Rotational Diffusion Model with a Variable Collision Distribution

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Starting with an m-diffusion model a matrix description is given of the rotational motion of a dipole molecule undergoing frequent collisions. This treatment gives rise to an analytical expression for the dipole correlation function and for the angular momentum correlation function in which a limited number of parameters from the model appear. It is argued that the collision distribution which determines the rotational diffusion process need not necessarily be a Poisson distribution. In liquids with strong interactions the distribution is governed by the frequency distribution of the medium. This leads to the inclusion of a librational motion in the rotational diffusion model. A comparison of simulations with different collision distributions and experimental data is given.

INTRODUCTION

Information about molecular motions in liquids and dense gases is contained in dipolar absorption spectra, which extend from the far infrared down into the microwave region. The absorption spectra are conveniently expressed as time correlation functions, which in this case reflect the molecular dynamics in the reorientation process of the dipole moment vector.

In order to obtain quantitative information about molecular motions in dense media several models have been developed.[1-5] All these models give the possibility of simulation of time correlation functions via computational techniques. Assuming that the dynamical variables obey a classical equation of motion in which the friction coefficient is frequency dependent, one can calculate ensemble averaged correlation functions. Agreement of the thus obtained correlation functions with the experimental ones is used as a justification of the particular model. The approach of simulation and subsequent comparison with experiment is prompted by the fact that the molecular motions extend continuously over such a wide frequency range. The complexity of molecular motion and the wide frequency range in which they occur, makes it virtually impossible to determine the frequency dependence of the frictional forces directly from experiment.

If we confine ourselves to dielectric relaxation at low frequencies only, we can describe the molecular motions by a simple Debye diffusion model.[6] Then the rate of randomization of the direction of the dipole moment vector is determined by a single diffusion coefficient, which is directly related to the experiment. Inclusion of higher frequency modes of motion necessitates the introduction of frequency dependent friction coefficients. The inadequacy of the Debye model for the description of higher frequency modes has been recognized before, since Gordon[1] showed how to include the possibility of free rotation over large angles in the description of the diffusion process. Two limiting cases can be recognized in the model that he suggested. At every interruption of the rotational motion by a collision both the direction and magnitude of the vector of angular momentum are randomized in the j-diffusion limit. In the m-diffusion limit just the direction of the vector of angular momentum is reoriented upon collision. The extent to which both effects come into play depend on the assumed interactions, the collision distribution and the molecular parameters of the system under consideration. In the earlier versions of this theory there are many implicit assumptions and approximations. Recently McClung[3] has given some thorough considerations on the limitations of the theory and made some progress to a wider applicability.

When experimental data on a greater variety of liquid systems[7-12] came to our disposition we felt the need for a more flexible presentation of the theory and in particular for a better way to compare theoretical assumptions with the experimental results. In this paper we give the result of our effort to modify the rotation diffusion model in such a way that fewer assumptions and restrictions are made implicity and at an early stage. The possibility then remains to adjust the model parameters to fit the simulations with the experiments in a more conspicuous fashion. We shall also derive an analytical expression for the correlation functions. Both assets are important for a wider applicability of the rotation diffusion model, because they both tend to diminish the needed computer times and make possible a qualitative comparison between calculations and experimental results.

Starting with an m-diffusion model we give a matrix description of the rotational motion. This allows us to derive a reorientation matrix for the motion of one single molecule. This matrix contains explicitly the probability that the molecule has undergone an n-collision process. Taking the ensemble average we arrive at an analytical expression for the correlation function for the dipole moment and the angular momentum supposing the collisions are Poisson distributed.

FORMALISM

We start with a consideration of the effect of molecular collisions on the orientation of the dipole moment vector and the vector of angular momentum of a linear dipole molecule.

