale has been reduced by 5·3.

It has been shown recently [7] that fine structure of the type illustrated in figure (*a*), appears in the far infrared (f.i.r.) power absorption coefficient ($\alpha(\bar{\nu})$/neper cm^{-1}) if the friction coefficient (or barrier crossing frequency) $\beta \rightarrow 0$ for a finite barrier height v_0. In this limit the broad f.i.r. power absorption band usually observable in dipolar liquids becomes resolved into its component frequencies (figure). In physical terms the spectrum is that of molecular rotational diffusion taking place in a liquid medium that is *highly* structured in the low friction limit. The curves of the figure are produced for a multiplicity $N = 2$, which, as mentioned already, is of practical importance [5] for the ordered smectic VI phase of TBBA. It is important in this context to note that far infrared fine structure has been reported by G. J. Evans [1] in liquid acetonitrile—known to have a low viscosity coefficient and to have crystal like structure properties at low temperatures, i.e. to have well-defined potential wells [6]. The paper by Evans [1] also reports the effect of a static electric field on the f.i.r. fine structure. The simplest way of incorporating an external electric field term into equation (4), in the special case $N = 2$ is to denote the angle between the electric field [**E**] and the molecular dipole moment (**μ**) by 2θ. The extra torque generated between **μ** and **E** then modifies equation (4) to

$$I\ddot{\theta}(t) + I\beta\dot{\theta}(t) + V'(\theta) + \mu E \sin 2\theta = \dot{W}(t). \tag{5}$$

Equation (5) has been solved for this note using the numerical method of Reid [4], and the results are discussed in the next section.

2. Results and discussion

The effect of increasing the electric field strength in equation (5) can be monitored as an effective increase in the parameter used by Reid [4] to denote the height of the effective barrier between potential wells:

$$\gamma = \frac{V_E}{2I\alpha}, \qquad \text{where} \qquad \alpha = \left(\frac{kT}{I}\right)^{1/2}, \qquad V_E = V_0 + \mu E$$

The effect on the far infrared power absorption coefficient from equation (5) of increasing γ for constant α and β is illustrated in figures (*b*) and (*c*). The panoply of peaks is shifted to higher frequencies, the relative peak intensities, frequencies and frequency intervals between peaks change, and there is an increase in the *number* of peaks as γ increases. At the same time the broad dielectric loss curve from equation (5) shifts to lower frequencies with increasing γ, as discussed by Reid [4].

These theoretical results are qualitatively similar to the experimental results of Evans [1] on liquid acetonitrile and of Evans and Evans on the nematic phase of 7CB [3], where an electric field appears to produce many peaks in the far infrared that are unresolved in the field-off case.

It is interesting to note finally that the inclusion of an electric field term with a potential of the type (3) in an equation such as (5) would produce, in theory, a very large number of far infrared peaks, because of the difference frequencies generated between the N coefficients in sin $N\theta$ and the usual electric field term $\mu E \sin\theta$. In this note difference-frequencies such as these have been eliminated for ease of calculation.

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Appendix

Notes on harmonic progression

At $\gamma = 10$ the natural non-linear harmonic progression (6) can be discerned, with peak structure centred at about 10, 20, 40 and 80 cm^{-1} with further overtone components at about 60 cm^{-1} and 120 cm^{-1}. The fundamental component at about 40 cm^{-1} is split into two or three parts. As γ is increased the pattern of splitting changes, and so do the relative peak intensities and positions. The splitting process has its origins in the fact that equation (1) deals with hopping and diffusion processes taking place at different frequencies.

References

[1] Evans, G. J., 1983, *J. chem. Soc. Faraday Trans. II*, **79**, 547.
[2] Evans, M. W., and Evans, G. J., 1980, *J. chem. Soc. Faraday Trans. II*, **76**.
[3] Evans, M. W., and Evans, G. J., 1978, *J. chem. Soc., Chem. Commun.*, p. 267.
[4] Reid, C. J., 1983, *Molec. Phys.*, **49**, 331.
[5] Dianoux, A., and Volino, F., 1977, *Molec. Phys.*; **34**, 1263.
[6] Evans, M. W., Evans, G. J., Coffey, W. T., and Grigolini, P., 1982, *Molecular Dynamics* (Wiley–Interscience), Chap. 1 and 2. Coffey, W. T., Evans, M. W., and Grigolini, P., 1984, *Molecular Diffusion and Spectra* (Wiley–Interscience), Chap. 3–9.
[7] Evans, M. W., 1984, *Physica scripta*, **30**, 222.