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Collapse of the rotational structure of Raman-scattering spectra in dense media

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A description of the shapes of the Raman-scattering spectra of linear molecules in inert solvents is obtained in mathematically closed form by employing the Keilson–Storer kernel in the integro-differential equations of the theory of pressure broadening. In the case of strong collisions an analytic solution is obtained that describes the transformation of the contour with increasing density. It is shown that in the high-density limit the rotational structure of the spectrum undergoes a collapse during which the intensity is shifted from the sidebands of the *O–Q–S* triplet to the central band, whose width decreases with further growth of density. The narrowing of this band is shown to be a spectral manifestation of the Hubbard relation $\tau_\Theta \tau_J = I/6kT$ (τ_J and τ_Θ are the rotational and orientational relaxation times), a relation reliably confirmed by magnetic resonance experiments.

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1. INTRODUCTION

Raman-scattering (RS) spectra in rarefied gases and liquids differ greatly in shape and in extent. The reserved rotational structure, or at least the less pronounced triplet of *O–Q–S* branches, which is characteristic of gases of moderate density, is transformed in liquids into a single diffuse line, which is much narrower than the width of the rotational band in the gas at comparable temperature.[1–4] Consequently, with increasing density, the structure is not simply smeared out, but is also averaged (collapsed); this gives rise to an over-all narrowing of the spectrum, similar to that observed in NMR and ESR spectra of dense gases and liquids.[5–7] How this takes place, however, has not been investigated so far either theoretically or experimentally. It is only clear that the rotational angular momentum **J** (in units of $\hbar$) is preserved for a long time in a gas, so that all the frequencies $\omega \sim 2J/I \sim 2\bar{\omega} \sim (kT/I)^{1/2}$, are represented in the spectrum, whereas in the liquid the axis of the molecule does not rotate, but executes diffuse motion,[8] and the slower this motion the narrower the spectrum (I is the moment of inertia of the molecule).

Yet it is very important to understand what it is that converts free rotation into Brownian rotation. Do the cohesion forces fix the molecule axis and permit it only rarely to become reoriented,[9–11] or does the reason lie simply in the collisions, which become more frequent with increasing density, and the motion between which is not as free as before. If the rotational diffusion is a consequence of random wandering of the molecule axis, which is forced to overcome energy barriers during each rotation,[12,13] then the liquid is in this respect perfectly similar to a solid medium, but if its axis is fixed exclusively as a result of frequent changes of the direction of rotation, then the liquid and the gas can and must be described in the same manner, and the transformation of the spectra can be traced in continuous fashion. This, in particular, is the purpose of the present work.

It should be noted that despite the extensive use of the rigid-body (hopping) model of orientational diffusion, recently obtained direct experimental evidence favors the free-rotation mechanism of reorientation of linear and spherical molecules in simple liquids. In exceptional cases, such as in solutions of HCl or N_2 in liquid SF_6, even a rotational structure identical to its gas analog has been resolved.[14,15] On the other hand, the presence of resolved and unresolved O and S bands, as in compressed CF_4,[16] offers evidence that the rotation is not fully suppressed and has not yet acquired a diffusion character. An idea of what takes place in denser media can be obtained from certain representations of NMR investigations of the relaxation times τ_J of the rotational angular momentum and τ_θ of the molecule orientation. They show that for heavy spherical molecules in the liquid phase, these times are connected by the Hubbard relation[17–20]

$$\tau_\theta\tau_J=I/6kT, \tag{1.1}$$

which can be explained only from the point of view of the free-rotational model of orientational diffusion (in the hopping variant $\tau_\theta=\tau_J\exp\{W/kT\}$, where W is the potential barrier that limits the frequency of the hops). Finally, assuming τ_J^{-1} to be the number of binary collisions that interrupt the free rotation, it is possible to calculate their cross section and to verify that in SF_6, for example, it turns out to be an almost linear function of the temperature, which experiences no changes whatever when the gas condenses into a liquid.[21] All this gives grounds for considering the behavior of simple molecules both in a gas and in a liquid, within the framework of the general formalism of impact theory, a quasiclassical variant of which was first proposed by Gordon.[22,23] By resorting to this theory[24,25] it was possible to account numerically for the experimentally established $\tau_\theta(\tau_J)$ dependence, starting with rarefied media, where $\tau_\theta\sim\tau_J$, and ending with a liquid, where the Hubbard relation (1.1) is valid. Following this example, we have improved the quasi-classical impact theory of Raman-scattering spectra, first recasting it in a mathematically closed form. This has uncovered a possibility of analytically solving the problem of collision broadening of a spectrum, at least when the latter can be regarded as strong. It has thus been established that the collapse of the rotational structure is the spectral equivalent of the $\tau_\theta(\tau_J)$ dependence, and the narrowing of the spectrum upon condensation of a gas, just as the Hubbard relation, can be attributed to the non-adiabatic character of the collisions that cause the transitions between the rotational sublevels without loss of phase coherence.

