Interpolation model for molecular reorientation in gases and liquids

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Abstract. The interpolation model for molecular reorientation in gases and liquids has been extended to the case for symmetric top molecules. It has been compared with experimental correlation functions for linear as well as prolate and oblate symmetric top molecules. The agreement is excellent for systems where the intermolecular torque is small. With increasing torque, there is discrepancy at short times whereas at intermediate and long times the decay is described quite well. However for liquids at low temperatures, the description of molecular reorientation within the framework of this model is unsatisfactory.

Keywords. Molecular rotations; infrared line shapes; Raman line shapes; generalized extended diffusion models; interpolation model.

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1. Introduction

Reorientation dynamics of molecules in gases and liquids is being studied by a number of experimental techniques—the infrared and Raman spectroscopic techniques being the most widely used. The time-correlation function for molecular orientation vector as well as the angular velocity vector can be obtained from Fourier transform of vibration-rotation band profile in infrared and Raman spectra. The different experimental techniques and the different types of information obtained from these along with their advantages and disadvantages are reviewed in several articles (Gordon 1968; Steele 1976; Berne and Pecora 1976; McClung 1977; Vincent-Geisse 1980; Yarwood 1983 etc.). A complete understanding of the reorientation dynamics, however requires comparison of the experimental data with theoretical models. Of the several theoretical models for molecular reorientation in gases and liquids, the rotational diffusion model proposed by Debye (1928) has been the earliest and by far the simplest. This was subsequently generalized by Gordon (1966). Unlike Debye's model where the molecule reorients by infinitesimal angle, Gordon had introduced free rotation by finite angle between successive collisions. The Gordon's model, also known as the extended diffusion model (EDM) has two versions—the M and J diffusion models. The two models are indistinguishable at short times but the J diffusion model decays much faster than the M diffusion at long times. The EDM was extended to include molecules of different shapes and compared with various experimental data to obtain a clear understanding of the reorientation dynamics (McClung 1977). However, in spite of comparing a large number of experimental data, no broad consensus could be arrived

at regarding the applicability of either of these two versions of EDM. For example, the NMR data relating the reorientational and angular momentum correlation times for spherical molecules (Maryott et al 1971; Gillen et al 1972; Marsault et al 1973) and symmetric top molecules (McClung 1973; Bull 1973, 1975; DeZwaan et al 1974) seems to be in accord with the J diffusion model. However, the situation is not so encouraging for linear molecules (Krynicki and Powels 1972; Krynicki et al 1975)—in a few cases (Boden and Folland 1975; Schwartz and Wang 1974) the experimental data lie between the J and M diffusion limits. The experimental correlation function for a few spherical molecules seems to be well described by the J diffusion model (Sunder et al 1974; Marsault-Herail et al 1975; Campbell et al 1973) but in other cases the situation is quite ambiguous (Eagles and McClung 1973; Sunder and McClung 1973). For example, although the correlation function for neopentane has been claimed to lie between the J and M diffusion limits (Livingstone et al 1973) the experimental data is ambiguous. The situation is also similar for linear (Marsault et al 1975; Levi et al 1972; Perrot et al 1975) and symmetric top molecules (Marsault et al 1973; Arndt and McClung 1978; Bansal and Roy 1979; Perry et al 1981). In some cases the experimental correlation function seems to lie between the J and M diffusion models (Marsault et al 1975; Dreyfus et al 1982; Rothschild et al 1975).

An attempt to improve the situation was undertaken by Dattagupta and Sood (1979) who proposed an 'interpolation' scheme where one could calculate the correlation function intermediate between the J and M diffusion limits by varying an interpolation parameter. Thus the M and J diffusion models could be treated as limiting cases of this model. This was achieved by incorporating partial randomization of the magnitude of angular momentum in a collision as opposed to no or complete randomization in M and J diffusion limits respectively. They had dealt with linear molecules and compared with infrared and NMR data. However, a careful survey of the experimental data in the literature reveals that a large number of accurate data exist for symmetric top molecules of both prolate and oblate shape (Griffiths 1977; Vincent-Geisse 1980; Perry et al 1981; Bansal et al 1981; Deb et al 1986). This is particularly true for reorientation of molecules in liquids. Thus it is of considerable interest to extend this scheme to the case of symmetric top molecules and compare with a wide variety of available experimental data. We would like to emphasize here that the NMR data, which deals only with correlation time, do not constitute a critical test for a theoretical model. Also, NMR data is not always unambiguous because of uncertainty in several experimental parameters. Thus it is essential to compare with correlation function to determine the applicability of a particular model. Further, it is preferable to compare with Raman correlation function rather than with infrared data because the latter also contain a contribution from vibrational relaxation. The effect of vibrational relaxation on molecular reorientation, although can be neglected in gases, becomes quite important in liquids. However, it has been shown that (Gordon 1968) for linear and symmetric top molecules, the reorientational correlation function for tumbling motion of the molecular axis obtained from Raman band profile analysis does not contain the effect of vibrational relaxation. It is also necessary to ensure that the experimental data is free from 'collision-induced-scattering'. Keeping these in mind, we generalize the interpolation model for symmetric top molecules and examine its applicability by comparing with infrared and Raman correlation function of linear as well as symmetric top prolate and oblate molecules.