At the time $t=t_0$ the x axis of the Cartesian frame coincides with the dipole moment vector and the z axis with the angular momentum vector. The rotation of

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the dipole moment vector can now be described by a rotation of the coordinate system in the xz plane with respect to the original position over an angle θ. Likewise the reorientation of the angular momentum vector which is the effect of one collision or interaction corresponds to a rotation of the coordinate system in the $y'z$ plane, over an angle γ (see Fig. 1). We consider an n-collision process in which the molecule rotates freely over angles $\theta = \omega\tau$ in which ω is the rotation frequency and τ the time between collisions. The free rotation steps are terminated by collisions of short duration which reorient the vector of angular momentum over an angle γ. These two events are in the following represented by a matrix $\mathbf{R}$ for the rotation and a matrix $\mathbf{O}$ for the orientation. The total effect of an n-collision process on the frame of axes can now be described by a matrix $\mathbf{M}_n(t)$ which is a product of n reorientation matrices and $n+1$ rotation matrices. Considering one reorientation denoted by $\mathbf{O}'$ following one rotation given by $\mathbf{R}$ we can write $\mathbf{O}' = \mathbf{R}^{-1}\mathbf{O}\mathbf{R}$ and hence the combined effect $\mathbf{O}'\mathbf{R} = \mathbf{R}\mathbf{O}\mathbf{R}^{-1}\mathbf{R} = \mathbf{R}\mathbf{O}$. For a succession of n collisions we write

$$\mathbf{M}_n(t) = \mathbf{R}(t_1 - t_0)\mathbf{O}(t_1)\mathbf{R}(t_2 - t_1)\mathbf{O}(t_2)\cdots$$
$$\times \mathbf{O}(t_n)\mathbf{R}(t - t_n). \quad (1)$$

To obtain the contribution of this n-collison matrix to the ensemble averaged matrix at time t it should be multiplied by the probability that this particular collision process occurs. The probability that collisions occur at times between t_1 and $t_1 + dt_1$, t_2, and $t_2 + dt_2$ etc., is denoted by $P_n(t_1, t_2, \cdots t_n; t)dt_1 dt_2\cdots dt_n$. This probability is to be multiplied by $P(\gamma_1, \gamma_2, \cdots \gamma_n)d\gamma_1 d\gamma_2\cdots d\gamma_n$, the probability that the reorientation angle resulting from a collision lies between γ_1 and $\gamma_1 + d\gamma_1$, $\gamma_2 + d\gamma_2$ etc. We now make two assumptions. First of all we assume the probability of any collision to depend only on the time of the preceding collision. Secondly the reorientation effect is assumed to be uncorrelated for successive collisions, moreover $P(\gamma) = P(-\gamma)$. The reorientation angle γ depends only on the frequency of the rotator.

$$P_n(t_1, t_2, \cdots t_n)dt_1 dt_2\cdots dt_n = Q'(t_1 - t_0)P_1(t_2 - t_1)\cdots$$
$$\times P_1(t_n - t_{n-1})Q''(t - t_n)dt_1 dt_2\cdots dt_n. \quad (2)$$

Here $P_1(t_2 - t_1)dt_2$ is the probability that a collision occurs between t_2 and $t_2 + dt_2$ after a preceeding collision at t_1 etc. It is to be noted that the probability for the first collision $Q'(t_1 - t_0)dt_1$ differs from the probabilities for the other collisions inasmuch as the molecule does not necessarily collide at $t = t_0$. It is the probability for any molecule that after time $t = t_0$, at which time the observation started, it will collide for the first time between t_1 and $t_1 + dt_1$. This probability is

$$Q'(t_1 - t_0)dt_1 = \frac{dt_1}{\tau}\left(1 - \int_0^{t_1} P(t_1 - t')dt'\right), \quad (3)$$

where τ is the average time interval between collisions. $Q''(t - t_n)dt$ is the probability that no collision will take place after the time of the nth collision. The molecule then rotates freely. This probability is

$$Q''(t - t_n) = \left(1 - \int_0^t P(t)dt\right). \quad (4)$$

One also has to include the probability that no collision takes place at all. This probability is denoted by $Q(t)$, and can be obtained by integration over the collision probability for all times between t_0 and t. The ensemble averaged collision matrix for one single rotation frequency ω_j can now be expressed as follows:

$$\mathbf{M}_j(t) = Q(t)\mathbf{R}(t) + \sum_{n=1}^{\infty}\int\cdots\int Q'(t_1 - t_0)\mathbf{R}(t - t_0)\mathbf{O}(t_1)$$
$$\times P(t_2 - t_1)\cdots\mathbf{O}(t_n)\mathbf{R}(t - t_n)Q''(t - t_n)dt_1\cdots dt_n. \quad (5)$$