2. THEORY OF RAMAN-SCATTERING SPECTRUM SHAPE

In comparison with NMR, investigations of the relaxation time, the spectroscopy of Raman scattering offers much greater possibilities. When parallel and perpendicular experimental geometries are combined, it makes it possible to determine in pure form the entire orientational-relaxation spectrum

$$G(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^\infty K(t)\exp\{-i\omega[t+i/2kT]\}dt=F(\omega)\exp\{\omega/2kT\}, \tag{2.1}$$

while the reorientation time

$$\tau_\theta=\int_0 K(t)\,dt=\pi G(0)$$

merely represents the intensity of the spectrum, normalized to unity, etc. Investigating its behavior, it is difficult to trace the fine points of the phenomenon, whereas the presence or absence of sideband components (O and S branches) makes it possible to ascertain directly whether the rotation is still preserved or whether it has turned into orientational diffusion of the Debye type. The orientational correlation function

$$K(t)=\frac{3}{2}\operatorname{Sp}\{\overline{\alpha_{ik}(t)\alpha_{ik}(0)}\} \tag{2.2}$$

is defined in terms of the anisotropic part of the polarizability tensor

$$\alpha_{ik}(t)=n_i(t)n_k(t)-{}^1/{}_3\delta_{ik}, \tag{2.3}$$

in which n_i are the Cartesian components of the unit vector $\mathbf{n}$ that is directed along the molecule axis. The latter is assumed, for the sake of argument, to be here linear. The combinations of the components

$$\begin{gathered}d_0=\frac{3}{2}\alpha_{zz},\qquad d_{\pm1}=\sqrt{\frac{3}{2}}(\mp\alpha_{zx}-i\alpha_{zy}),\\ d_{\pm2}=\frac{1}{2}\sqrt{\frac{3}{2}}(\alpha_{xx}-\alpha_{yy})\pm i\sqrt{\frac{3}{2}}\alpha_{xy},\end{gathered} \tag{2.4}$$

which is transformed under spatial rotations as the corresponding spherical harmonics of second rank, change (2.2) into the scalar product

$$K(t)=\sum_{q=-2}^{2}(-1)^q\overline{d_q(t)}d_{-q}(0). \tag{2.5}$$

The bar, which denotes in (2.2) averaging over the collisions, i.e., over all possible realizations of the random process of the variation of $\alpha_{ik}(t)$, now pertains to $d_q(t)$ (from now on we leave out the averaging sign).

Proceeding as in[26], we can derive by the general method of summation of realizations[27] a closed integral-differential equation that describes the behavior of d_q averaged over all the collisions and free rotations, with the exception of the latter, in which the angular momentum is an argument of the dependence of the sought function $d_q(t,J)$.

$$\frac{\partial}{\partial t}d_q(t,J)=\frac{iJ}{I}qd_q(t,J)-\frac{1}{\tau_0}\Bigg[d_q(t,J)$$

$$-\sum_{q'}\int_0^{\pi}d\alpha\int_{-\pi}^{\pi}d\theta\int_{-\pi}^{\pi}d\eta\mathscr{D}^2_{q'q}\left(\theta-\frac{\pi}{2};\alpha;\eta+\frac{\pi}{2}\right)\int_0^{\infty}d_{q'}(t,J')\mathscr{F}(J',J,\theta,\alpha,\eta)\,dJ'\Bigg],\tag{2.6}$$

where τ_0 is the free path time and $q=0$ or ± 2.[1)] As to the angular momentum, in contrast to d_q there is a purely discontinuous Markov variable, which is conserved during the time of free rotation and is altered only by the collisions. The probability that in the course of time the angular momentum will change from J_0 to J and will be inclined by an angle φ from its initial direction is determined by Feller's equation[27]

$$\frac{\partial}{\partial t}\Phi(J,\varphi,J_0,t)=-\frac{1}{\tau_0}\Phi(J,\varphi,J_0,t)$$

$$+\frac{1}{\tau_0}\int\mathscr{F}(J',J,\theta,\varphi-\varphi',\eta)\,\Phi(J',\varphi',J_0,t)\,dJ'\,d\varphi'\,d\theta\,d\eta,\tag{2.7}$$

the kernel of which is the same distribution function $\mathscr{F}(J',J,\theta,\alpha,\eta)$, by which the result of the impact is specified in (2.6). The integration of the angles and momenta over this distribution has the meaning of averaging over the collision impact parameters, the only result of which in classical language is a rotation, determined by three Euler angles (θ,α,η), of the plane of rotation and of the axis of the molecule, and also a change in the rotation frequency from J'/I to J/I. The transformation of the components to d_q in the case of rotations of the rotational and dipole moments is specified by the Wigner functions $\mathscr{D}^2_{q'q}$, which are defined in[28], and the change of the angular momentum J is assumed to be continuous. The last circumstance limits region of applicability of the theory to spectra with unresolved rotational structure of the bands. In conjunction with the usual impact conditions, this establishes the following time hierarchy:

$$2/I\ll 1/\tau_J\ll 1/\tau_{\text{coll}},\tag{2.8}$$

in which τ_{coll} is the average duration of the collisions that change the rotational state of the module. The initial conditions for (2.6)

$$d_q(0,J)=d_q(0)\varphi_B(J)\tag{2.9}$$

are defined in terms of the equilibrium distribution of the molecules over the rotational moments

$$\varphi_B(J)=2\beta J\exp(-\beta J^2),\quad \beta=1/2IkT,\tag{2.10}$$

and finally, the average contained in (2.6) is given by

$$d_q(t)=\int_0^{\infty}d_q(t,J)\,dJ.\tag{2.11}$$

Bearing this in mind, we can greatly simplify the calculation of the spectrum, expressing it in terms of the Fourier transforms of the partial components

$$d_q(\omega,J)=\int_0^{\infty}\exp(-i\omega t)\,d_q(t,J)\,dt.$$

As a result we get

$$G(\omega)=\frac{1}{\pi}\operatorname{Re}\sum_q(-1)^q\int_0^{\infty}d_q(\omega,J)\,d_{-q}(0)\,dJ\exp(\omega/2kT).\tag{2.12}$$

Thus, the matter reduces to a solution of the Fourier-transformed Eq. (2.6) with the initial condition (2.9).