The plan of the paper is as follows. In § 2, we present the calculation of correlation

function for symmetric top molecule. We follow an approach similar to Dattagupta and Sood (1979), but the details are similar to that of EDM for symmetric top molecules by McClung (1977). The times (t), frequencies (ω) and angular momenta (J) are expressed in reduced units (r.u.) i.e. in units of $(I/k_B T)^{1/2}$, $(k_B T/I)^{1/2}$ and $(I k_B T)^{1/2}$ respectively, where I is the moment of inertia perpendicular to the molecular axis, k_B the Boltzmann constant and T the absolute temperature. In § 3, we present comparison with experimental correlation function for OCS, CD_3H, propyne and CH_3I. The applicability and limitations of the model are discussed in § 4.

2. Mathematical approach

The fundamental mechanism for reorientation is the same as that of EDM where the molecule is assumed to rotate freely between successive collisions. The rotational motion of a freely rotating symmetric top molecule is described by McClung (1972). The set of Eulerian angles specifying the orientation of the symmetric top molecule with respect to a space fixed frame is denoted, for brevity, by Ω. The essential features of EDM have been retained by Dattagupta and Sood (1979) except that the change in angular momentum in a collision is represented by a collision operator which allows an interpolation between the M and J diffusion limits. The angular momentum is represented by an operator in an infinite-dimensional vector space spanned by the angular momentum. Thus the angular momentum operator ($\tilde{J}$) is a diagonal matrix whose elements are the possible values of the angular momenta.

Thus

$$\langle J|\tilde{J}|J_0\rangle = J_0\,\delta(J-J_0), \tag{1}$$

where $\delta(J-J_0)$ is the Dirac delta function.

The feature common to M and J diffusion, i.e. the complete randomization of the angular momentum direction is also retained in this scheme. Unlike in linear molecules where the angular momentum vector is normal to the molecular axis, the angular momentum has both polar and azimuthal angles for a symmetric top molecule. Therefore, both these angles are randomized in a collision. The azimuthal angle (α) is randomized to an isotropic distribution, whereas the polar angle (β) is randomized to the distribution (McClung 1977)

$$W(J, \beta) = \frac{J(\xi/2\pi)^{1/2}}{\mathrm{erf}\,[J(\xi/2)^{1/2}]}\,\exp(-\xi J^2 x^2/2), \tag{2}$$

where $x = \cos\beta$ and $\mathrm{erf}(y)$ denote the error function. The change in the magnitude of angular momentum in a collision is represented by a collision operator $\tilde{T}$, whose elements $\langle J|\tilde{T}|J_0\rangle$ denote the probability that the angular momentum changes from J_0 to J in a collision.

Suppose at $t = 0$, the orientation of the molecular frame with respect to the space fixed frame is denoted by Ω_0. The rotational motion of the molecule can be described by defining a diffusion trajectory of the angular momentum vectors $\mathbf{J}_0$, $\mathbf{J}_1$, $\mathbf{J}_2$, .. , $\mathbf{J}_{n-1}$, ... of the molecule during successive diffusion steps and times $t_1, t_2, t_3, \ldots t_n, \ldots$ at which the first, second, third, ... nth diffusive steps terminate. Then following

McClung (1977), after n collisions, the transformation from the laboratory to the molecular frame is given by

$$D^{(l)}[\Omega(t)]_n = D^{(l)}[\Omega_0] D^{(l)}[\Delta\Omega(\mathbf{J}_0; t_1)] D^{(l)}[\Delta\Omega(\mathbf{J}_1; t_2 - t_1)]$$

$$\ldots D^{(l)}[\Delta\Omega(\mathbf{J}_n; t - t_n)], \tag{3}$$

where $\Delta\Omega(\mathbf{J}_i; t_{i+1} - t_i)$ is the orientation by which the molecular frame rotates between the i-th and $(i+1)$th collision and $D^{(l)}$ represents the corresponding transformation matrix, which are nothing but rotation matrices representing transformation of a spherical tensor of rank l (Rose 1957). Here $l=1$ and $l=2$ correspond to infrared and Raman correlation functions respectively.