In order to obtain a closed analytic expression for the dipolar correlation function $C(t) = \langle M(0)M(t)\rangle$ and for the directional correlation function $D(t) = \langle J(0)J(t)\rangle$[13] we solve Eq. (5) by Laplace transformation. Making use of the definitions

$$\mathcal{L}\{f(t)\cos\omega t\} = \tfrac{1}{2}(f(s - i\omega) + f(s + i\omega)) = f_+,$$

$$\mathcal{L}\{f(t)\sin\omega t\} = (1/2i)(f(s - i\omega) - f(s + i\omega)) = f_-,$$

we can write for the Laplace transformed collision matrix for a single rotator with frequency ω_j as follows:

$$M_j(s) = \begin{pmatrix} Q_+ & -Q_- & 0 \\ Q_- & Q_+ & 0 \\ 0 & 0 & Q(s) \end{pmatrix}$$
$$+ \sum_{n=0}^{\infty}\begin{pmatrix} P_+ & -P_- & 0 \\ P_- & P_+ & 0 \\ 0 & 0 & P(s) \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\gamma_j & 0 \\ 0 & 0 & \cos\gamma_j \end{pmatrix}$$
$$\times \left[\begin{pmatrix} P_+ & -P_- & 0 \\ P_- & P_+ & 0 \\ 0 & 0 & P(s) \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\gamma_j & 0 \\ 0 & 0 & \cos\gamma_j \end{pmatrix}\right]^n$$
$$\times \begin{pmatrix} Q_+'' & -Q_-'' & 0 \\ Q_- & Q_+ & 0 \\ 0 & 0 & Q(s) \end{pmatrix}, \quad (6)$$

where $\sin\gamma_j$ is put equal to zero because of the assumption that the sense of reorientation of successive collisions is uncorrelated and evenly likely to be right handed or left handed. Because of the choice of the coordinate system with respect to the direction of the

dipole and its sense of rotation, the (1, 1) element of this matrix is just the Laplace transform of $\langle M(0)M(t)\rangle_j$ and the (3, 3) element the Laplace transform of $D_j(t)$. As before the subscript j denotes that the correlation functions reflect the relaxation process for just one single rotator with frequency ω_j.

Straightforward calculation gives

$$C(s) = s/(s^2+\omega^2)$$

$$+\omega^2(1-\alpha)[1-p(s+i\omega)][1-p(s-i\omega)]/(\tau(s^2+\omega^2)^2\{1-\tfrac{1}{2}(1+\alpha)[p(s+i\omega)+p(s-i\omega)]\}+\alpha p(s+i\omega)p(s-i\omega)) \tag{7}$$

and

$$D_j(s) = \{\tau s[1-\alpha p(s)]-(1-\alpha)[1-p(s)]\}/\{\tau s^2[1-\alpha p(s)]\}, \tag{8}$$

where

$$p(s) = \int_0^\infty P(t)\exp(-st)dt \quad \text{and} \quad \alpha = \cos\gamma_j.$$

By integration of $C_j(s)$ and $D_j(s)$ over the thermal distribution of rotation frequencies one obtains the spectral distributions $A(\omega)$. Successively Fourier transformation yields the ensemble averaged correlation functions $\langle M(0)M(t)\rangle$ and $\langle J(0)J(t)\rangle$.

COLLISION DISTRIBUTIONS

Since in the expressions (7) and (8), $P(t)$ appears, it allows us to use a collision distribution at choice in the calculation of the correlation function. This is one of the main advantages of the above described formalism. For a dilute gas in which all collisions take place independently of each other, the collision probabilities $P(t)$ can be taken to be Poisson distributed. For liquids specific characteristics of the dynamics can give rise to deviations of the Poisson distribution. By adjustment of the collision distribution one can now describe these systems without modification of the model itself. Then the physical interpretation of certain colli-

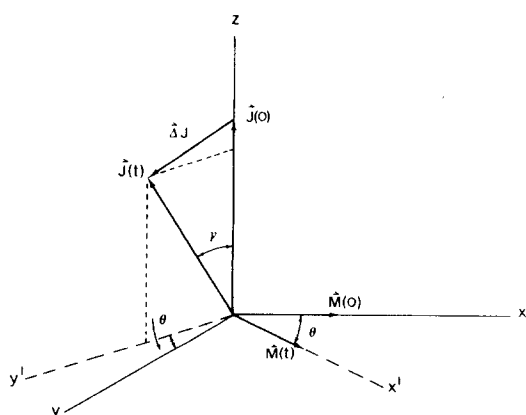
FIG. 1. Rotation of the molecular frame in the xy plane over an angle $\theta = \omega t$ is followed by a reorientation of J over an angle γ due to a collision at time t. If m diffusion is assumed, $|J(0)| = |J(t)|$ for linear molecules. J is perpendicular to the dipole moment vector.

sion distributions can be given afterwards within the limits set by the m-diffusion model.

