Physica Scripta. Vol. 30, 222–224, 1984.

Barrier Crossing Theory for Ultra-Fine Far Infrared Structure in the Liquid State*

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Received April 16, 1984; accepted April 28, 1984

Abstract

The possibility of very sharp peaks in the far infrared power absorption of liquid acetonitrile is analysed with the simple Kramers theory of Brownian motion in potential well, which is shown to be capable of describing the new type of absorption using a combination of low friction and deep wells.

1. Introduction

The recent discovery [1] of very sharp peaks in the far infrared power absorption spectrum of liquid acetonitrile is, if corroborated, fundamentally important to our understanding of the liquid state. One of the challenges now is to try to reproduce the features of the spectrum in a manner that is consistent with accepted theories of the broad-bands usually observable in liquids. The *complete* frequency range from static to terahertz must be taken as one set of data for the purposes of interpretation [2]. The model chosen for the molecular dynamics must be capable of reproducing the dielectric loss profile *and* power absorption profile with the same set of input parameters. In this communication we outline the performance of the simplest available theory that is capable of producing simultaneously a broad, low frequency loss profile and a series of ultra sharp peaks in the far infrared.

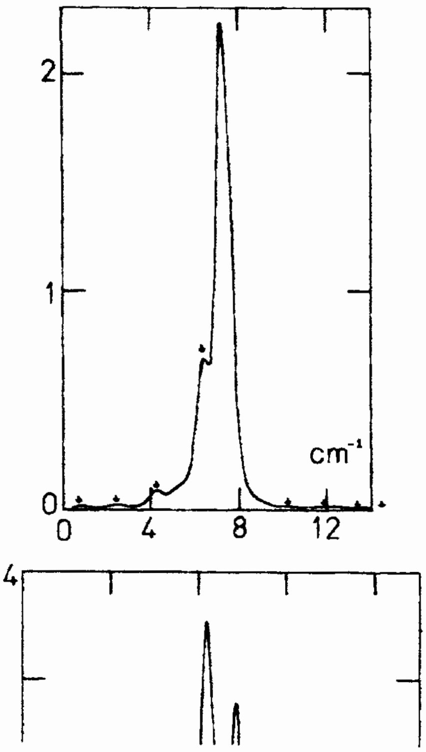
2. Theory

The starting equation for the analysis is

$$I\ddot{\theta}(t) + I\beta\dot{\theta}(t) + MV_0\cos(M\theta(t)) = \dot{W}(t) \quad (1)$$

Here the rotational motion of the molecule in the liquid state is confined to one coordinate, θ, in order to keep the analysis tractable. I is the effective molecular moment of inertia, β the friction coefficient, V_0 the well depth and M the number of

therefore capable of producing loss and power absorption profiles through the parameters: $\alpha = (kT/I)^{1/2}$; $\gamma = V_0/(2(IkT)^{1/2})$, β and M. The effect of these on the broad-band spectral profiles is discussed in detail by Reid [4]. In this communication we wish to show how the sharp absorption peaks discovered by G. J. Evans [1] may be reproduced qualitatively using this model in the limit $\gamma \gg \beta$, i.e., for low friction (or low viscosity) and steep, deep potential wells (well defined liquid structure). The physical picture we have is therefore one of molecular tor-



sional oscillation [2] within well defined potential wells, with occasional barrier crossing processes giving rise to a low frequency loss curve and a number of sharp, far infrared peaks.

3. Results and discussion

Power absorption profiles in the far infrared produced by eq. (1) for two sets of parameters α, β, γ, M are illustrated in Fig. 1. For a multiplicity $M = 2$ narrow substructure appears on the overall far infrared power absorption spectrum – the half width of the theoretical absorption lines is $< 1\ \mathrm{cm}^{-1}$, and the peaks can be approximately equally spaced (Fig. 1a) or unequally spaced (Fig. 1b) depending on the relative magnitude of α, β, and γ. If the ratio (γ/α) is increased for constant β and M the result is as illustrated in Figs. 1(a) and (b). The absolute value of α depends on the temperature and effective molecular moment of inertia. If the latter is decreased, keeping everything else constant, the complete spectrum is shifted to higher frequencies. In addition to the far infrared detail, eq. (1) produces a standard Debye type loss profile (1.12 decades half-width) at low frequencies as discussed by Reid [4], and Evans et al. [5, 6].

It is not our purpose here to attempt to describe accurately the complete observable loss and power absorption processes of liquid acetonitrile. These have been reviewed recently by Evans [7] and are compounded, complicated processes involving many body polarizability effects. We wish to focus our attention entirely on the appearance of the sharp sub-structure, and on the possibility of building this up eventually with equations of the type (1). The parameters α, β, γ and M can be adjusted to position the theoretical maximum peak underneath the experimental peak frequency (Fig. 2) of $\bar{\nu}_{\max} = 90\ \mathrm{cm}^{-1}$. In this event the theoretical spectrum from eq. (1) can be adjusted to produce sub-structure as sharp as any observed experimentally [1]. Any attempt to broaden the underlying absorption profile will, however, wash out these peaks Fig. 1(b), if we do not impose the condition $\gamma \to \infty$. In this limit, Reid's numerical method of solution becomes unreliable, and there is the further problem that the loss profile in this limit would peak at far too low a frequency in comparison with the observed [8, 9] dielectric relaxation time of 3.3 ps.

