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VIBRATIONAL DEPHASING AND INTERMOLECULAR INTERACTIONS IN LIQUIDS*

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A simple approach to the problem of the influence of intermolecular interactions on the isotropic Raman band profile $I_{\text{vib}}(\omega)$ based on the idea of different time scales for electronic and nuclear motion is given. The proposed method gives a physical insight into short-time fluctuations of the intermolecular potential and helps to find the dominant type of the intermolecular interactions in the picosecond time region.

1. *Introduction*

Nafie and Peticolas [1], Sykora [2], Bartoli and Litovitz [3], Bratos et al. [4] have developed theories of the spontaneous Raman scattering that explicitly take into account vibrational relaxation. They derive the following expression:

$$G_{\text{vib}}(t) = \langle Q(t)Q(0)\rangle \sim \int\limits_{-\infty}^{\infty} I_{\text{vib}}(\omega)e^{-i\omega t}d\omega, \tag{1}$$

$$I_{\text{vib}}(\omega) = I_{||}(\omega)-\tfrac{4}{3}I_{\perp}(\omega),$$

where the bracket $\langle\ldots\rangle$ represents an equilibrium statistical average, zero frequency in (1) corresponds in fact to the frequency of the band centre ω_0, $Q(t)$ is the normal coordinate associated with the investigated normal mode; $I_{||}(\omega)$ and $I_{\perp}(\omega)$ are the polarized and depolarized component of the Raman-scattered light respectively. Equation (1) gives the time-correlation function of $Q(t)$ as the Fourier transform of the "isotropic" Raman intensity $I_{\text{vib}}(\omega)$. Thus, if $G_{\text{vib}}(t)$ decays, for example, exponentially with a time constant $\tau_0-\tau_0$ is related to the width at half-height of $I_{\text{vib}}(\omega)$. Consequently, $G_{\text{vib}}(t)$ provides a measure of the rate of loss of "memory" of $Q(t)$. i.e. the rate of dephasing of $Q(t)$ and τ_0 is the dephasing time of the incoherent molecular normal vibration Q. Information on vibrational dephasing is also obtained from experiments of von der Linde, Laubereau, Kaiser [5, 6].

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At present there exist several hipotheses accenting various possible mechanisms which may contribute to the broadening of the $I_{\text{vib}}(\omega)$ such as: a) translational collisions [7, 9], b) intermolecular energy transfer [8], c) resonance energy transfer (flip-flop) [10, 12, 13]. However, to our knowledge there is no convincing theory or experiment which can clearly show what kind of interactions are indeed efficient and give main, most dominant contribution to the isotropic band broadening. In this paper we present a procedure which, we hope, although partially will be able to help to answer that question.

2. *Theory*

The influence of the intermolecular potential on the Raman line shape can be investigated by considering, for simplicity, a homonuclear diatomic molecule in a liquid perturbed by the local field associated with sourrounding molecules. The essence of our approach consists in the use of different time scales of response to the external perturbation for the electronic and nuclear motion in a molecule. Since the electrons move much more rapidly than nuclei – due to their small mass — their response to an external field is relatively rapid and they, in turn, or more precisely their shift in energy or density, serves as the actual perturbation experienced by the nuclei. In other words, we assume that relatively slowly moving nuclei experience external interactions indirectly through perturbations of the electronic density, i.e. there is no direct interaction between the fluctuating local field and the nuclei themselves. The situation here is similar, in the spirit, to that of the Born–Oppenheimer approximation [14] in the theory of intermolecular potential. What we are doing here is the transfer of the Born–Oppenheimer idea to the theory of intermolecular interactions. As one knows, in the equation of motion for the vibrating nuclei, the force constant is represented phenomenologically by $\hat{f} = \left(\frac{d^2V}{dQ^2}\right)_0$, where V is the intramolecular potential [14]. In agreement with our concept, the molecular oscillator feels stochastic fluctuations of the intermolecular potential as a time modulation of its force constant. Therefore, if we can find the time dependence of $\tilde{f}(t)$ we can indicate the dominant mechanism perturbing the harmonic motion of a molecular vibrator in liquid. For instance, modulation of the $\tilde{f}(t)$ with a frequency ω_0 suggests resonance energy transfer; modulation of the $\tilde{f}(t)$ with a characteristic frequency $\omega_{\text{coll}} \ll \omega_0$ suggests rather a collisionlike model of the interaction, ...etc.

