QUANTISED ROTATION OF HBr IN LIQUID SF_6

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Absorption data on HBr in liquid SF_6 at 296 K are presented in the frequency range 20–200 cm^{-1}. The broadened $J \to J + 1$ transitions are clearly resolved, more so at the higher frequencies. Although noisy, the data are good enough to discriminate between two models of liquid phase rotational dynamics. It is found that the modified M and J diffusion model of Frenkel and Wegdam rests on sounder hypotheses than a formalism, based on a truncated Mori expansion, that does not predict preferential broadening of the lower frequency $J \to J + 1$ lines.

1. Introduction

At present there is a limited number of liquid systems known which exhibit the remains of rotational fine structure in their far infrared spectra [1,2]. This is made up of the solutions in liquid noble gases and SF_6 of HCl, HF, DF and NH_3. In each case the lower frequency lines have nearly disappeared while at high frequencies they persist as in the compressed gas. The overall spectral envelope remains that of the free rotor distribution. The existence of fine structure implies that these small anisotropic molecules can be used as sensitive probes for the dynamical behaviour of their solvents, even at liquid densities: they themselves retaining considerable angular freedom of movement.

An attempt has been made [3] to describe these spectra in terms of a quantum mechanical calculation of the perturbation on a dipolar molecule in a cubic cage of spherical solvent molecules. A clearer dynamical insight is offered by Frenkel and Wegdam [4] who developed a stochastic model based upon the original M and J-diffusion representation of Gordon [5]. We use this model to describe the data on the HBr-system presented in this preliminary note. Since the J-diffusion model itself corresponds to a very early truncation [6] of the Mori continued fraction series approximation to the dipolar autocorrelation function, we shall study below the effect of including one more term in this series.

Our present data on HBr in liquid SF_6 are presented to help to assess the validity of the assumptions made in the above models. More are needed over a large range of temperature and density; although data at the same density on different but comparable systems can be used to assess the intermolecular effects and average kinetic parameters.

The fine structure which we can see in $HBr/SF_6(l)$ can be used to differentiate between the last two stochastic models mentioned above: models which stress respectively the influence of correlation between collisions [4] and the mean square torque [7] on molecular motion.

2. Experimental

The spectrum was measured with a prototype Grubb-Parsons/N.P.L. interferometer at a resolution of 2 cm^{-1}, using an optical system consisting of a TPX plano-convex lens and a melinex beam splitter. The submillimetre radiation [8] was detected with a diamond-windowed Golay pneumatic cell. The sample was contained in a specially constructed [9] stainless steel, variable path length, high pressure cell with TPX windows fitted with a drying chamber where the HBr and SF_6 gases were condensed, dried, and mixed over type 3A zeolite. In computing the absorption coeffi-

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cient α (neper cm^{-1}), path length difference was used rather than a ratio of sample to background so that spurious effects due to refractive index changes [10, 11] were virtually eliminated and an indefinite number of runs could be made with one specimen. The quality of the spectrum given here is such that the individual $J \to J+1$ absorptions can be seen clearly, but it is too noisy to discriminate entirely satisfactorily between the theoretical models of the absorption. Further measurements will be made with an improved mark III interferometer, incorporating phase modulation of the radiation, and a transistorised detector.

3. Results and discussion

The rotational dynamics of the HBr molecule are dependent to a great extent on its environment in the liquid phase, and like [2] HF and HCl, may be used as a probe. The fine structure evident in the liquid phase (fig. 1) is a clear manifestation of this property. A quantitative estimate has been introduced by van Aalst and van der Elsken in the phase persistence ϕ, which for HBr/SF$_6$ we find to be 0.03 (fig. 2), compared with 0.02 for HCl/SF$_6$. The dependence of ϕ for HCl upon environment (different solvents) indicates that this molecule moves in a fluctuating cage of solvent molecules from which it occasionally diffused with complete loss of dynamical memory.

