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Advances in Molecular Relaxation and Interaction Processes, 15 (1979) 273–279
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CHARGE-CHARGE ELECTRODYNAMICS OF THE C_6H_6 .... C_6F_6 COMPLEX

MYRON EVANS
Chemistry Department, University College of Wales, Aberystwyth, SY23 1NE, U.K.
(Received 30th. May 1979)

ABSTRACT

Molecular motion in the solid 1:1 complex of C_6H_6 and C_6F_6 is considered from the point of view of Brownian motion modulated by a strong atom-atom electrostatic interaction. The depolarised Rayleigh bandshape is found to consist of an infinite number of Lorentzians, in contrast to the recent results of Bauer et al.

INTRODUCTION

An equimolar solution of liquid benzene and liquid hexafluorobenzene is a solid at temperatures much higher than the melting point of either component. The solid solution has therefore been called a 1:1 complex and has been extensively studied in an attempt to uncover the molecular basis for its existence. It is known that charge-transfer is not a factor but X-ray studies prove that the configuration taken up in the complex is that with alternately parallel rings, in contrast to the mutually perpendicular packing in either component in the crystalline state. A recent Rayleigh scattering study by Bauer et al. (1) has revealed strong static and dynamic cross-correlation in the solid 1:1 solution which affects the individual molecular reorientational diffusion. No significant contribution was found from a "long-lived complex" in the 1:1 mixture. Pair-correlations were analysed with the theory of Kivelson and Keyes (2) which links the macroscopic (observable) orientation time (τ_{LS}) to the single molecule reorientation time (τ_{SP}). In their analysis Bauer et al. took the line that in a solution containing two anisotropic components, the light scattering spectrum should consist of the sum of two Lorentzians (neglecting inertial and memory effects) and be affected by factors F_{11}, F_{22}, F_{12}, G_{11}, G_{22} and G_{12} are analogous dynamic pair correlations defined within the structure of Mori statistical mechanics. In a C_6H_6/C_6F_6 mixture, there will be <u>more than two</u> effective components if the (C_6H_6 .... C_6F_6) entity is long lived. This would imply the presence of a narrow Lorentzian in the overall spectrum.

In this paper the distribution will be examined of one particle and two particle relaxation times appropriate to the theory of Rayleigh scattering by extending to intermolecular interactions a theory of Brownian motion with intramolecular freedom developed by Budo (3) and generalised by Coffey (4). In so doing we shall ignore all pair correlations except those between distinct molecules. The intermolecular correlation in this case is treated in terms of point quadrupole interactions (5,6) and also by summing the 144 Coulomb interactions which result by splitting up each quadrupole into point charges localised atomically on each molecule of the C_6H_6 .... C_6F_6 pair. There is no loss of generality in ignoring C_6H_6 .... C_6H_6 and C_6F_6 .... C_6F_6 interactions; our primary purpose is to demonstrate that the strong electrodynamic C_6H_6 .... C_6F_6 interaction generates an infinite number of two-particle correlation times in addition to those single-particle times associated with each component. Taking account of the relatively much weaker C_6H_6 .... C_6H_6 and C_6F_6 .... C_6F_6 interactions merely adds to the number of two-particle Lorentzians.

Bauer et al. assume that if the lifetime of the C_6H_6 .... C_6F_6 entity is short compared with its reorientation time, then only two components should exist in the Rayleigh spectrum. In the light of the following analysis this is clearly an oversimplification which works because the Rayleigh spectrum is relatively insensitive to the details of molecular motion compared with, for example, the far infra-red. Their claim that much important information about intermolecular interactions can be obtained by depolarised Rayleigh scattering is obviously encouraging, but sometimes (as in this instance) this information can be oversimplified. To resolve the full implications of electrodynamic interactions in the C_6H_6 .... C_6F_6 complex, a semi-stochastic Monte-Carlo simulation along the lines of that of Brot and Darmon (7) is strongly recommended. This will remove the need to consider only pair-correlations, which is restrictive. It would also be useful to gather complementary data on complexes of C_6F_6 with dipolar aromatics in the whole zero-TH_z range of electromagnetic frequencies.

THE C_6H_6 .... C_6F_6 INTERACTION POTENTIAL

Apart from the usual repulsion between van der Waals profiles, London dispersion forces and second-order induced dipoles (giving rise to far infra-red induced absorptions), the electrostatic attraction between C_6H_6 and C_6F_6 is overwhelmingly important in determining the structure of the 1:1 solid solution (5). This part of the intermolecular potential may be treated in terms of point-quadrupoles or point charges.