In order to find time correlation function of the $\tilde{f}(t)$ we write the equation of motion:

$$\mu\ddot{\tilde{Q}}(t) = -\tilde{f}(t)\tilde{Q}(t), \tag{2}$$

where μ is the reduced mass and $\ddot{\tilde{Q}}(t)$ is a shorthand notation of the second time derivative of the normal coordinate $\tilde{Q}$. Since we are interested in the broadening of the "isotropic" intensity $I_{\text{vib}}(\omega)$ around the band centre ω_0, it is convenient to write:

$$\tilde{f}(t) = f_0 + f(t), \tag{3'}$$

$$\tilde{Q}(t) = Q(t) \cdot e^{i\omega_0 t}, \tag{3''}$$

where $f_0 = \omega_0^2\mu$. relations (3) equation (2) reduces to

$$\ddot{Q}(t)+2i\omega_0\dot{Q}(t) = -\frac{f(t)}{\mu}Q(t). \tag{4}$$

Hence we obtain the following expression for the correlation functions:

$$\langle\ddot{Q}(t)\ddot{Q}(0)\rangle-4\omega_0\langle\dot{Q}(t)\dot{Q}(0)\rangle \sim \langle f(t)f(0)\rangle\,\langle Q(t)Q(0)\rangle. \tag{5}$$

The separate averaging of $f(t)$ and $Q(t)$ on the right hand side of Eq. (5) is justified if we take into account that a time fluctuation of $f(t)$ is of the order of 10^{-13} sec — much shorter than correlation time describing vibrational motion $Q(t)$ [17]. Notice, that

$$\langle\dot{Q}(t)\dot{Q}(0)\rangle \sim \int_{-\infty}^{\infty} \omega^2 I_{\text{vib}}(\omega)e^{-i\omega t}d\omega \tag{6'}$$

and

$$\langle\ddot{Q}(t)\ddot{Q}(0)\rangle \sim \int_{-\infty}^{\infty} \omega^4 I_{\text{vib}}(\omega)e^{-i\omega t}d\omega. \tag{6''}$$

In both Eqs. (6) we have employed an expression from the transform theory which deals with relationship of a transform to its derivative [15].

Using relations (1) and (6) in Eq. (5) we have

$$\langle f(t)f(0)\rangle \sim \frac{\int\limits_{-\infty}^{\infty} [\omega^4-(2\omega_0\omega)^2]I_{\text{vib}}(\omega)e^{-i\omega t}d\omega}{\int\limits_{-\infty}^{\infty} I_{\text{vib}}(\omega)e^{-i\omega t}d\omega}. \tag{7}$$

Therefore we get the goal of this paper.

It is clear from Eq. (7) that the main contribution to the function $\langle f(t)f(0)\rangle$ gives the Fourier transform of the term $(2\omega_0\omega)^2 I_{\text{vib}}(\omega)$ because $(2\omega_0\omega)^2 \gg \omega^4$ for reasonable values of ω (except very wide lines). Therefore, we can neglect the term $\omega^4 I_{\text{vib}}(\omega)$ in Eq. (7) and consequently the term $\ddot{Q}(t)$ in Eq. (4). Let us introduce time dependent angular frequency $\tilde{\omega}(t) = \omega_0+\omega(t) = (\tilde{f}(t)/\mu)^{1/2}$. Hence $f(t)/\mu = 2\omega_0\omega(t)+\omega^2(t) \cong 2\omega_0\omega(t)$ and Eq. (4) becomes

$$\dot{Q}(t) = i\omega(t)Q(t). \tag{8}$$

The vibrational correlation function after these approximations is given by

$$G_{\text{vib}}(t) = \frac{\langle Q(t)Q(0)\rangle}{\langle Q^2(0)\rangle} = \langle e^{i\int_0^t \omega(t')dt'}\rangle. \tag{9}$$

Here we catch contact with previous stochastic-type considerations where the possibility of this type of vibrational correlation function was suggested [4] and applied [16–18].