The correlation functions are calculated by evaluating the expression

$$\langle D^{(l)}[\Omega_0] D^{(l)*}[\Omega(t)] \rangle, \tag{4}$$

where $\langle \ \rangle$ represents ensemble average over all possible trajectories and involves averages over: (i) the number of collisions experienced by the molecule upto time t, (ii) the times at which the collisions occurred, (iii) the angular momentum in each diffusive step, and (iv) the initial molecular orientation.

As in EDM, the 'collisions' are idealized events, where the rotational motion of the molecule is instantaneously interrupted by torques which change the angular momentum state of the molecule. The collisions are completely uncorrelated and collision times follow a Poisson distribution with average time τ_J between the collisions. Then following Dattagupta and Sood (1979) and McClung (1977), the correlation function can be shown to be given by

$$C^{(l,k)}(t) = \int dJ \int dJ_0 \ W(J_0) \sum_{n=1}^{\infty} \tau_J^{-n} \exp(-t/\tau_J) \int_0^t dt_n \int_0^{t_n} dt_{n-1} \ldots \int_0^{t_2} dt_1$$

$$\int dJ_{n-1} \ldots \int dJ_1 \, g(J; t - t_n) \langle J|\tilde{T}|J_{n-1}\rangle \, g(J_{n-1}; t_n - t_{n-1}) \ldots$$

$$\ldots \langle J_2|\tilde{T}|J_1\rangle \, g(J_1; t_2 - t_1) \langle J_1|\tilde{T}|J_0\rangle \, g(J_0; t_1). \tag{5}$$

In the above J_0 and J are the magnitudes of angular momentum at the beginning and end of a particular collision sequence and $g(J_i; t_{i+1} - t_i)$ is given by (McClung 1977)

$$g(J_i; t_{i+1} - t_i) = \sum_{m=-l}^{l} \int W(J_i, \beta_i) \sin \beta_i |d_{km}^{(l)}(\beta_i)|^2$$

$$\exp[-i(t_{i+1} - t_i)J_i(m + k\xi \cos \beta_i)]. \tag{6}$$

The probability distribution function for angular momentum magnitude is given by

$$W(J) = [(1+\xi)/\xi]^{1/2} J \exp(-J^2/2) \operatorname{erf}[J(\xi/2)^{1/2}]. \tag{7}$$

In (6), the integration over β_i represents averaging corresponding to the randomization of polar angle of angular momentum. The averaging with respect to azimuthal angle

has already been performed. ξ is the asymmetry parameter defined by

$$\xi = (I/I_z - 1),$$ (8)

where I_z is the moment of inertia around the molecular symmetry axis. $\xi > 0$ for 'prolate' molecules and $\xi < 0$ for 'oblate' molecules. The averaging with respect to β_i does not arise for linear molecules.

Then by taking Laplace transform it can be shown that

$$\tilde{\tilde{C}}^{(l,k)}(p) \equiv \int_0^\infty C^{(l,k)}(t)\exp(-pt)\mathrm{d}t$$

$$= \int \mathrm{d}J \int \mathrm{d}J_0\, W(J_0) \left\langle J \left| \frac{G_{\mathrm{FR}}^{(l)}(p+\lambda; \tilde{J})}{1 - \lambda \tilde{T} G_{\mathrm{FR}}^{(l)}(p+\lambda; \tilde{J})} \right| J_0 \right\rangle,$$ (9)

where

$$G_{\mathrm{FR}}^{(l)}(S; \tilde{J}) = \sum_{m=-l}^{l} \int \mathrm{d}\beta \sin\beta |\mathrm{d}_{km}^{(l)}(\beta)|^2\, W(\tilde{J}, \beta).$$

$$\frac{1}{S + i\tilde{J}(m + k\xi\cos\beta)}.$$ (10)