QUADRUPOLE-QUADRUPOLE INTERACTION (Q - Q)

Brown and Swinton (5) have recently reproduced X-ray results by considering simple forms of C_6H_6 .... C_6F_6 Q - Q interaction. Using the method of Gierke et al. (6) these authors show that the quadrupoles (Q_1, Q_2) are of opposite sign, and that a form:

$$V_{QQ}(R_0) = \frac{9Q_1Q_2}{4R_0^{\,5}} \qquad (1)$$

for face to face quadrupolar interaction is energetically the most favoured in the 1:1 mixture. Here R_0 is the inter-ring-centre separation. There is no angular dependence of any nature in eqn. (1) because this is the expression for the quadrupole-quadrupole interaction between axially symmetric charge distributions with parallel symmetry axes (8). This is to say that the charge is not atomically localised but smeared evenly perpendicular to the molecular hexad axis. Even in the absence of angular dependence eqn. (1) is sufficient to imply the existence of an infinite number of two-particle (C_6H_6 .... C_6F_6) relaxation times for Rayleigh scattering.

CHARGE-CHARGE INTERACTION (q - q)

As demonstrated clearly by Brot and Darmon (7) in a dielectric context, and by G.J. Davies et al. (9) for far infra-red induced absorption, the point quadrupole limit is unrealistic when dealing with molecules whose dimensions and separations are commensurate. We have therefore decomposed the C_6H_6 and C_6F_6 quadrupoles used by Brown and Swinton into atom-localised point charges (q). Assuming that the C_6H_6 and C_6F_6 molecules are parallel, with inter-ring-centre axis (R_0) perpendicular to the plane of each ring, the charge-charge interaction is then:

$$V_{qq}(R_0,\eta) = \sum_{ij} \frac{q_iq_j}{[R_0^{\,2} + r_i^{\,2} + r_j^{\,2} - 2r_ir_j \cos 2\eta_{ij}]^{1/2}} \qquad (2)$$

where r_i is the ring centre to atom distance in molecule i. We define the angle (2η) as follows. Set up a pair of two fold symmetry axes (H - C_1 .... C_6H) (μ_1) and (F - C_1 .... C_6 - F) (μ_2) in each face to face molecule and project these on to a common parallel plane. The angle subtended by the two axes is then 2η. From X-ray studies we have R_0 = 3.5 Å at ambient temperature. We note that V_{qq} is angle dependent with a periodicity in 2η of $\pi/6$ as the C_6H_6 molecule rotates with respect to C_6F_6 about the common hexad axis under the influence of thermal angular Brownian motion.

Therefore in what follows we shall regard V_{QQ} and V_{qq} as potentials which modulate strongly an underlying thermally stimulated rotational diffusion in each molecule of the (C_6H_6 .... C_6F_6) pair. The situation is therefore precisely that considered by Budó in a dielectric context associated with the rotational diffusion of a molecule with internally rotating dipolar groups. Some very recent advances (10) in computer software have obviated the need for a laborious algebraic analysis in solving the Sturm-Liouville type of eigenvalue problem which governs the two-particle molecular dynamics, given a form for the interaction potential V.

THEORETICAL SYNOPSIS

If the overall Brownian motion of the (C_6H_6 .... C_6F_6) entity be considered isotropic, the probability density function underlying the process is governed by the following Smoluchowski equation (3,4):

$$\frac{\partial f}{\partial t} = \frac{kT}{\zeta}\left[\frac{\partial^2 f}{\partial \theta^2} + \operatorname{cotan}\,\theta\frac{\partial f}{\partial \theta} + \left(\operatorname{cotan}^2\theta + \frac{\zeta}{\zeta_1}\right)\left(\frac{\partial^2 f}{\partial \phi_1^2} + \frac{\partial^2 f}{\partial \phi_2^2}\right)\right.$$

$$\left. + \, 2\operatorname{cotan}^2\theta\,\frac{\partial^2 f}{\partial \phi_1 \partial \phi_2}\right] + \frac{\partial}{\partial \phi_1}\left[\frac{f\sin\theta}{\zeta_1}\frac{\partial V}{\partial \phi_1}\right] + \frac{\partial}{\partial \phi_2}\left[\frac{f\sin\theta}{\zeta_1}\frac{\partial V}{\partial \phi_2}\right]; \quad t>0 \qquad (3)$$

Here $f \sin\theta d\theta\, d\psi\, d\phi_1\, d\phi_2 = f\, d\Omega$ is the number of molecules whose axes μ_1 and μ_2 have orientations between Ω and $\Omega + d\Omega$ at time t; θ and ψ are the polar angles which specify the direction of the molecular axis relative to that of E, the unidirectional measuring field, while ϕ_1 and ϕ_2 are the azimuthal angles of μ_1 and μ_2 measured from the plane containing E and the axis of R_0. V is the interaction potential taking the argument $(\phi_1 - \phi_2)$.

It may be shown that the relaxation times related to the governing equation are given by:

$$\tau_{\lambda_{nm}} = \frac{b}{\lambda_{nm} + n(n+1)(a-1) - m^2(a-2)} \qquad (4)$$

In eqn. (4) $b = 2\zeta_1/kT$; $a = 1 + \frac{2\zeta_1}{\zeta}$; where ζ_1 is the coefficient of friction acting on the C_6H_6 or C_6F_6 component as it undergoes rotational Brownian motion and ζ is that on the (C_6H_6 .... C_6F_6) entity. In the case of depolarised Rayleigh scattering m = n = 2, so that

$$\tau_{\lambda_{22}} = \frac{b}{\lambda_{22} + 2a + 2} \qquad (5)$$

In eqns. (4) and (5) λ is an eigenvalue of the Sturm Liouville equation:

$$\frac{d^2 z_\lambda(\eta)}{d\eta^2} - \frac{2\phi(\eta)dz_\lambda(\eta)}{d\eta} + \lambda z_\lambda(\eta) = 0 \qquad (6)$$

with $\phi(\eta) = \frac{1}{kT}\frac{d}{d(2\eta)}V(2\eta)$.