Our next step is the second cumulant approximation of the $G_{\text{vib}}(t)$ defined by Eq. (9),

$$G_{\text{vib}}(t) \cong e^{-\int_0^t\int_0^{t'} \langle\omega(t')\omega(t'')\rangle dt'dt''} \tag{10}$$

and

$$\langle\omega(t)\omega(0)\rangle = -\frac{d^2}{dt^2}\{\ln G_{\text{vib}}(t)\}. \tag{11}$$

We can also write the relation (11) in the Fourier transform representation,

$$\langle\omega(t)\omega(0)\rangle = \frac{\int\limits_{-\infty}^{\infty} \omega^2 I_{\text{vib}}(\omega)e^{-i\omega t}d\omega}{\int\limits_{-\infty}^{\infty} I_{\text{vib}}(\omega)e^{-i\omega t}d\omega} - \left[\frac{\int\limits_{-\infty}^{\infty} \omega I_{\text{vib}}(\omega)e^{-i\omega t}d\omega}{\int\limits_{-\infty}^{\infty} I_{\text{vib}}(\omega)e^{-i\omega t}d\omega}\right]^2. \tag{12}$$

At last, it is worth to mention here that Eqs. (7), (11) and (12) are valid not only for diatomic molecules but also for nondegenerate modes in polyatomic molecules. Moreover, in our classical approach, the intermolecular potential perturbed by the external forces is represented phenomenologically by the force constant $f(t)$. The more rigorous, quantum mechanical approach, needs explicit definition of the intermolecular potentali and leads to the quite complicated molecular dynamics calculations [11]. In the next section we will show an application of Eqs. (7) and (12) to the study of the short-time behaviour of molecules in liquid methyl iodide.

3. Experimental

Measurements were made by means of spectrophotometer Cary 82 with the slit 1.2 cm^{-1} for pure liquid CH_3J at the temperature 300 K. This molecule has one well separated band with $\nu_0 = 525$ cm^{-1}. The discussed band is asymmetric due to the presence of the hot band. This hot band can be extracted by the method described by Goldberg [19]. The band profile was measured up to 125 cm^{-1} from ν_0. The slit width was narrower about six times than the measured $I_{||}(\omega)$ band width and about four times than $I_{\perp}(\omega)$ band width. The numerical deconvolution method proposed by Jones [20] was applied. In the observed time scale (0÷2 psec) no differences between Fourier transforms of the convoluted and deconvoluted band profiles have been found.

4. Results and discussion

Both Fourier transforms obtained according to Eqs. (7) and (12) are presented in Fig. 1. Moreover, for comparison, in Fig. 1 we present also the common vibrational correlation function

$$\langle Q(t)Q(0)\rangle \sim \int\limits_{-\infty}^{\infty} I_{\text{vib}}(\omega)e^{-i\omega t}d\omega = G_{\text{vib}}(t). \tag{13}$$

Fig. 1 shows generally satisfactory agreement between functions $\langle f(t)f(0)\rangle$ and $\langle\omega(t)\omega(0)\rangle$, so for the investigated band the second cumulant approximation is quite good.

Let us firstly discuss the errors of the correlation functions. Our estimates have indicated that among several factors which contribute to the experimental error (slit function, accuracy in determining ω_0 and baseline) the most important is the error produced by the cut-off of the experimental curve — in the present case $I_{\text{vib}}(\omega)$. In practice, one can measure the intensity $I^{\text{obs}}(\omega)$ in the finite frequency region $\omega_0-\omega_c < \omega < \omega_0+\omega_c$. In other words