Proceeding to the analysis of (2.6), we must first take into account the difference between the adiabatic and the non-adiabatic collisions. Non-adiabatic broadening is experienced only by the central part of the spectrum with components $J\lesssim I\tau^{-1}_{\text{coll}}$ (or respectively $\omega\lesssim 2\tau^{-1}_{\text{coll}}$), and its periphery broadens adiabatically. On the other hand, the difference lies in the fact that the adiabatic collisions only rotate the axis of the molecule and the vector of the angular momentum, without changing the value of the latter (m-diffusion), owing to which all the components broaden independently of one another,[26] whereas the non-adiabatic collisions, besides producing disorientation, change also the value of the angular momentum (J-diffusion), i.e., they induce transitions between rotational terms, through which the spectral exchange is effected. Of particular importance is the fact that besides the frequencies, the non-adiabatic collisions exchange also the components d_q with different q, thus effecting a coupling between the O, Q, and S branches of the spectrum (Fig. 1). This phenomenon, which plays a decisive role in the collapse of the rotational structure, was first pointed out by Gordon.[22] Gordon has assumed, however, that this phenomenon has an adiabatic nature and consequently should accompany not only J diffusion but also m diffusion. Actually, the O–Q–S exchange is a typical interference effect of non-adiabatic origin,[29,30] and as shown recently[26] vanishes on going into the adiabatic approach both in the classical and in the quantum formalism. However, if the collisions are short enough, then the non-adiabatically broadened part of the spectrum extends far beyond the middle frequencies and it can be assumed that J-diffusion, meaning also O–Q–S exchange, extends over the entire spectrum.

To make the problem mathematically closed, we consider a collision model wherein the change of the plane and frequency of the rotation take place independently of the reorientation of the molecule axis, so that

$$\mathscr{F}(J',J,\theta,\varphi-\varphi',\eta)=f(\mathbf{J}',\mathbf{J})f(\theta,\eta).\tag{2.13}$$

This makes it possible to establish the possible form of the distribution function $f(\mathbf{J}',\mathbf{J})=f(J',\varphi',J,\varphi)$ by starting from the fact that must satisfy the detailed balancing principle or the "stationarity condition"

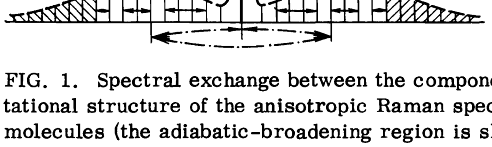

FIG. 1. Spectral exchange between the components of the rotational structure of the anisotropic Raman spectrum of linear molecules (the adiabatic-broadening region is shaded); $\leftarrow\cdot\rightarrow$ 0 – Q – S exchange; $\leftrightarrow$ J – J exchange.

$$\varphi_B(\mathbf{J})=\int f(\mathbf{J}',\mathbf{J})\varphi_B(\mathbf{J}')d\mathbf{J}', \tag{2.14}$$

which ensures constancy of the equilibrium distribution of the molecule with respect to the angular momenta $\varphi_B(J)$. A condition of exactly this type guarantees conservation of the Maxwellian distribution with respect to the velocities in the collision process. On the basis of precedent, which was considered by Keilson and Storer,[31] it is natural to adapt the general form $f(\mathbf{J}',\mathbf{J})=f(\mathbf{J}-\gamma\mathbf{J}')$. This is perfectly sufficient, knowing $\varphi_B(J)$, to determine uniquely from the integral equation (2.14) the actual form of its kernel.[32] In our case it turns out to be

$$f(\mathbf{J}-\gamma\mathbf{J}')=f(J'\,J,\alpha)=\frac{2\beta J}{\pi(1-\gamma^2)}\exp\left\{-\frac{\beta}{1-\gamma^2}\left[J^2+\gamma^2J'^2-2\gamma J'J\cos\alpha\right]\right\}, \tag{2.15}$$

where, as usual, $0\leqslant\gamma\leqslant1$. When $\gamma=0$, the collisions are so strong that after each of them the angular momentum can assume an arbitrary value with an equilibrium $\varphi_B(J)$. On the other hand if the collisions are weak, then $1-\gamma\ll1$, and the angular momentum J after the collision differs insignificantly from the value J' that precedes the collision.