To begin with we will describe rotational diffusion in a system in which the collisions exerted on the rotating dipole are supposed to be Poisson distributed. The collision probability $P(t)$ then becomes:

$$P(t) = \tau_p^{-1}\exp(-t/\tau_p),$$

where τ_p is the Poisson relaxation time. This relaxation time gives an average time between collisions.

For a dipole having a single rotation frequency ω_j the expressions (7) and (8) now become:

$$(C_j(s) = (s+R_j)/(s^2+2R_j+\omega_j^2) \tag{9}$$

for the Laplace transformed correlation function $C_j(t)$ and

$$D_j(s) = 1/(s+2R_j) \tag{10}$$

for the Laplace transformed orientational correlation function $D_j(t)$, where the parameter $R_j = (1-\cos\gamma_j)/2\tau_p$ and $s = -i\omega$. τ_p is the Poisson relaxation time. Laplace transformation of $C_j(s)$ and $D_j(s)$ leads straightforwardly to analytical expressions for the correlations functions $C_j(t)$ and $D_j(t)$:

$$C_j(t) = \exp\{-R_jt\}[\cos\omega_j't+(R_j/\omega_j')\sin\omega_j't], \tag{11}$$

where $\omega_j'^2 = \omega_j^2-R_j^2$ and $\omega_j'^2 > 0$.

If $\omega_j'^2 < 0$ the expression becomes

$$C_j(t) = \exp\{-R_jt\}[\cosh\omega_j't-(R_j/\omega_j')\sinh\omega_j't]. \tag{12}$$

The analytical expression for $D_j(t)$ becomes:

$$D_j(t) = \exp\{-2R_jt\}. \tag{13}$$

For an ensemble of rotators with a set of frequencies $\{\omega_j\}$ the correlation functions $C_j(s)$ have to be summed:

$$C(s) = \sum_j A(\omega_j)C_j(s).$$

The time correlation functions are then summations over terms as in Formulas (11) and (13) in which each term is characterized by the variables ω_j' and R_j. In
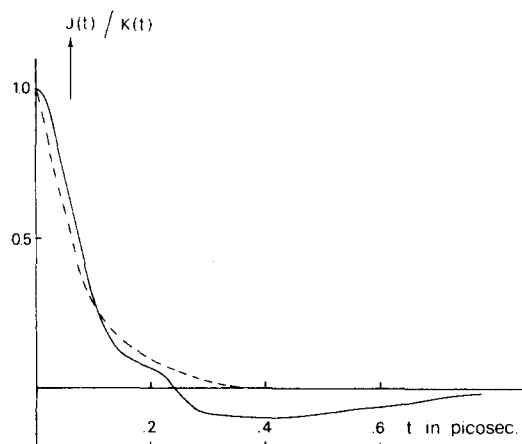
FIG. 2. If collisions are Poisson distributed, $D_j(t) = \omega_j^2 K_j(t)$ for a single rotation frequency. This relation does not hold if both functions are calculated for a thermal distribution of classical rotators. Shown in the figure are the normalized functions $K(t)$ (solid line) and $D(t)$ (dotted line) drawn to the same scale as calculated for CH$_3$CN ($I = 91.3 \times 10^{-40}$ g·cm^2, $T = 314°$K) with a Poisson collision distribution; $\tau_p = 1.0 \times 10^{-13}$ sec, the maximum amount of angular momentum ΔJ transferred in one collision is 6.2×10^{-26} g·cm^2 sec^{-1}.

the actual calculations of the correlation functions we sum over an ensemble of classical rotators. In that case the frequency dependence of the friction coefficient R_j is derived by considering a classical rotator under the influence of an applied torque. Using the symbols defined above the frequency dependence of R_j is given by the relation

$$R_j = (1 - \cos\gamma_j)/2\tau_p = (1/4\tau_p)(\Delta J/J)^2. \quad (14)$$

The dipole correlation function $C_j(t)$ shows the correct behavior at $t = 0$. The first and second derivatives with respect to the time at $t = 0$ are

$$(\delta C_j(t)/\delta t)_{t=0} = 0, \quad (\delta^2 C_j(t)/\delta t^2)_{t=0} = -\omega_j^2. \quad (15a)$$

The derivatives of the directional correlation function $D_j(t)$ are not defined at $t = 0$. However, if t approaches zero from the positive time direction

$$\lim_{t \to 0+} (d/dt) D_j(t) = -(1 - \cos\gamma_j)/\tau_p. \quad (15b)$$

The relations (15a) and (15b) hold for any collision distribution.