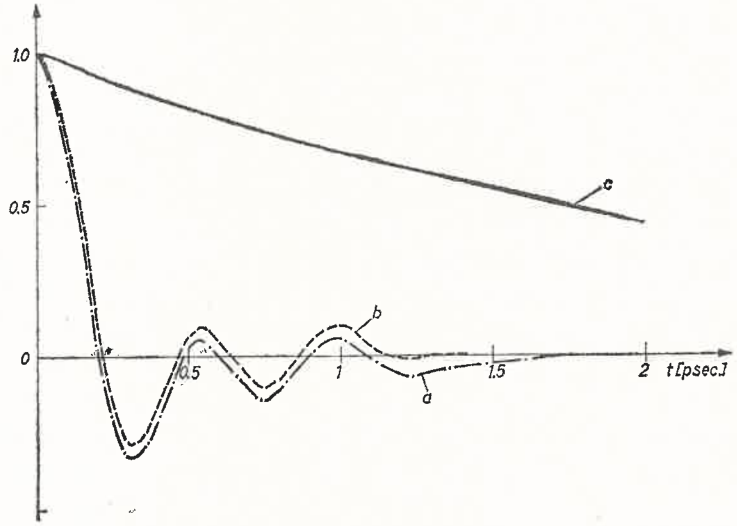

Fig. 1. Experimental correlation functions for A_1 band (C–J stretch, $\nu_0 = 525$ cm^{-1}, temperature $T = 300$°K) of pure liquid CH$_3$J; a) $\langle f(t)f(0)\rangle$ computed according to Eq. (7), b) $\langle\omega(t)\omega(0)\rangle$ computed according to Eq. (12), c) vibrational correlation function $\langle Q(t)Q(0)\rangle \sim \int_{-\infty}^{\infty} I_{\text{vib}}(\omega)e^{-i\omega t}d\omega$. Note a great difference between

$$\tau_0 = \int_0^{\infty} G_{\text{vib}}(t)dt = 2.4 \text{ psec and } \tau = \int_0^{\infty} \langle f(t)f(0)\rangle dt = 0.05 \text{ psec}$$

$$I^{\text{obs}}(\omega) = I^{\text{true}}(\omega)\cdot\pi(\omega), \tag{14}$$

where

$$\pi(\omega) = \begin{cases} 1 \text{ for } \omega_0-\omega_c \leqslant \omega \leqslant \omega_0+\omega_c \\ 0 \text{ for } \omega < \omega_0-\omega_c \text{ and } \omega > \omega_0+\omega_c. \end{cases}$$

Hence

$$\begin{aligned} \langle f(t)f(0)\rangle^{\text{obs}} &\sim \mathscr{F}\{[\omega^4-(2\omega_0\omega)^2]I^{\text{obs}}(\omega)\} \\ &= \mathscr{F}\{[\omega^4-(2\omega_0\omega)^2]I^{\text{true}}(\omega)\} * \mathscr{F}\{\pi(\omega)\} \\ &= \langle f(t)f(0)\rangle^{\text{true}} * 2\omega_c \operatorname{sinc}(\omega_c t), \end{aligned} \tag{15}$$

where $\mathscr{F}$ denotes frequency Fourier transform and star denotes convolution,

$$\operatorname{sinc}(\omega_c t) = \frac{\sin(\omega_c t)}{\omega_c t}.$$

The above equation indicates that the correlation function $\langle f(t)f(0)\rangle^{\text{true}}$ is convoluted with a periodical function $2\omega_c \operatorname{sinc}(\omega_c t)$. In order to obtain $\langle f(t)f(0)\rangle^{\text{true}}$ the deconvolution procedure ought to be applied. In our case $\nu_c = 125\ \text{cm}^{-1}$ ($\omega_c = 2\pi c\nu_c$) so the value $\operatorname{sinc}(\omega_c t)$ equals zero in the time points $t_n = n\pi/\omega_c$ ($t_1 = 0.13$ psec, $t_2 = 0.26$ psec, ...). Our experimentally obtained function $\langle f(t)f(0)\rangle^{\text{obs}}$ looks like a damped cosine first time cutting through t-axis at 0.2 psec. In this unfortunate case—similar periods—deconvolution procedure cannot be applied effectively.

It is usually assumed that the correlation function approaches an exponential function of the form $\exp(-t/\tau)$. Let us then consider this simple form of the $\langle f(t)f(0)\rangle^{\text{true}}$ relaxation process, which has been already applied by Rothschild [17]. It is true that the convolution $\exp(-t/\tau) * \operatorname{sinc}(\omega_c t)$ provides the periodical damping function if $\tau < 0.04$ psec, but it is impossible to achieve a reasonable fitting to $\langle f(t)f(0)\rangle^{\text{obs}}$($\langle f(t)f(0)\rangle^{\text{obs}}$ and $\exp(-t/\tau)$ $* \operatorname{sinc}(\omega_c t)$ cross the time axis at different points). When the relaxation time τ increases, the negative part of the computed function $\exp(-t/\tau) * \operatorname{sinc}(\omega_c t)$ decreases and at last for $\tau > 0.1$ psec it becomes completely positive (see Fig. 2). It is clear that the exponential form of the $\langle f(t)f(0)\rangle^{\text{true}}$ is not a satisfactory approximation.