3. ROTATIONAL RELAXATION

An equation describing the relaxation of the angular momentum is simplified with the aid of the obtained distributions and takes the form

$$\frac{\partial}{\partial t}\Phi(\mathbf{J},\mathbf{J}_0,t)=-\frac{1}{\tau_0}\Phi(\mathbf{J},\mathbf{J}_0,t)+\frac{1}{\tau_0}\int\Phi(\mathbf{J}',\mathbf{J}_0,t)f(\mathbf{J}-\gamma\mathbf{J}')d\mathbf{J}'. \tag{3.1}$$

Multiplying it by J and integrating, we obtain after simple transformations

$$\frac{\partial}{\partial t}\langle\mathbf{J}\rangle=-\frac{1-\gamma}{\tau_0}\langle\mathbf{J}\rangle, \tag{3.2}$$

where $\langle\mathbf{J}\rangle=\int\mathbf{J}\Phi(\mathbf{J},\mathbf{J}_0,t)d\mathbf{J}$ is the mean value of the angular-momentum vector, and is equal to $\mathbf{J}_0$ at $t=0$. Just as in the Langevin approach which was used by Hubbard,[17,18] this mean value relaxes exponentially to zero with a friction coefficient $(1-\gamma)/\tau_0$ due to the collisions. Since it is the collisions that play the role of a random Langevin force, at the same time an increase takes place in the scatter of the angular momenta about the mean value, a scatter that changes their initial distribution $\Phi(\mathbf{J},\mathbf{J}_0,0)=\delta(\mathbf{J}-\mathbf{J}_0)$ into an equilibrium distribution $\Phi(\mathbf{J},\mathbf{J}_0,\infty)=\varphi_B(\mathbf{J})$. The rate of relaxation of the angular momentum

$$1/\tau_J=(1-\gamma)/\tau_0 \tag{3.3}$$

depends on the effectiveness of the collisions.

In the case of weak collisions ($\gamma\to1$), by means of a standard expansion[27] in the small parameter $(1-\gamma)$, the Feller Eq. (3.1) is reduced to a Fokker-Planck equation

$$\frac{\partial}{\partial t}\Phi=2uI\Phi+uI(\mathbf{J}\nabla_J)\Phi+D\Delta\Phi. \tag{3.4}$$

Here $D=(1-\gamma)/2\tau_0\beta$ is the coefficient of the diffusion made up of numerous but small jumps $\mathbf{J}(\Delta J\sim(1-\gamma)J)$, which occur in the collisions, and $u=1/I\tau_J$ is the mobility in J-space and satisfies the relation $u=D/kT$ which is customary in random-walk problems. The process of the correlated J-diffusion is described by the solution of the equation (3.4)

$$\Phi(\mathbf{J},\mathbf{J}_0,t)=\frac{1}{2\pi IkT[1-\exp(-2t/\tau_J)]}\exp\left\{-\frac{[\mathbf{J}-\exp(-t/\tau_J)\mathbf{J}']^2}{2IkT[1-\exp(-2t/\tau_J)]}\right\}, \tag{3.5}$$

which was obtained by Hubbard[17] within the framework of the Langevin phenomenology, which can now be identified with the limiting case of "weak collisions." In addition, the physical meaning of the phenomenological parameters D and u becomes clear in terms of the free-rotational mechanism of J-diffusion.

The concrete specification of the collisions, which leads to the Feller equation, has also one more advantage over the phenomenological theory in that it allows us to consider, besides the weak collisions, also strong collisions that restore immediately the equilibrium distribution in J. In this limit, similar to τ approximation to the Boltzmann equation, we have $\gamma=0$, so that we obtain the identity

$$\tau_0=\tau_J, \tag{3.6}$$

and from Feller's equation we obtain in place of (3.4)

$$\frac{\partial}{\partial t}\Phi=-\frac{1}{\tau_0}\Phi+\frac{1}{\tau_0}\varphi_B. \tag{3.7}$$

The "J-diffusion" approach process described by this equation is in essence not even a diffusion of the angular momentum in the true sense of the word, since the spreading over all of J space takes place as a result of the very first collision by one impact, and not by a sequence of such impacts. The change of J has in this case an uncorrelated character (all the subsequent values do not depend on the preceding ones) and is described by the distribution

$$\Phi(\mathbf{J},\mathbf{J}_0,t)=\varphi_B(\mathbf{J}_0)[1-\exp(-t/\tau_0)]+\delta(\mathbf{J}-\mathbf{J}_0)\exp(-t/\tau_J), \tag{3.8}$$

which has nothing in common with (3.5). Thus, strong collisions give rise to the hopping mechanism of J relaxation, which is always an alternative of the diffusion mechanism.[27,32] However, since the term "J diffusion" has become standard, we can retain it but must not take it literally but in a broader sense, in the sense of "J-migration" or "rotational relaxation," which is true with respect to both types of collisions, both weak and strong.

4. ORIENTATIONAL RELAXATION

The presence of the distributions (2.13) and (2.15), which satisfy the stationarity condition, make it possible also to reduce the orientational-relaxation problem to a mathematically closed formulation. Carrying out the necessary averaging in (2.6), we obtain for the Fourier component

$$-d_q(0)\varphi_B(J)=i\left[\frac{1}{I}qJ-\omega\right]d_q(\omega,J)-\frac{1}{\tau_0}\left[d_q(\omega,J)-\sum_{q'}\int_0^\infty T_{q'q}(J',J)d_{q'}(\omega,J')dJ'\right], \tag{4.1}$$

where the operator $T_{q'q}(J',J)$, which effects the exchange in J and q spaces, is