At this point we want to make the remark that starting from the obtained analytical expression it is easy to show that a direct relation exists between $D_j(t)$ and the memory function of the dipole correlation function $K_j(t)$ which is defined by the equation

$$\frac{\delta}{\delta t} C(t) = -\int_0^t dt' K(t - t') C(t'). \quad (16)$$

From formulas (15a) and (16) one finds that

$$K_j(t) = \langle \omega_j^2 \rangle D_j(t). \quad (17)$$

Berne and Harpe[14] have already indicated that in general this same relationship holds for an ensemble of rotators, though under certain conditions. Under the condition that large torques are exerted on the dipole in short during collisions, the first few coefficients in the time development of both functions are approximately equal. Hence for short times this relation holds. Moreover, Berne and Harpe found from their molecular dynamics calculations of the correlation functions of liquid CO that even at long times both functions showed the same behaviour.

In the model which we are discussing here $K_j(t)$ and $D_j(t)$ are identical for a Poisson collision distribution. This is not true for an ensemble of rotators and an arbitrary collision distribution, then $K(t)$ and $D(t)$ will be different. However, in accordance with the observation made by Berne and Harp, we find that for large torques the resemblance between $K(t)$ and $D(t)$ is maintained.

A difficulty is that in the m-diffusion model, the fourth moment of the power spectrum of $C(t)$ is not defined. Hence no finite value of the mean squared torque can be calculated. This is a consequence of the assumption that a finite amount of angular momentum ΔJ is transferred in infinitely short collisions. We can, however, obtain a rough estimate for the mean squared torque if we make a guess about the actual collision time. As ΔJ is a parameter in the model the mean squared torque $\langle N^2 \rangle$ can be calculated according to the relation

$$(d(\Delta J)/dt) = \langle N^2 \rangle. \quad (18)$$

For large values of ΔJ we have simulated $K(t)$ and $D(t)$. A typical example is shown in Fig. 2 for the normalized correlation function. The time in which they decay to zero is practically the same. Only for larger times $K(t)$ deviates and goes negative.

Another important feature of the m-diffusion model in which the collisions are Poisson distributed is the limiting case of R large in comparison with ω_j, the rotation frequency. It can easily be deduced from Formula (12) that in the limit of large R the analytical expression for the correlation function reduces to

$$C_j(t) = \exp(-\omega_j^2/2R_j)t.$$

In this limit the rotational motion as simulated by the m-diffusion model is essentially a Debye type of rotational diffusion. Since for low frequencies R_j is proportional to ω^2 the relaxation time $\tau_c = 2R_j/\omega_j^2$ is even a constant, independent of ω. The correlation function of the low frequency part of the spectrum then has the same form as predicted by the Debye model. Since the limit is only valid for low frequencies the dipole rotates freely over small angles interrupted by collisions, which reorient the angular momentum vector over quite large angles. In this limit the relaxation

time for $D(t)$ is $\tau_J = (2R_j)^{-1}$. Consequently $\tau_J\tau_c = (\omega_j^2)^{-1}$, known as Hubbard's rule.[15]