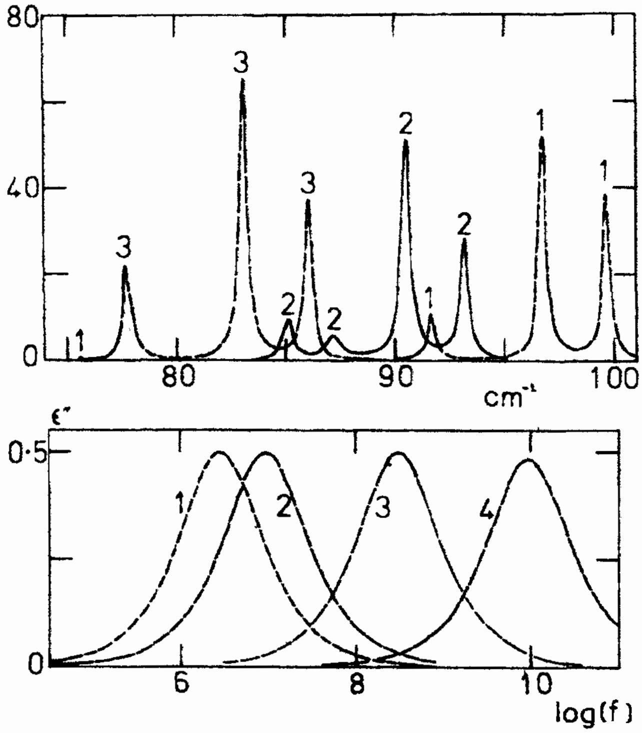


Fig. 2. (a) Positioning of the ultra-fine substructure in the region of $84\ \mathrm{cm}^{-1}$ – where experimental evidence for the effect is available from submillimeter laser spectroscopy [1]. (1) -------, $N = 2$, $\alpha = 8.0$, $\beta = 0.1$, $\gamma = 40.0$; (s) ———, $N = 2$, $\alpha = 8.0$, $\beta = 0.1$, $\gamma = 35.0$; (3) -------, $N = 2$, $\alpha = 8.0$, $\beta = 0.1$, $\gamma = 30.0$. Ordinate and Abscissa as for Fig. (1). (b) Loss curves corresponding to (1)–(4). *Ordinate*: ϵ''. *Abscissa*: log (frequency). (1) $N = 2$, $\alpha = 8.0$, $\beta = 0.1$; $\gamma = 40$; (2) $\gamma = 30$; (3) $\gamma = 20$; (4) $\gamma = 10$, $f = 2\pi\bar{\nu}c$.

It seems to be clear, however, that a broad band power absorption profile, with sharp superimposed structure, and a corresponding Debye-like loss profile, could be synthesized by introducing a thermodynamic averaging in eq. (1) over *the barrier height* V_0, i.e., by using a discrete distribution of barrier heights (or, in alternative parlance, well depths). The effect of this would be to build up a very detailed far infrared spectrum with many individual sub-structures of the type illustrated in Figs. 1 and 2. The effect of an external electric field is always to sharpen a far infrared spectrum [5], and it will be of great interest to solve the governing differential equation in this case, viz.

$$I\ddot{\theta}(t) + I(\beta - \mathrm{i}\omega_1)\dot{\theta}(t) + MV_0 \sin(M\theta(t)) = \dot{W}(t) \qquad (2)$$

by transforming it into a Kramers equation and solving this in turn with differential difference equations [4], or by using the very powerful and general methods developed by the Pisa group [10] – the continued fraction and adiabatic elimination procedures.

In conclusion, therefore, we intend this communication to show that very sharp sub-structures in the far infrared *can* be produced by a seemingly simple equation such as eq. (1) in the low friction, deep well limit. We *do not* intend to go into a detailed analysis of the complete far infrared sub-structure of acetonitrile (this is insufficiently resolved as yet), but we believe it to be important and timely to show that there is a sound theoretical basis for the discovery by G. J. Evans [1] of these peaks, *and therefore to encourage further experimental work at very high resolution*. Finally it is suggestive that liquid acetonitrole is known to have a very low viscosity (i.e., low friction β) at room temperature and to become highly structured as the normal freezing point is approached from the high temperature side [1, 7, 10].

Acknowledgements

The University of Wales is thanked for a Fellowship, and Dr G. J. Evans, Prof. P. Grigolini and Dr F. Marchesoni for illuminating discussions. The Nuffield Foundation is thanked for a bursary. I am greatly indebted to Dr Colin Reid for a copy of his algorithm, which was adapted for the UMRCC CDC 7600 computer.

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