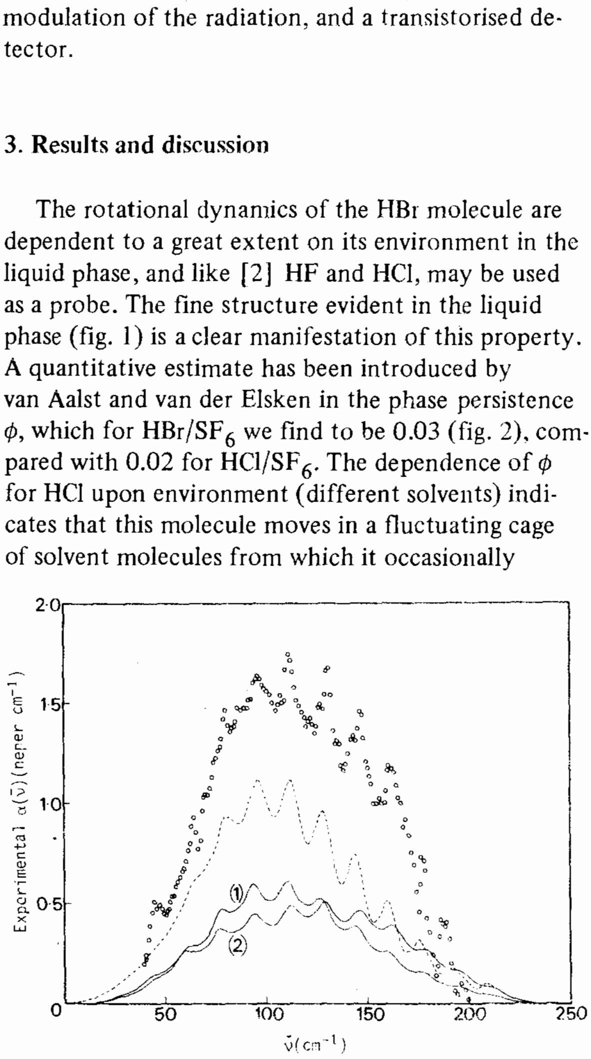

Fig. 1. ○ Experimental absorption of HBr/SF$_6$ liquid mixture at 296 K. --- Frenkel/Wegdam formalism, ordinate scale unnormalised. —— (1) Truncated Mori formalism of Bliot et al., $\beta_2 = 1$; (2) $\beta_2 = 1.2$. Both curves (1) and (2) are unnormalised to the experimental data on the ordinate scale.

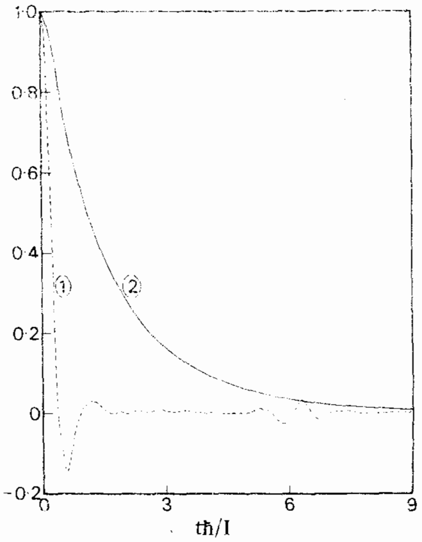

Fig. 2. --- (1) Dipole autocorrelation function from the Frenkel/Wegdam curve of fig. 1. —— (2) Normalised angular momentum autocorrelation function i.e. $\langle J(0)\cdot J(t)\rangle / \langle J(0)\cdot J(0)\rangle$.

The technique of solving the equations of notion by computer for a large number ($\approx 10^2$) of molecules suggests that collective motions of a host fluid, originating obviously in the rotational motion of individual molecules may be discerned in the long time hydrodynamic tails of any rotational type correlation function. Thus we have a fairly clear picture of motions between interactions whose magnitude and duration are still badly understood. Comparison of different probes may help to remedy this, and help to discern those facets of current models of molecular behaviour in the fluid which rest on unrealistic hypotheses. With this in mind we use two models, one of which assumes interactions of very short duration compared with the relaxation time of the dipole vector and molecular angular momentum; and the other interactions of finite duration.

The first approximates the autocorrelation function, $C(t)$, of the dipole moment $\mu(t)$ with a set of memory functions $K_0(t), ..., K_n(t)$. These are related to $C(t)$ by a set of integro-differential equations described by Bliot et al. [7]. It is assumed that the stochastic nth order interaction force of which $K_n(t)$ is the autocorrelation function follows a statistical law where the interaction probabilities are Poisson distributed. Thus:

$$K_n(t) = \beta_n K_{n\mathrm{FR}}(t) \exp(-|t|/\tau), \tag{1}$$

where $K_{n\mathrm{FR}}(t)$ is the nth order memory function associated with the free rotor autocorrelation function $C_{\mathrm{FR}}(t)$. For example, $K_{n\mathrm{FR}}(0)$ depends only on the natural angular velocities, and in particular, $K_{0\mathrm{FR}}(0) = 2\,kT/I = \omega_0^2$, where I is the moment of inertia for a linear molecule. In eq. (1), β_n and τ are stochastic parameters, β_2, for example, being related to the phase-space averaged mean square torque $\langle O(V)^2\rangle$ by:

$$\langle O(V)^2\rangle = I^2\omega_0^4(\beta_2 - 1) \qquad (2)$$

in a linear molecule. Here τ has the dimensions of time. Eq. (1) with $n = 1$ describes the J-diffusion model [5] of extended rotational diffusion, which uses elastic collisions and thus involves singularities in $\langle O(V)^2\rangle$, since this becomes infinite at every impact. To keep the torque finite for all positive times, Bliot et al. use $n = 2$ which leads to an equation for the absorption coefficient (not given in their paper) which we write using Baise's definition [12] of the free rotor autocorrelation $C_{\mathrm{FR}}(t)$:

$$\alpha(\omega) \propto \frac{\omega[1 - \exp(-\hbar\omega/kT)]\,(B - \beta_2/\tau)K_{0\mathrm{FR}}(0)}{x^2 + y^2}, \qquad (3)$$

where

$$x = \omega(B - \beta_2/\tau), \qquad y = K_{0\mathrm{FR}}(0) - \omega[A + \omega(1 - \beta_2)],$$

$$A = K_{0\mathrm{FR}}(0)\beta_2[\Lambda + \omega(\Lambda^2 + \Gamma^2)]/D,$$

$$B = K_{0\mathrm{FR}}(0)\beta_2[\Gamma - (\Lambda^2 + \Gamma^2)/\tau]/D,$$

$$D = (1 + \Lambda\omega - \Gamma/\tau]^2 + (\Lambda/\tau + \Gamma\omega)^2,$$

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

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

$$f(\Omega) = \frac{\Omega}{2\pi c}\exp\left[-\frac{h\Omega}{8\pi B_0 kT}\left(\frac{\Omega}{2\pi c} - 2B_0\right)\right],$$

$$E = \int_0^\infty f(\Omega)\,\mathrm{d}\Omega.$$

In this set of relations, B_0 is the rotational constant (in cm^{-1}) and ω the angular velocity (rad s^{-1}). Curves from eq. (3) are illustrated in fig. 1 for $\tau = 0.75$ ps; $\beta_2 = 1$ and $\beta_2 = 1.2$. It is seen that each $J \to J + 1$ feature is broadened by the same amount and independently of the torque. The observed peak absorption at 110 cm^{-1} corresponds to $\beta_2 = 1$ in this model, so that thermal interactions only are significant, i.e. according to this model, $\langle O(V)^2\rangle$ is effectively zero. The rotational fine structure of eq. (3) is very sensitive to small changes in β_2 (see fig. 1 for $\beta_2 = 1.2$, where the peak has shifted already to 130 cm^{-1}). Data such as those for [1,2] $\mathrm{HCl/SF_6}$ or HCl/A liquid mixtures show a very small shift to higher frequency of the maximum absorption over a large range of molecular number density, but this is inevitably accompanied by the disappearance of the low J bands, these being broadened more than those at higher frequencies.

This model is incapable of such differential broadening since it is based on an assumed Poisson randomisation of the torque derivative at each collision, independently of the initial value of the molecular angular acceleration $\dot{J}$. The original J-diffusion model analogously randomises the torque itself independently of the J vector associated with each molecule prior to impact, and thus suffers the same inability to broaden each line in deference to observation.

To remedy this Frenkel and Wegdam [4] have developed recently a modified M and J-diffusion formalism, our second model. In the limit of very slow energy relaxation (M-diffusion) the effect of a collision is an average momentum transfer to or from the rotator, which results in a J^2 dependence of the width of successive lines. The energy relaxation can be made progressively faster up to the J-diffusion limit by the introduction of a probability that upon each reorientation by a collision the energy attains the equilibrium value. This is unity in the limit. The frequency dependence of the width of successive lines alters on going from M to J diffusion and the value for the probability of occurrence of an inelastic collision is adjusted to fit the observed frequency dependence of the width. The best fit to our admittedly crude data is shown in fig. 1, the overall contours of experiment and theory matching fairly well. The parameters used are the elastic momentum transfer, $\langle \Delta J^2\rangle_\mathrm{d} = 40$, the probability P of occurrence of an inelastic event (defined as above), $P = 0.25$, and the time between collisions $\tau_\mathrm{c} = 95\,\hbar/I$. The value for the time between collisions can be compared with that calculated for a rough sphere in the Enskog approximation according to [13]:

$$\tau^{-1} = 4\pi\sigma^2\rho g(\sigma)(kT/\pi m)^{1/2},$$

where ρ is the molecular number density, m the molecular mass, and $g(\sigma)$ the contact pair correlation function given by:

$$g(\sigma) = (2 - \eta)/2(1 - \eta)^3,$$

where $\eta = \pi(\rho\sigma^3)/6$, σ being the molecular diameter. For HBr in SF_6 this value is 0.8 $\hbar/I$, which compares favourably with the value derived from the fitting procedure. The result is not surprising, as already pointed out by O'Dell and Berne [13], diffusion models work quite well in the liquid phase of rough spheres.

Looking at the spectra of HCl and HBr in solvents such as SF_6 and A, it is not possible to justify the inclusion of one further term of the Mori continued fraction approximation. However, these are exceptional systems in which quantisation is retained, and more anisotropic molecules show a distinct shift [14] in the frequency of maximum absorption as a function of number density. Molecules like HCl in SF_6 behave more like rough spheres, certainly for high J quantum numbers, and the J dependence of the width is an important feature giving information on the relative significance of the rate of energy and the rate of momenta relaxation. This ratio in itself produces a slight shift in the frequency of maximum absorption. It is important to gather more data about these systems since they yield with facility information about molecular interactions otherwise difficult to obtain.

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