In general, equation (6) has an infinite number of eigenvalues λ for each $V(2\eta)$, so that whatever the form of a non-zero $V(2\eta)$, there will always be an infinite distribution of relaxation times $\tau_{\lambda_{22}}$ of the (C_6H_6 .... C_6F_6) entity. The depolarised Rayleigh spectrum will consist therefore of a weighted sum:

$$\sum_\lambda \frac{I_\lambda}{1 + \omega^2\tau_\lambda^2} \qquad (7)$$

of Lorentzians corresponding to the reorientation of the strongly interacting entity C_6H_6 .... C_6F_6. From the sum (7) we expect the two Lorentzians considered by Bauer, Brauman and Pecora as those of C_6H_6 and C_6F_6 modified by their mutual interaction; but in addition many more, weighted by the factor I_λ. the derivation of which is appended.

NUMERICAL SOLUTION OF EQN. (6)

If the mutual interaction of C_6H_6 and C_6F_6 is considered to be governed by Coulomb forces, then eqn. (6) may only be solved numerically. The algorithm we have used is one based on a shooting method and Prufer transformation developed recently by Pryce and Hargrave (10). The Prufer form of eqn. (6) is integrated using a Runge-Kutta formula devised by Merson. The computed values of λ have an adjustable, mixed, absolute/relative uncertainty, those in table 2 below being set accurate to one part in 10^6. In common with the Mathieu and Hill equations, the periodicity of the eigenfunctions of eqn. (6) is that of the potential $V(2\eta)$.

RESULTS AND DISCUSSION

In table 1 we list the atomic charges and ring-centre to atom distances for C_6H_6 and C_6F_6 used in the computation of the Coulomb potential, and its variation with 2η (periodic in $\pi/3$). These are obtained from the values of Q_1 and Q_2 used by Brown and Swinton.

TABLE 1

Coulomb Charges (in 10^{-10} e.s.u.) (q, q_1) and ring centre to atom distances (r, r_1) for C_6F_6 and C_6H_6 respectively

Molecule	Atom	Coulomb Charge $/10^{-10}$ e.s.u.	Ring Centre to Atom Distance/Å
C_6F_6	F	-2.16	2.68
C_6F_6	C	2.16	1.36
C_6H_6	H	1.05	2.48
C_6H_6	C	-1.05	1.39

As one component of the complex rotates with respect to the other the Coulomb potential is periodic. By using this potential in eqn. (6) an infinite number of correlation times (corresponding to the range of λ) is extracted and summarised as in Table 2. For quadrupole-quadrupole interaction eqn. (6) reduces to:

$$\frac{d^2 z_\lambda(\eta)}{d\eta^2} + \lambda z_\lambda(\eta) = 0 \qquad (8)$$

giving a quadratic measure of increasing λ. It is reasonable to assume that the friction coefficients acting on C_6H_6 and C_6F_6 are similar, or the same, so that $\zeta = \zeta_1$. Whatever the values of ζ and ζ_1, however, the series of increasing λ implies that there will be in the depolarised Rayleigh spectrum a series of correlation times τ_λ shorter than that for the reorientation of the C_6H_6 or C_6F_6. The spectrum will consist theoretically therefore of many more than two Lorentzians, and it should be particularly interesting to reinvestigate it at high frequencies.

TABLE 2

First few Eigenvalues of eqn. (8) and eqn. (6)

Index	λ for Quadrupole-Quadrupole Interaction (eqn. 8)	λ for Coulomb Interaction (eqn. 6)
0	1	0.000000 ± 0.0000001
1	4	33.19595 ± 0.000021
2	9	144.1547 ± 0.00009
3	16	324.1314 ± 0.00021
4	25	
5	36	
6	49	
7	64	

The specific face to face interaction disappears as the solid complex melts so that the geometry of the intermolecular interaction is considerably complicated. It would no longer be valid in the liquid complex to use simply a face Coulomb potential or quadrupole-quadrupole potential of the form utilized for the solid. If a strong C_6H_6 .... C_6F_6 intereaction persists into the liquid, however, the high frequency end of the Rayleigh scattering should be affected in a manner similar to that of the solid. A project of study of solutions of dipolar aromatics in C_6F_6 by use of far infra-red methods should be particularly informative in conjunction with dielectric relaxation results at lower frequencies, where the Budó model for internal rotation has been useful for a long time. To describe the complete zero-THz spectral region, a consideration of memory and inertial effects in eqn. (1) is essential, and such work is under way at present.

ACKNOWLEDGEMENTS

The S.R.C. is thanked for an equipment grant and T.C.D. for their hospitality to M.W.E.

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