$$\hat{T}=\begin{pmatrix} \left\langle\cos^4\frac{\alpha}{2}\right\rangle\overline{e^{2i(\theta+\eta)}} & \frac{\sqrt{6}}{4}\langle\sin^2\alpha\rangle\overline{e^{2i\eta}} & \left\langle\sin^4\frac{\alpha}{2}\right\rangle\overline{e^{-2i(\theta-\eta)}} \\ \frac{\sqrt{6}}{4}\langle\sin^2\alpha\rangle\overline{e^{2i\theta}} & \frac{1}{2}\langle 3\cos^2\alpha-1\rangle & \frac{\sqrt{6}}{4}\langle\sin^2\alpha\rangle\overline{e^{-2i\theta}} \\ \left\langle\sin^4\frac{\alpha}{2}\right\rangle\overline{e^{2i(\theta-\eta)}} & \frac{\sqrt{6}}{4}\langle\sin^2\alpha\rangle\overline{e^{-2i\eta}} & \left\langle\cos^4\frac{\alpha}{2}\right\rangle\overline{e^{-2i(\theta+\eta)}} \end{pmatrix} \tag{4.2}$$

(here and below the sign of the component d_0 is reversed). The bar denotes averaging over the distribution $\tilde{f}(\theta,\eta)$, while the angle brackets denote averaging over $f(\mathbf{J}-\gamma\mathbf{J}')$. In contrast to the analogous matrix used by Gordon,[26] all three Euler angles are retained in the present matrix, a procedure which is far from unnecessary. Only because of this, as already indicated,[26] does the averaging over the distribution of the angles, which occurs in adiabatic collisions, cause all the nonsecular terms to vanish, including by the same token the O–Q–S exchange. For non-adiabatic collisions, the presence of all angles is also most important, since it makes it possible to reduce the matrix to a symmetrical form, which should be inherent in it by virtue of most general considerations.[33] After independence of the angles θ and η is assumed, symmetrization by means of averaging is possible only in the case when these angles are distributed in the same manner: $\tilde{f}(\theta,\eta)=\psi(\theta)\psi(\eta)$. Taking this into consideration, we have

$$\hat{T}=\frac{2\beta J}{1-\gamma^2}\exp\left\{-\frac{\beta}{1-\gamma^2}[J^2+\gamma^2J'^2]\right\}\times\begin{pmatrix} \mathcal{I}_+(z')x^2 & \frac{\sqrt{6}}{4}\mathcal{I}_0(z')x & \mathcal{I}_-(z')|x|^2 \\ \frac{\sqrt{6}}{4}\mathcal{I}_0(z')x & \mathcal{I}_\sim(z') & \frac{\sqrt{6}}{4}\mathcal{I}_0(z')x^* \\ \mathcal{I}_-(z')|x|^2 & \frac{\sqrt{6}}{4}\mathcal{I}_0(z')x^* & \mathcal{I}_+(z')(x^*)^2 \end{pmatrix}. \tag{4.3}$$

Here

$$x=\int\exp(2i\theta)\psi(\theta)d\theta, \tag{4.4}$$

and

$$\mathcal{I}_0(z')=\frac{1}{2}[I_0(z')-I_2(z')],\quad \mathcal{I}_\sim(z')=I_0(z')-\frac{3}{2}\mathcal{I}_0(z'),$$
$$\mathcal{I}_\pm(z')=\frac{3}{8}I_0(z')\pm\frac{1}{2}I_1(z')+\frac{1}{8}I_2(z'), \tag{4.5}$$

where $I_i(z')$ are modified Bessel functions with $z'=2\gamma\beta J'J/(1-\gamma^2)$.

From the physical point of view, Eq. (4.1) describes orientational relaxation, just as the Fourier-transformed Eq. (3.1) describes rotational relaxation. From the mathematical point of view, however, it is incomparably more complicated. Even in comparison with Teller's equation there are considerable complications connected with the presence of the dynamic term and of the much more complicated structure of the nucleus. Therefore an analytic solution of the problem, not only in the general case but also in the limiting situations of weak ($\gamma\to 1$) and strong ($\gamma=0$) collisions, encounters appreciable difficulties. The extent of these difficulties, however, is not the same. In the case of correlated variation of $\mathbf{J}(\gamma\sim 1)$, the same expansion in $(1-\gamma)$ which had transformed (3.1) into (3.4) and (4.1) reduces to a difficultly-solved system of three coupled partial differential equations of second order. Only by ignoring this coupling, i.e., by assuming the plane of rotation unchanged and the O–Q–S exchange insignificant, is it possible to obtain lucid solutions in both the linear and nonlinear formulation of the problem.[35] On the other hand, if $\mathbf{J}$ varies in uncorrelative fashion ($\gamma=0$), then we can resort to the general method that makes it possible to reduce the system of integral equations into algebraic equations.[27] We shall make use of this possibility to obtain lucid results.