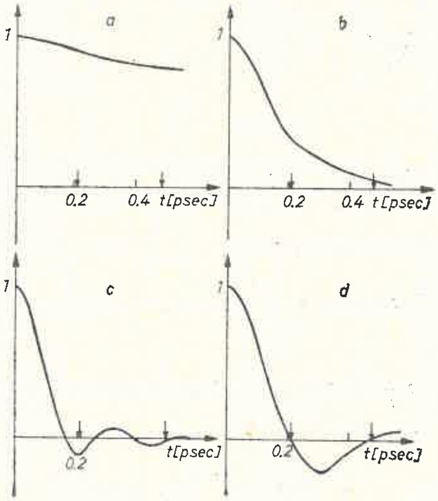

Fig. 2. The functions describing the time development of sinc($\omega_c t$) ($\nu_c = 125\ \text{cm}^{-1}$) convoluted with exponential functions (with damping factors a — $\tau = 2$ psec; b — $\tau = 0.16$ psec; c — $\tau = 0.05$ psec) and damping cosine $e(-t/\tau)\cos\omega_L t$ ($\tau = 0.16$ psec, $\nu_L = 50\ \text{cm}^{-1}$). Arrows indicate the points on t-axis where the experimental curve $\langle f(t)f(0)\rangle$ equals zero

However, we can get easily a good agreement with the experimental curve if we assume $\langle f(t)f(0)\rangle^{\text{true}}$ in the form $\exp(-t/\tau)\cdot\cos\omega_L t$ with the parameters value: $\tau = 0.16$ psec,

$\omega_L = 2\pi c\nu_L$, $\nu_L = 50 \pm 10\ \text{cm}^{-1}$. We emphasize that only pulsed functions with a negative part convoluted with sinc $(\omega_c t)$ can reproduce observed curve. Of course, the damped cosine proposed here is only one example from the large class of such functions.

Now we want to focus our attention on a characteristic time behaviour of the $\langle f(t)f(0)\rangle$ and we want to try to explain quantitatively this interesting plot. To do this we assume that the time dependence of the force constant $\tilde{f}(t)$ arises from translational motion, reorientational processes and other vibrational motions of the same and adjacent molecules i.e. $\tilde{f}(t) = f(R(t), \Omega(t), q(t)) = f(\varepsilon(t))$, where $\varepsilon(t) = \{R(t), \Omega(t), q(t)\}$ represents the set of the translational, angular and vibrational coordinates. The force constant $\tilde{f}(t)$ can be expanded around temporary equilibrium position as follows

$$\tilde{f}(t) = f_0 + f(t) = f(\varepsilon_0) + \sum \left(\frac{\partial f}{\partial \varepsilon_i}\right) \delta\varepsilon_i(t). \tag{16}$$

The summations are made on translational, angular and vibrational coordinates of the nearest molecules.

Consequently,

$$\langle f(t)f(0)\rangle \sim \sum_{i,j} \left(\frac{\partial f}{\partial \varepsilon_i}\right)_0 \cdot \left(\frac{\partial f}{\partial \varepsilon_j}\right)_0 \cdot \langle \delta\varepsilon_i(t)\delta\varepsilon_j(0)\rangle. \tag{17}$$

Above equation shows that even in the simple case of binary interactions there are several different relaxation mechanisms such as: translational $\langle \delta R(t)\delta R(0)\rangle$, rotational $\langle \delta\Omega(t)\delta\Omega(0)\rangle$, vibrational $\langle q(t)q(0)\rangle$, fluctuations and cross terms $\langle \delta R(t)\delta\Omega(0)\rangle$, $\langle \delta\Omega(t)\delta q(0)\rangle$ e.t.c. It is not easy to establish here, on the basis of one experiment at one temperature, which mechanism gives the main contribution to the investigated band, but the characteristic frequency of this process is $50 \pm 10\ \text{cm}^{-1}$. Note, that "far infrared" value $\nu_L = 50 \pm 10\ \text{cm}^{-1}$ is not unrealistic. It is known [21] that large amplitude translatory-rotatory fluctuations occur in liquids with peak frequencies of the order of 50–100 cm^{-1}. It would be interesting to apply this procedure to experimental study of the temperature, pressure and solvent effects on Raman and IR line shapes in order to establish the detailed nature of the perturbation process.

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