Here $\lambda = \tau_J^{-1}$ is a measure of the average collision frequency. The expression for Laplace transform of the correlation function is essentially similar to that given by Dattagupta and Sood (1979) except that the form of $G_{\mathrm{FR}}^{(l)}$ is much more complicated. The spectral density $I^{(l,k)}(\omega)$ is obtained from $\tilde{\tilde{C}}^{(l,k)}(p)$ by using the relation

$$I^{(l,k)}(\omega) = (1/\pi)\,\mathrm{Re}[\tilde{\tilde{C}}^{(l,k)}(i\omega)],$$ (11)

and the corresponding correlation function $C^{(l,k)}(t)$ is calculated from the Fourier transform of $I^{(l,k)}(\omega)$. Equation (9) is a general expression with $\tilde{T}$ as the transition operator and a particular model is obtained with a specific form of its matrix element. In the interpolation model it is given by

$$\langle J | \tilde{T} | J_0 \rangle = \gamma W(J) + (1-\gamma)\,\delta(J - J_0),$$ (12)

where γ is the interpolation parameter. $\gamma = 0$ and $\gamma = 1$ correspond to the M and J diffusion limits respectively. We are interested in the correlation functions representing reorientation of the symmetry axis and the corresponding spectral densities can be obtained with $k = 0$ from (9), (11) and (12) as

$$I_l(\omega) \equiv I^{(l,0)}(\omega) = \frac{1}{\pi}\mathrm{Re}\left[\frac{A}{1 - \lambda\gamma A}\right],$$ (13)

where

$$A = \int \mathrm{d}J_0\, W(J_0)\, G_{\mathrm{FR}}^1(\lambda + i\omega; J_0),$$ (14)

and

$$G_{\mathrm{FR}}^1(S; J) = G_{\mathrm{FR}}^{(l)}(S; J)/[1 - \lambda(1-\gamma)G_{\mathrm{FR}}^{(l)}(S; J)].$$ (15)

The infrared and Raman correlation functions $C_1(t)$ and $C_2(t)$ are calculated by using the relation

$$C_l(t) = \int_0^\infty I_l(\omega) \cos \omega t \, d\omega. \tag{16}$$

The different expressions required to calculate $I_1(\omega)$, $I_2(\omega)$ and hence $C_1(t)$, $C_2(t)$ are given in the Appendix. The $C_1(t)$ and $C_2(t)$ as functions of λ and γ show similar behaviour as that for linear molecules (Dattagupta and Sood 1979). The principal difference is that the correlation time, defined as the first moment of the line shape, for a symmetric top molecule in the limit of M diffusion is finite.

3. Numerical results and comparison with experiments

The correlation functions have been obtained by first calculating the spectral densities and then taking their Fourier transform. The numerical calculations were verified by reproducing the M and J diffusion correlation functions of McClung (1977) for various values of ξ. They were also checked by reproducing correlation functions given by Dattagupta and Sood (1979) for linear molecules in the limit of large values of ξ. In the following we compare this model with a few experimental data to examine its applicability. We do not intend to compare with NMR data for the reasons stated earlier and confine to infrared and Raman correlation function for reorientation of symmetry axis of linear and symmetric top molecules only. We consider only those experimental data which are accurate and unambiguous.