Besides the purely methodological advantages, the model of strong collisions is preferable also from the point of view of the realistically attainable collision effectiveness. Experiment indicates that the cross sections of the collisions that lead to J diffusion are close to the gaskinetics cross sections,[34] and are not much smaller, as might be expected were we to have $1-\gamma\ll 1$. Furthermore, small changes in the angular momentum as well as in the momentum can be naturally expected in collisions between heavy particles and light ones, and not with partners of comparable mass. It is also equally clear from the quantum-mechanical point of view that the probability of non-adiabatic processes which lead, in particular, to J–J and O–Q–S exchange,[26] increases no slower than $1/R^6$ with decreasing impact distance. This means that the strong-interaction region is reached quite rapidly and its contribution to the J-diffusion cross section can be decisive. In the case of long paths, when the interaction is weak, mainly dipole-allowed transitions with $\Delta J=\pm 1$ take place. However, in the case of close paths, transitions with $|\Delta J|=2,3,\ldots$ become allowed with increasing order and with increasing multipolarity of the interaction, so that in the case of strong interaction transitions with any ΔJ are possible, a fact indeed corresponding to the approximation (3.6).

The fact that impact theory, in contrast to the Hubbard diffusion approximation, can describe, in addition to the weakly-disorienting collisions ($\alpha\ll\pi$), also collisions that spread $\mathbf{J}$ out over all directions ($\alpha\lesssim\pi$), is well known and is frequently used.[23–25] Less known is the fact that collisions that disorient $\mathbf{J}$ completely cannot be weak in the sense of J exchange if the molecule axis is not displaced during the collision time. The converse is also true: if all the hindrances on ΔJ are lifted, then the collision "spreads out" $\mathbf{J}$ both in magnitude and direction. Therefore at $\gamma=0$ we obtain from (4.3)

$$\hat{T}=\varphi_B(J)\begin{pmatrix} \frac{3}{8}x^2 & \frac{\sqrt{6}}{8}x & \frac{3}{8}|x|^2 \\ \frac{\sqrt{6}}{8}x & \frac{1}{4} & \frac{\sqrt{6}}{8}x^* \\ \frac{3}{8}|x|^2 & \frac{\sqrt{6}}{8}x^* & \frac{3}{8}(x^*)^2 \end{pmatrix}=\varphi_B(J)T_{q'q}. \tag{4.6}$$

The numerical values of the matrix elements stem from the averaging marked by the angle brackets in (4.2), which is carried out, by virtue of the strong collisions, over the uniform $d\alpha/\pi$ distribution.

The assumption that the spreading out in J space is not adiabatic must inevitably be used when attempt is made to extend the impact theory to dense media. In fact, even by virtue of the very condition that the impact theory (2.8) we must have the inequality

$$(\overline{\theta^2})^{1/2} \lessapprox \bar{\omega}\tau_{coll} \ll \bar{\omega}\tau_J = \lambda \quad (\bar{\omega} = \bar{J}/I = (\pi/4\beta I^2)^{1/2}).$$

However, if the impact theory remains valid also at $\lambda \ll 1$, when Hubbard's relation is satisfied, then we also have

$$(\overline{\theta^2})^{1/2} \ll 1. \tag{4.7}$$

Moreover, Hubbard's relation itself, as we shall see below, is obtained strictly speaking only at $\overline{\theta^2} = 0$, as was indeed assumed in all the studies that reproduced this result within the framework of the impact theory.[24,25] There is no need, however, for such an excessive enhancement of the inequaltiy (4.7). The phase-coherence loss, even if small, may turn out to be significant after complete averaging of the rotation, when it becomes the only cause of the broadening of the spectrum, a cause corresponding to the classical model of random warps of the axis. It is important only that unit step of these warps be small by virtue of (4.7) so that when the integrand of (4.4) is expanded in its terms we have

$$x \approx 1 - 2\overline{\theta^2} \tag{4.8}$$

with allowance for the fact that, owing to the symmetry of the collision, the odd terms vanish as a result of the averaging.

5. COLLAPSE OF STRUCTURE

Under the assumptions made, the solution of (4.1) can be obtained in quadratures. Indeed, finding the partial $d_q(\omega, J)$ and averaging them over J, we have

$$d_q(\omega) = A_q\left[d_q(0) + \tau_J^{-1}\sum_{q'} T_{q'q} d_{q'}(\omega)\right],$$

whence

$$d_q(\omega) = \sum_{q'}\left[\frac{\delta_{q'q}}{A_q} - \frac{1}{\tau_J}T_{q'q}\right]^{-1} d_{q'}(0) = \sum_{q'} G^{-1}_{q'q} d_{q'}(0). \tag{5.1}$$

We have introduced here the notation

$$A_q = \int_0^\infty \frac{\varphi_B(J)\,dJ}{i\omega - iq\omega_0 J + \tau_J^{-1}} = \frac{iq\sqrt{\pi\beta}}{4\omega_0} + \frac{qz\sqrt{\pi\beta}}{2\omega_0}\exp(-z^2)\,[1 - \Phi(iz)]$$
$$- \frac{iz\sqrt{\beta}}{2\omega_0}\exp(-z^2)\,\mathrm{Ei}(z^2), \quad q = \pm 2, \tag{5.2}$$
$$A_0 = (i\omega + \tau_J^{-1})^{-1},$$

where $\omega_0 = 1/I$ is the frequency corresponding to the smallest rotational quantum, $z = (\sqrt{\beta}/2)(\omega/\omega_0 - i/\omega_0\tau_J)$, while $\Phi(iz)$ and $\mathrm{Ei}(z^2)$ are respectively the error integral and the integral exponential function (the notation for the special functions is in accordance with Jahnke, Emde, and Lösch.[36] Using (5.1), we obtain ultimately in (2.1)

$$F(\omega) = \frac{1}{\pi}\,\mathrm{Re}\sum_{q'q} G^{-1}_{q'q} d_{-q}(0)\, d_{q'}(0). \tag{5.3}$$