Apart from the possibility of inserting a conventional Poisson distribution the formalism gives also the possibility to work with a different distribution of collisions. The model is therefore also suited for the description of a dense medium, in which a strong correlation exists between successive collisions. This strong correlation may arise from collective motions of strongly interacting molecules in the medium. If in a liquid, one thinks the dipole molecule enclosed by a cage of solvent molecules one should reconsider the choice of the distribution of collisions. A stationary cage will give rise to a very specific distribution depending on the shape of the cage. It has been suggested that large random fluctuations of the cage walls results again in a Poisson collision process.[16] However, it should be realized that by an effective coupling between the motion of the dipole and a restricted number of phonon modes of the medium the dipole molecules experience a less random motion of the cage wall. It is for instance to be expected, that the rotational diffusion process will be influenced strongly by the longitudinal modes of short wave vector. Especially in media consisting of organic molecules having high polarizabilities and low lying phonon modes coupling between these modes and the rotation will certainly occur. This effect has already been discussed by Morawitz and Eisenthal.[17] In their treatment of the near infrared vibration–rotation bands it results into a value of the second moment deviating from the average classical rotation
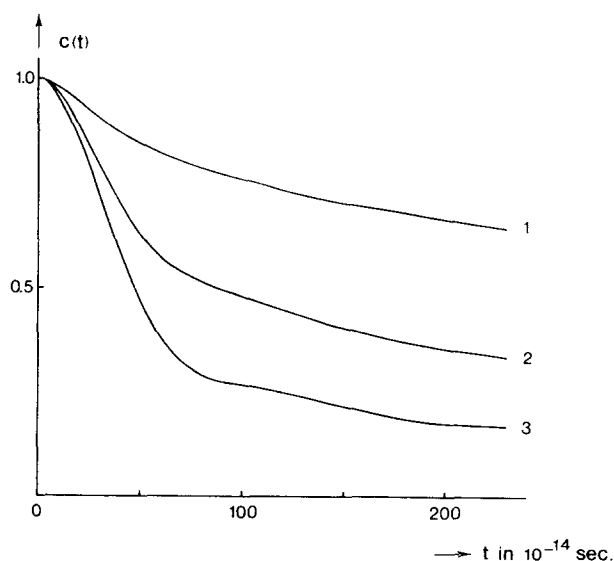

Fig. 4. Simulated correlation functions for CH_3CN ($I = 91.30\times10^{-40}$ g·cm², $T=314°K$) with a Poisson collision distribution; $\tau_p = 1.0\times10^{-13}$ sec. The simulations differ only in the amount of angular momentum transferred in one collision: (1) $\Delta J = 9.1\times10^{-26}$ g·cm² sec⁻¹, (2) $\Delta J = 2.4\times10^{-26}$ g·cm² sec⁻¹, (3) $\Delta J = 0.85\times10^{-26}$ g·cm² sec⁻¹.

energy. In our model these effects can be translated into deviations in the Poisson distribution of collisions.

It is elucidating to consider a dipole molecule on a site in a crystal lattice at very low temperatures. Then, the collisions suffered by the dipole are governed by the phonon density of states multiplied by the appropriate weight factors which are determined by the specific interactions and the extent to which the dipole participates in the different phonon modes. This results in a collision distribution, which shows a limited number of peaks and is zero between $t=0$ and the time $t=1/\omega_{max}$, where ω_{max} is the highest frequency in the corrected phonon density of states. For larger values of t, it will roughly follow the phonon density of states. With increasing temperature a broadening of the collision distribution towards shorter times will arise as a consequence of the higher population of phonon states. Evidently this population depends on the value of the frequency with respect to the temperature. In a liquid the phonon distribution will in general be very much the same as the distribution in the corresponding solid apart from some minor differences in the low frequency part of the acoustical branches. The collision distribution in the liquid therefore is determined in exactly the same way by the frequency distribution and the temperature. At a given temperature liquids with low molecular interactions and hence low frequencies will have higher phonon states densely populated. This situation leads to a collision distribution resembling a Poisson distribution. Liquids with high molecular interactions and comparatively high frequencies will