3.1 *Linear molecule: Carbonyl sulphide (OCS)*

Dreyfus *et al* (1982) determined the infrared correlation function for OCS, N_2O and CO_2 mixed with rare gases in the density range 15–300 amagat. They compared their data with EDM and other models. At low densities, the M diffusion model agrees with the experimental data quite well, but it worsens at higher densities. In particular, the correlation function obtained from ν_1 mode of OCS mixed in Kr at 300 amagat lies between the J and M diffusion limits for $\lambda = 1$. Thus this is an ideal situation for examining the usefulness of the interpolation model and the fit to experimental data is shown in figure 1. The calculated correlation function for $\lambda = 1{\cdot}0$ and $\gamma = 0{\cdot}28$ fit the experimental points quite well. The agreement is excellent except at long times ($t > 3{\cdot}5$ r.u.) where the experimental $C_1(t)$ seems to decay faster. We have also shown the calculated curves for M and J diffusion and Fokker-Planck-Langevin (FPL) model and it shows that the agreement with the interpolation model is far better than with any of the models. Dreyfus *et al* do not show comparison with Steele memory function model (1981) at 300 amagat, but the curve for 272 amagat shows discrepancy after $t \approx 2$ r.u. and decays to zero beyond $t \approx 3$ r.u. However the agreement with interpolation model is better than that obtained by Dreyfus *et al* with either Fokker-Planck-Langevin or Steel memory function model. We should also mention that the contribution of vibrational relaxation in this case could be neglected because the
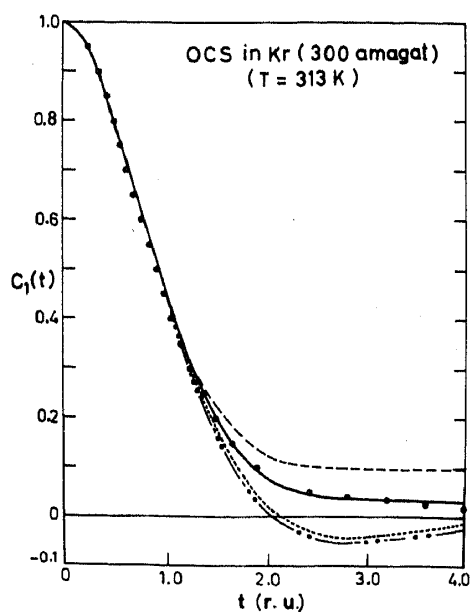
Figure 1. Experimental $C_1(t)$ for OCS in Kr (· · ·)(Dreyfus *et al* 1982) and comparison with interpolation model (——) for $\lambda = 1$ and $\gamma = 0.28$. The M diffusion (– – –), J diffusion (–··–) and FPL (– – – – –) curves are shown for comparison.
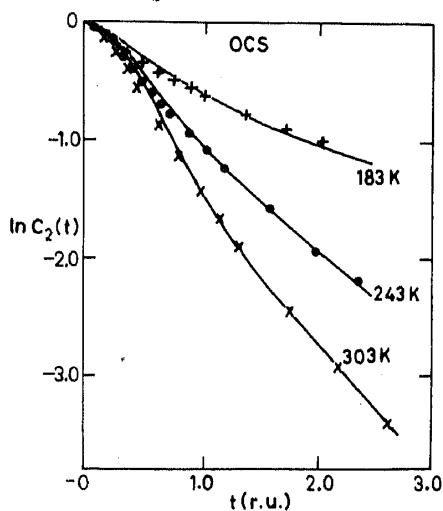

Figure 2. Raman correlation function for OCS at 183 K (+ + +), 243 K (· · ·) and 303 K (× × ×) (Hegemann and Jonas 1983) and interpolation model fit (——) for (i) $\lambda = 6.7$, $\gamma = 0.01$ at 183 K; (ii) $\lambda = 3.2$, $\gamma = 0.25$ at 243 K; (iii) $\lambda = 2.0$, $\gamma = 0.65$ at 303 K respectively.

isotropic Raman width has been found to be much smaller than the rotational width (Dreyfus *et al* 1982).

Hegemann and Jonas (1983) had obtained Raman correlation function for liquid OCS over a temperature range 183 K to 303 K. The contribution from the collision-induced scattering had been subtracted assuming the second moment criterion. Figure 2 shows comparison of the experimental $C_2(t)$ at 303 K, 243 K and 183 K with interpolation model. At short times ($t < 0.8$ r.u.) the agreement is poor—the calculated $C_2(t)$ being always larger than the experiment. At long times, the experimental $C_2(t)$ at 303 K and 243 K are well reproduced for $\lambda = 2.0$, $\gamma = 0.65$ and $\lambda = 3.2$, $\gamma = 0.25$ respectively. But at 183 K, the agreement is poor even at long times. We note that, with decreasing temperature, λ increases and γ decreases such that the product $\lambda\gamma$ decreases. This agrees with the interpretation of γ by Dattagupta and Sood (1979) and Balakrishnan (1979) where $\lambda\gamma$ is an effective rate of randomization of angular momentum. The long time decay of the correlation function is governed by the angular momentum randomization and thus a larger value of $\lambda\gamma$ corresponds to faster decay.

3.2 *Symmetric top molecules*

3.2a *CD₃H in liquid Ar*: Marsault *et al* (1973) have determined the infrared correlation function for CH_3D and CD_3H molecules in some inert liquids. They assume that the contribution from vibrational relaxation is negligible. The reorientation in liquid CH_4 and CF_4 were reasonably well described by the J diffusion model, but in other liquids neither of the versions of EDM seemed to be applicable. CD_3H is an oblate symmetric top molecule with $\zeta = -0.2$ and figure 3 shows an interpolation model fit to the experimental $C_1(t)$ for CD_3H in liquid Ar at 84 K. The calculated $C_1(t)$ for $\lambda = 1.4$ and $\gamma = 0.15$ is in excellent agreement with the experiment. Marsault *et al* observe that the M diffusion curve for $\lambda = 1.25$ agrees well only up to $t \approx 2$. r.u. but decays much slower at long times. This is evident from the M and J diffusion curves shown in the same figure for $\lambda = 1.25$. Similar agreement can be obtained for other cases also.