Diagonalizing the matrix G by means of a similar transformation

$$\Omega_{q'q} = \sum_{p'p} U^{-1}_{q'p'} G_{p'p} U_{pq} = \Omega_{qq}\delta_{q'q}, \tag{5.4}$$

we can represent the spectrum (5.3) in the form of a sum of three lines

$$F(\omega) = \frac{1}{\pi}\,\mathrm{Re}\sum_{q} \tilde{d}_q \Omega_{qq}^{-1} \tilde{\tilde{d}}_q, \tag{5.5}$$

the intensity of which depends on the products of the corresponding elements of the transform vectors

$$\tilde{d}_q = \sum_{q'} U_{q'q} d_{q'}(0), \quad \tilde{\tilde{d}}_q = \sum_{q'} U^{-1}_{qq'} d_{q'}(0). \tag{5.6}$$

These results enable us to describe quantitatively the change in the form of the spectrum, starting with the instant of time when the rotational structure of the sidebands becomes smeared out and the Q band appears in the form of a homogeneously broadened component. At low densities we have $\lambda \gg 1$, which makes it possible, by using the smallness of the off-diagonal elements of the matrix G (of order λ^{-1}), to simplify (5.5) and to obtain for the central part of the spectrum the expression

$$F(\omega) = \pi^{-1}[d_0(0)]^2\Gamma/(\omega^2 + \Gamma^2), \quad \Gamma = 3/4\tau_J. \tag{5.7}$$

From (5.7) we can find the relation between the times of the orientational and rotational relaxation of a linear molecule in the quasi-static limit:

$$\tau_\theta = \pi F(0) = \tau_J/3. \tag{5.8}$$

Comparison of (5.8) with the analogous relation ($\tau_\theta = \tau_J/4$) for spherical tops[24] shows that at identical pressures the orientational relaxation of linear molecules is slower than that of spherical ones, which have one additional rotational degree of freedom.

With further increase of the density, besides the central band and the side bands, broadening will take place in the O and S bands; this broadening is particularly noticable for the narrowest Q line. The broadening of the bands ends with their coalescence into one (collapse), which should be followed either by further broadening or by a narrowing of the spectrum as a whole. Which of the two possibilities is realized in fact can be assessed only from the actual form of the solution at

$$\lambda \ll 1. \tag{5.9}$$

We shall dwell separately on this limiting case, in order to demonstrate that the narrowing by pressure does indeed take place. Its analysis is greatly facilitated by the fact that the inequalities (4.7) and (4.9) make it possible to carry out first an asymptotic expansion of $\Phi(iz)$ and $\mathrm{Ei}(z^2)$, and then use the diagonalization procedure (5.4) for the matrix G by perturbation theory. Using the matrix U of the eigenvectors G in (5.6) and confining ourselves in (5.5) to terms of second order of smallness, we obtain the following expression for the spectrum:

$$F(\omega)=-\frac{3\lambda^2}{2\pi}\left\{\frac{\Gamma_O(\omega)}{[\omega+\bar{\omega}-{}^5/_2\omega B(\omega)]^2+\Gamma_O^2(\omega)}\right.$$

$$\left.+\frac{\Gamma_S(\omega)}{[\omega-\bar{\omega}-{}^5/_2\omega B(\omega)]^2+\Gamma_S^2(\omega)}\right\}+\frac{1+3\lambda^2}{\pi}\frac{\Gamma_Q(\omega)}{\omega^2[1-3B(\omega)]^2+\Gamma_Q^2(\omega)},$$

$$B(\omega)=\frac{(\overline{\omega^2}-\bar{\omega}^2)\tau_J^2}{1+\omega^2\tau_J^2},$$

$$\Gamma_O(\omega)=\Gamma_S(\omega)=\tau_J^{-1}-\frac{3}{2}\bar{\omega}^2\tau_J+\frac{5}{2}\tau_J^{-1}B(\omega), \tag{5.10}$$

$$\Gamma_Q(\omega)=3\bar{\omega}^2\tau_J^{-1}-3\tau_J^{-1}B(\omega)+3\frac{\overline{\theta^2}}{\tau_J},$$

where $\overline{\omega}^2=\overline{J^2}/I^2$. The first two terms are the "remnants" of the O and S branches. They can be interpreted as Lorentzian lines with a width of scale τ_J^{-1} that varies insignificantly along the contour; the line centers coincide with the frequency centers of the bands $\pm\bar{\omega}$. With increasing density, they continue to broaden, but their amplitude tends to zero. Thus, as a result of the collapse, the side band branches become forbidden and the entire intensity is pumped over in final analysis to the central component (Fig. 2). The shape of the latter is also close to Lorentzian, as is evidenced by the insignificant variation of $\Gamma_Q(\omega)$ over the spectrum. Its width, which is inversely proportional to the intensity at the maximum (at zero frequency) actually coincides with $1/\tau_\theta$. Whether the residual width of the spectrum decreases or increases with increasing density depends entirely on whether the Hubbard relation holds or not. To answer this question we investigate the density dependence of the orientational-relaxation time