Fig. 3. Simulated correlation functions for CH_3CN ($I = 91.3\times10^{-40}$ g·cm², $T=314°K$) with a Poisson collision distribution; the amount of angular momentum transferred in one collision is 6.2×10^{-26} g·cm² sec⁻¹. The simulations differ in the average time between collisions: (1) $\tau_p = 1.0\times10^{-13}$ sec, (2) $\tau_p = 2.8\times10^{-13}$ sec, (3) $\tau_p = 5.6\times10^{-13}$ sec.
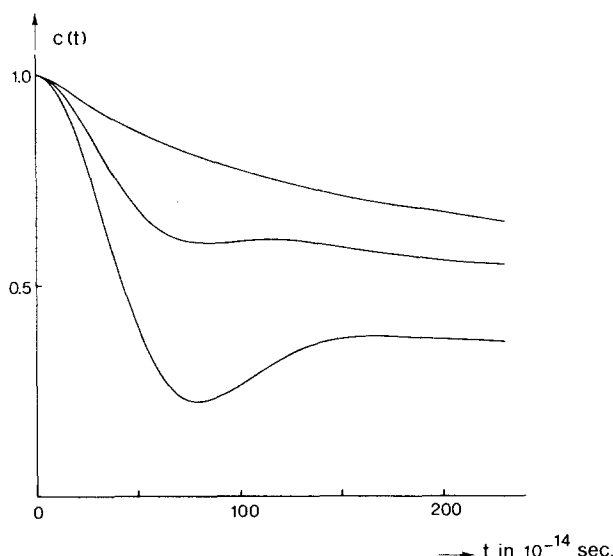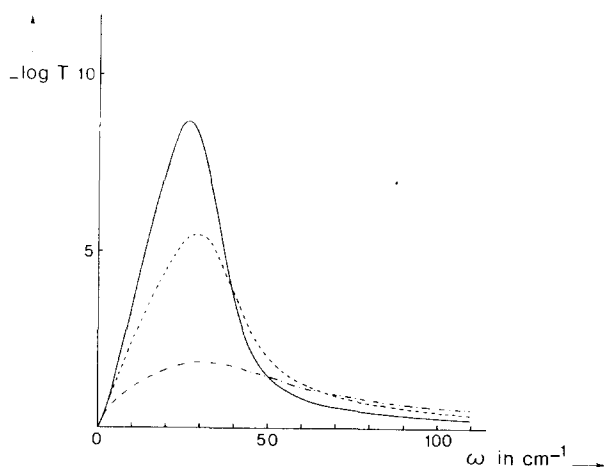
FIG. 5. Simulated absorption spectra for CH_3CN ($I = 91.3 \times 10^{-40}$ g·cm², $T = 314°K$) with a Poisson collision distribution. The amount of angular momentum transferred in one collision is 6.2×10^{-26} g·cm² sec⁻¹ for all simulations. The Poisson relaxation times are $\tau_p = 5.6 \times 10^{-13}$ sec (—), $\tau_p = 2.8 \times 10^{-13}$ sec (- - -), and $\tau_p = 1.0 \times 10^{-13}$ sec (-·-·).

have on the contrary a collision distribution that is mainly determined by the phonon density of states. In this case the collision distribution might exhibit a peak at a time later than zero.

An interesting feature emerging from the above considerations is the introduction of a librational motion which follows quite naturally from the model and need not be introduced as a separate possibility.[18,4] For those rotators, which have a frequency such that the average reorientation angle γ equals $\omega\tau$ a peak in the collision distribution causes the dipole to have an increased probability to turn the sense of rotation a number of times in succession. This event clearly manifests a librational motion.

RESULTS

In order to test the above described formalism and to examine the influence of the parameters and the shape of the collision distribution we compare the calculations with experimental data.

First of all we have calculated the absorption spectra and correlation functions for systems in which the collisions are supposed to be Poisson distributed. From Formulas (11) and (14) it can be seen that given the moment of inertia of the dipole molecule, the shape of the correlation function will be determined by two parameters, ΔJ, the reorientation vector, and by the Poisson relaxation time τ_p. The influence of these two parameters is shown in Figs. 3 and 4. The Poisson relaxation time determines mainly the rate at which the correlation function goes over in an exponential function, whereas the reorientation vector determines the more characteristics features such as the steepness of the descent and the appearance of periodic maxima

and minima. This last effect is caused by the frequency dependence of the reorientation angle. The simulations are carried out for a dipole having a moment of inertia of 90×10^{-40} g·cm² which equals the moment of inertia of CH_3CN.

The relaxation time τ_p is a parameter characteristic for the medium, while the reorientation vector ΔJ describes the collision process and the torques acting on the dipole. Arguments for the separation of properties of the medium from interactions of the dipole with the medium can be found in experimental observations that have been made on solutions of HCl in some liquids. The far-infrared absorption spectrum of HCl in liquid krypton does show considerable rotational fine structure, whereas in the spectrum of HCl in liquid argon the rotational fine structure is barely observable.[10] This observation is in contradiction with the expectation based on a consideration of the interactions. It has therefore been concluded that characteristic motions in the medium must come into play. Similar considerations hold for systems like HCl in SF_6[11] and CCl_4.[12]