3.2b *CH₃I in cyclohexane*: CH_3I is a prolate symmetric top molecule with $\zeta = 19.3$. Recently Deb *et al* (1986) have obtained Raman correlation function for CH_3I dissolved in cyclohexane at several molar concentrations. The experimental data satisfy the second moment criterion and has no contribution from collision-induced-scattering. Figure 4 shows comparison with interpolation model for pure liquid as well as in mixtures. The situation is similar to that for OCS where the agreement at long times is excellent whereas at short times the calculated $C_2(t)$ are always greater than the
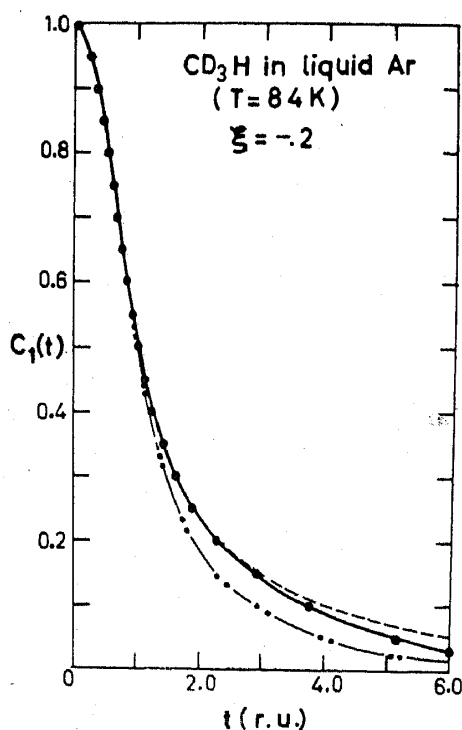

Figure 3. Comparison of calculated $C_1(t)$ (———) for $\lambda = 1.4$ and $\gamma = 0.15$ with the experimental data (· · ·) for CD_3H (Marsault *et al* 1973). The M diffusion (– – –) and J diffusion (–··–) curves are also shown.
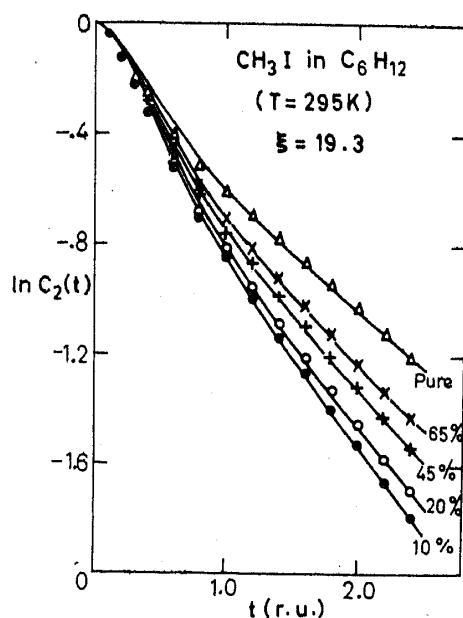
Figure 4. Comparison of experimental $C_2(t)$ (Deb *et al* 1986) and interpolation model fit (———) for CH_3I in C_6H_{12}. (i) Pure CH_3I, ($\triangle\triangle\triangle$) $\lambda = 7.0$, $\gamma = 0.03$; (ii) 65% mole fraction ($\times \times \times$) $\lambda = 5.8$, $\gamma = 0.07$ (iii) 45% mole fraction ($+ + +$) $\lambda = 5.3$, $\gamma = 0.09$ (iv) 20% mole fraction (o o o) $\lambda = 4.7$, $\gamma = 0.12$ (v) 10% mole fraction (· · ·) $\lambda = 4.5$, $\gamma = 0.15$.
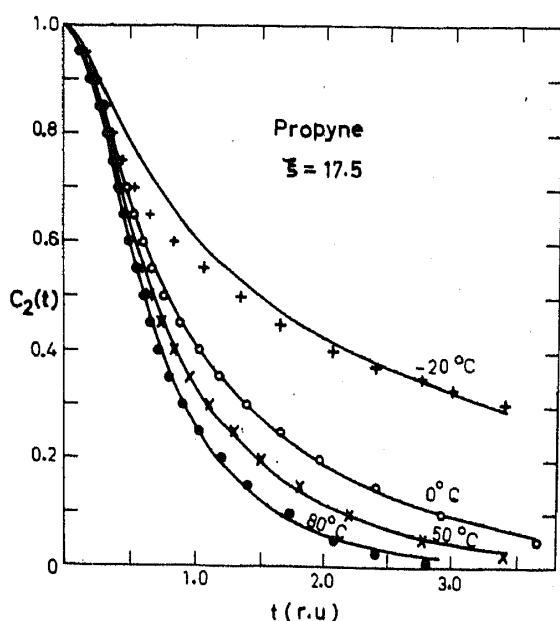
Figure 5. Experimental $C_2(t)$ for Propyne at 80°C (· · ·), 50°C (× × ×), 0°C (o o o) and −20°C (+ + +) (Perry *et al* 1981) and interpolation model fit (———) for (i) $\lambda = 2·5, \gamma = 0·8$ at 80°C; (ii) $\lambda = 3·2$, $\gamma = 0·4$ at 50°C (iii) $\lambda = 4·2$, $\gamma = 0·2$ at 0°C and (iv) $\lambda = 8·5$, $\gamma = 0·0$ (*M*-diffusion) at −20°C.