$$\tau_\theta=\pi F(0)=\tau_J\left[\frac{1}{3\overline{\omega^2}\tau_J^2+3\overline{\theta^2}}-3\bar{\omega}^2\tau_J^2\right], \tag{5.11}$$

bearing in mind the fact that $\tau_J\sim\rho^{-1}$. If we assume that there is no loss of phase coherence in the collisions, then in the limit as $\rho\to\infty$ we obtain from (5.11)

$$\tau_\theta=\frac{1}{3\overline{\omega^2}\tau_J}=\frac{I}{6kT}\frac{1}{\tau_J}, \tag{5.12}$$

inasmuch as $\overline{\omega^2}=2kT/I$ for linear molecules. This is in fact the Hubbard relation, and its experimental confirmation can be regarded as evidence favoring the narrowing of the Raman-scattering spectrum by collisions. As shown in the Appendix, for spherical molecules it is valid to the same extent as for linear ones.2) The universality of relation (5.12), which contains no parameters except the moment of inertia of the molecule, is a guarantee that it is precisely the free rotation, modulated by the collisions in frequency and in direction, which collapses to orientational relaxation. If, in addition to all other, the phase coherence also collapses ($\overline{\theta^2}\neq 0$), then this establishes the limit of applicability of the Hubbard relation on the high-density side.

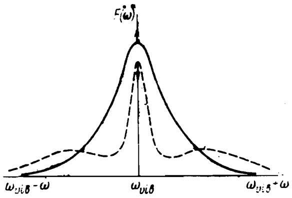

FIG. 2. Transformation of spectral contour with increasing density (the arrows mark the intensity transfer). Dashed—$\lambda>1$, solid line—$\lambda<1$.

APPENDIX

We write down for the unit vector **n**, which is rigidly connected with the core of the spherical top, the equation of motion in the form

$$\frac{\partial}{\partial t}\mathbf{n}(t)=\frac{1}{I}[\mathbf{J}(t)\mathbf{n}(t)], \tag{A.1}$$

which is valid if the phase coherence is not lost in the collisions. Solving (A.1) formally and substituting the obtained solution in the right-hand side, we arrive at

$$\frac{\partial}{\partial t}\mathbf{n}(t)=\frac{1}{I^2}\int_0^t[\mathbf{J}(t)[\mathbf{J}(t')\mathbf{n}(t')]]dt'+\frac{1}{I}[\mathbf{J}(t)\mathbf{n}(0)]. \tag{A.2}$$

Averaging over the realizations, we obtain for each of the components $\overline{n_\alpha(t)}$

$$\frac{\partial}{\partial t}\overline{n_\alpha(t)}=\sum_\beta\frac{1}{I^2}\int_0^t\overline{J_\alpha(t')J_\beta(t)n_\beta(t')}dt'-\frac{1}{I^2}\overline{J^2}\int_0^t\overline{n_\alpha(t')}dt', \tag{A.3}$$

where account is taken of the fact that $\overline{J_\alpha}=0$. Using the uncoupling procedure of[27] as well as the fact that the different spatial projections of the angular-momentum vector of the spherical top are not correlated

$$\overline{J_\alpha(t')J_\beta(t)}=K(t-t')\cdot{}^1/_3\overline{J^2}\delta_{\alpha\beta}, \tag{A.4}$$

we obtain under the usual assumptions $t\gg\tau_J$ and $\overline{J}^2\tau_J^2/I^2\ll 1$

$$\frac{\partial}{\partial t}\overline{n_\alpha(t)}=-\frac{2}{3}\frac{\overline{J^2}}{I^2}\int_0^\infty K(\tau)d\tau\,\overline{n_\alpha(t)}=-\frac{2}{3}\frac{\overline{J^2}}{I^2}\tau_J\overline{n_\alpha(t)}. \tag{A.5}$$

Equation (A.5) leads to an exponential correlation function

$$\overline{\mathbf{n}(t)\mathbf{n}(0)}=\exp\left\{-\frac{2}{3}\frac{\overline{J^2}}{I^2}\tau_J t\right\} \tag{A.6}$$

with a characteristic damping time

$$\tau_n=\frac{3}{2}\frac{I^2}{\overline{J^2}\tau_J}. \tag{A.7}$$

Analogous reasoning can be used also directly for the polarizability tensor, which is expressed in accordance with (2.3) in terms of bilinear combinations of the components n_α, but it is simpler to use the known relation[11]

$$\tau_\theta = \frac{1}{3}\tau_n \tag{A.8}$$

and to obtain from (A.7)

$$\tau_\theta = \frac{1}{2}\frac{I^2}{\overline{J^2}\tau_J}. \tag{A.9}$$

Substitution of the value of $\overline{J^2}$, which equals for spherical tops

$$\overline{J^2} = 3kTI,$$

again leads to the expression (5.12)

$$\tau_\theta\tau_J = I/6kT.$$

1) The reasons for the absence of the $d_{\pm 1}$ components are the same as those for the absence of the d_0 component in the IR spectra of linear molecules.[26]

2) In an investigation of the density dependence of the time of nuclear quadrupole relaxation, which, like the width of the Raman spectrum, is proportional to $1/\tau_\theta$, Neilsen and Gordon[37] reached conclusions that contradict (5.11). The reason for this is the attempt to integrate the spectrum (5.5) without taking into account the complicated transformation of the eigenfrequencies and eigenvectors of the matrix G during the collapse process.

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