It is clear that in the proposed formalism the influence of such characteristic motions of the medium on the motion of the dipole should be reflected in deviations from the Poisson collisions distribution. An even stronger motive to consider nonrandom collisions on the dipole is that simulations with a Poisson distribution show that the frequency of maximum absorption is solely determined by the temperature and the moment of inertia and is practically independent of the value of the parameters ΔJ and τ_p. This can be seen in Fig. 5. However, a great many cases have been reported in the literature where the frequency of maximum absorption is shifted towards much higher values than one should expect from the temperature and the moment of inertia. This has been noted for dilute solutions of dipole molecules as well as for neat liquids with dipolar or ionic species.[8,9,18] An example is aceto-
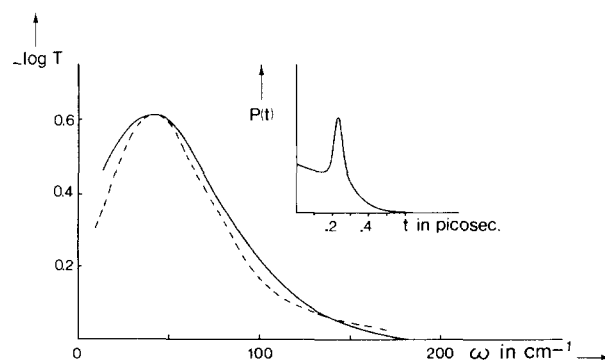

FIG. 6. Simulated (- - -) and experimental (—) spectrum of a dilute solution of CH_3CN at 314°K. The collision distribution used in the simulation is shown in the insert. The amount of angular momentum transferred in one collision is 7.5×10^{-26} g·cm² sec⁻¹.

nitrile. If one compares the simulated absorption spectra in Fig. 5 with the experimental absorption spectrum of acetonitrile in Fig. 6, the maximum of absorption in the experimental spectrum is situated at 60 cm^{-1}, whereas the spectra simulated with a Poisson distribution have a maximum at 25 cm^{-1}.

To examine the influence of a collision distribution which reflects the characteristic motions of the medium we tried a collision distribution as shown in the insert of Fig. 6. This distribution should be considered as arising from the effect of a mean phonon frequency together with a more gaslike Poisson distribution. The resulting simulated absorption spectrum and the experimentally determined spectrum are also shown in this figure. Apart from minor differences in the high frequency wing both spectra coincide within experimental error.

From the relaxation time of the underlying Poisson distribution and the maximum at 22.8×10^{-14} sec one can estimate an average time between collisions τ_{BC} of about 25×10^{-14} sec. This value is orders of magnitude higher than the value obtained by Litovitz et al.,[5] but then a jump diffusion model is not comparable with an m-diffusion model. In the first model it is the dipole moment vector, while in the last one it is essentially the angular momentum vector which is considered as the primary random variable.

The time of the peak in the collision distribution corresponds to a frequency of approximately 200 cm^{-1}. The high value of this frequency seems to indicate that internal vibrations couple to a considerable extent with the rotational motions. In view of the number of parameters involved in the characterization of the shape of the collision distribution one should not draw any quantitative conclusions about the details of this vibration–rotation interaction. Nevertheless, the influence of high frequency modes on the rotational motion of CH$_3$CN is unmistakeable. Moreover, the effect of the temperature on the maximum of absorption[8] can now be attributed to the temperature dependence of the collective modes of the medium. The need to imply the properties of the medium to account for this effect has been recognized before.[18]

As a last point, from the amount of angular momentum ΔJ transferred during a collision we can estimate a value of the mean squared torque exerted on a CH$_3$CN molecule by the n-heptane molecules. For a gas the mean squared torque is $(\Delta J/\tau_c)^2$, where τ_c is the time of a collision. For a system like CH$_3$CN in n-heptane some CH$_3$CN molecules can execute a librational motion. Then the torque acts on the dipole during the librational period and the amount of angular momentum transferred in two successive hard collisions

is $2J$. Hence we may write for the mean squared torque

$$\langle N^2 \rangle \simeq (\Delta J)^2/(\tau_{BC})^2,$$

where τ_{BC} is the time between collisions. This expression sets a lower limit to the value of the torque. For the simulation shown in Fig. 6 we then calculate a value for the mean squared torque of approximately 12×10^{-26} (dyn cm)^2. As far as we know no experimental values are known for CH$_3$CN. However, for liquid CO Gordon[19] calculated a value of 21×10^{-28} (dyn cm)^2 for the mean squared torque at 77.5°K. It is not surprising that the mean squared torque seems to be at least a factor 100 larger as it has been pointed out[14] that this quantity is very strongly dependent on the noncentral parts of the intermolecular potential.

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