experimental value. With decreasing concentration of CH_3I, λ decreases and γ increases such that the product $\lambda\gamma$ increases. This fact is also in agreement with the interpretation of γ.

3.2c *Liquid propyne*: Propyne is also a prolate symmetric top molecule with $\xi = 17·5$. Perry *et al* (1981) studied its reorientation dynamics in pure liquid as well as in mixture. They observe that in pure liquid, the J diffusion model agrees quite well with the experimental $C_2(t)$ at 80°C, but with decreasing temperature there is increasing discrepancy between J diffusion and experiment. Figure 5 shows comparison with interpolation model with data at 80°C, 50°C, 0°C and −20°C. At 80°C the interpolation model with $\lambda = 2·5$ and $\gamma = 0·8$ does not provide any agreement better than the J diffusion model of Perry *et al*. But at 50°C and 0°C the interpolation model agrees very well with the experimental $C_2(t)$. At −20°C, a satisfactory agreement with the interpolation model could not be obtained. This can be seen from the fact that the M diffusion $C_2(t)$ for $\lambda = 8·5$ differs considerably from the experiment. An effort to obtain agreement at short times results in much faster decay at long times even at the M diffusion limit whereas a corresponding effort at long times results in slower decay at short and intermediate time. The variation of λ, γ and the product $\lambda\gamma$ at 80°C, 50°C and 0°C is similar to that for carbonyl sulphide.

4. Discussion and conclusions

We have generalized the interpolation model to the case of symmetric top molecules and compared with several experimental data. We observe that the data for systems

where either the density is low, like gases or where the intermolecular torque is low agrees very well with the interpolation model. In these cases, the intermolecular collisions are less frequent and the underlying assumption in the model that the molecule rotates freely between successive collisions is justified. For example, CD_3H is although a symmetric top molecule, its shape is quite close to spherical and in mixtures of inert liquid, the intermolecular torque, which is related to the anisotropy of the potential is quite small. The situation is not encouraging for other liquids, particularly at low temperature. Here, the agreement at long and intermediate times is quite good, but at short times, the calculated correlation function is always greater than the experiment. The decay of the correlation function has been found to be determined by the product $\lambda \gamma$ rather than λ or γ alone. As has been pointed out by Dattagupta and Sood (1979) the product $\lambda \gamma$ corresponds to an effective rate of randomization of the angular momentum magnitude, and thus determines the rate of decay of the correlation function at long times. This has been observed for OCS, CH_3I in C_6H_{12} and propyne and agrees with the meaning of the interpolation parameter γ. Thus a fractional randomization of the angular momentum in a collision, rather than complete or no randomization is more appropriate for describing molecular reorientation within the framework of EDM.

The discrepancy at short times can be understood from the power series expansion of correlation function $(C_l(t))$ as $t \to 0$. Lindenberg and Cukier (1975) have shown that, in a collision interrupted free rotation model the $C_l(t)$ has a positive contribution from the t^3 term which is proportional to the parameter λ. The experimental $C_l(t)$, obtained from a symmetric band profile does not have t^3 contribution. This results in theoretical $C_l(t)$ being larger than the experiment at short time. We have seen that at low temperature and for hindered systems (where the intermolecular torque is large) the value of λ is large and hence there is larger deviation at short times in such cases.

Thus in conclusion the interpolation model works very well for situations where the density is low and the intermolecular torque is small. However, in dense systems like liquids with large torque, the success of the model is limited, in the sense that the intermediate and long time behaviour of $C_l(t)$ is explained much better than either the M or J diffusion limits, whereas at short times there is considerable discrepancy. On the other hand for liquids at low temperature, the reorientation of molecules cannot be described within the framework of this model.

Appendix

Here we give the expressions used to calculate the infrared and Raman line shapes and hence the correlation functions $C_1(t)$ and $C_2(t)$. The line shapes are given by

$$I_l(\omega) = \frac{1}{\pi} \left[\frac{A_1(1 - \gamma \lambda A_1) - \gamma \lambda A_2^2}{(1 - \gamma \lambda A_1)^2 + \gamma^2 \lambda^2 A_2^2} \right],$$

where

$$A_1 = \int dJ_0 \, W(J_0) \, G^{(1)},$$

$$A_2 = \int dJ_0 \, W(J_0) \, G^{(2)}.$$

The $G^{(1)}$ and $G^{(2)}$ are given by

$$G^{(1)} = [\{1 - \lambda(1-\gamma)G_1\}G_1 - G_2^2\lambda(1-\gamma)]/Z,$$

$$G^{(2)} = [G_2\{1 - \lambda(1-\gamma)G_1\} + G_1G_2\lambda(1-\gamma)]/Z,$$

where

$$Z = \{1 - \lambda(1-\gamma)G_1\}^2 + \lambda^2(1-\gamma)^2 G_2^2.$$

The expressions for G_1 and G_2 are different for infrared and Raman cases and are given below.

(a) *Infrared*

$$G_1 = \frac{J\lambda(\xi/2\pi)^{1/2}}{\mathrm{erf}[J\xi/2)^{1/2}]}\left[\frac{2I_0}{\lambda^2+\omega^2}+I_1\left\{\frac{1}{\lambda^2+(\omega-J)^2}+\frac{1}{\lambda^2+(\omega+J)^2}\right\}\right],$$

$$G_2 = -\frac{J(\xi/2\pi)^{1/2}}{\mathrm{erf}[J(\xi/2)^{1/2}]}\left[\frac{2I_0\omega}{\lambda^2+\omega^2}+I_1\left\{\frac{\omega-J}{\lambda^2+(\omega-J)^2}+\frac{\omega+J}{\lambda^2+(\omega+J)^2}\right\}\right],$$

where

$$I_0 = \int_0^1 x^2\exp(-\xi J^2 x^2/2)\,\mathrm{d}x,$$

$$I_1 = \int_0^1 (1-x^2)\exp(-\xi J^2 x^2/2)\,\mathrm{d}x,$$

(b) *Raman*

$$G_1 = \frac{\lambda J(\xi/2\pi)^{1/2}}{\mathrm{erf}[J(\xi/2)^{1/2}]}\left[\frac{1}{2}\frac{I_0}{\lambda^2+\omega^2}+3I_1\left\{\frac{1}{\lambda^2+(\omega-J)^2}+\frac{1}{\lambda^2+(\omega+J)^2}\right\}\right.$$

$$\left.+\frac{3}{4}I_2\left\{\frac{1}{\lambda^2+(\omega-2J)^2}+\frac{1}{\lambda^2+(\omega+2J)^2}\right\}\right],$$

$$G_2 = -\frac{J(\xi/2\pi)^{1/2}}{\mathrm{erf}[J(\xi/2)^{1/2}]}\left[\frac{1}{2}\frac{I_0\omega}{\lambda^2+\omega^2}+3I_1\left\{\frac{\omega-J}{\lambda^2+(\omega-J)^2}+\frac{\omega+J}{\lambda^2+(\omega+J)^2}\right\}\right.$$

$$\left.+\frac{3}{4}I_2\left\{\frac{\omega-2J}{\lambda^2+(\omega-2J)^2}+\frac{\omega+2J}{\lambda^2+(\omega+2J)^2}\right\}\right],$$

where

$$I_0 = \int_0^1 \mathrm{d}x(3x^2-1)^2\exp(-\xi J^2 x^2/2),$$

$$I_1 = \int_0^1 \mathrm{d}x\, x^2(1-x^2)\exp(-\xi J^2 x^2/2),$$

$$I_2 = \int_0^1 \mathrm{d}x(1-x^2)^2\exp(-\xi J^2 x^2/2).$$

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