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ON THE THEORY OF ENERGY DISSIPATION PROCESSES OF MOLECULAR OSCILLATIONS IN LIQUIDS

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The probabilities for energy dissipation of molecular oscillations in liquids are calculated. Exchange (short range) and electrostatic interaction forces between the molecules are taken into account. It is found that dissipation of vibrational energy due to exchange forces may explain the temperature course and the order of magnitude of the line widths of the molecular vibrational spectra in liquids. The role of electrostatic forces in energy dissipation is comparable with the role of exchange forces only in the case of complexes consisting of charged particles.

INTRODUCTION

THIS paper is devoted to a calculation of the lifetime of a liquid molecule in a definite vibrational state. The calculation has been carried out in order to elucidate the nature of the line widths of the vibrational (infrared and Raman) spectra of liquid molecules. The prevalent notion is that the width of the depolarization vibrational lines ($\rho \approx 6/7$) is due to a considerable extent to Brownian rotation of the anisotropic liquid molecules.[1,2] Estimates of the broadening due to dissipation of the vibrational energy have not yet been made. We consider first dissipation processes due to exchange short-range molecular interaction forces. Such forces act between all molecules, and the broadening that they induce will be present in the spectra of all liquids. We shall then consider dissipation processes due to electrostatic interaction between molecules in dipole liquids. In conclusion we shall discuss briefly the experimental data.

2. DISSIPATION OF VIBRATIONAL ENERGY OF MOLECULES. EXCHANGE INTERACTION OF PARTICLES

We single out one molecule in the liquid and describe its internal vibration by a set of normal coordinates Q_j; the atoms making up this molecule will be assigned numbers i; the atoms of the neighboring molecules will be designated A. In accordance with the problem posed, we must separate that part of the energy of exchange interaction of atoms i and A of two molecules, which depends on the coordinates Q_j. According to quantum-mechanical calculations, we choose for the exchange-interaction energy the expression (see Seitz[3])

$$H(R) = V_0 \exp(-\alpha R), \tag{1}$$

where R is the distance between the nuclei of the interacting atoms. We obviously have

$$R_{iA} = |\mathbf{r}_i^0 + \mathbf{s}_i - \mathbf{r}_A| = R_{iA}^0 - (\mathbf{R}_{iA}^0 \mathbf{s}_i)/R_{iA}^0, \tag{2}$$

where $\mathbf{r}_i^0 + \mathbf{s}_i$ and $\mathbf{r}_A$ are respectively the radius-vectors of atoms i and A; $\mathbf{s}_i$ is a small displacement of the atom i, due to the internal vibrations of the molecule.

Expanding (1) we obtain for the sought energy

$$H' = -\alpha V_0 \sum_{i,A} \exp(-\alpha R_{iA}^0)(\mathbf{R}_{iA}^0 \mathbf{s}_i)/R_{iA}^0. \tag{3}$$

We introduce the unit vector $\mathbf{n}_{iA}$, directed along $\mathbf{R}_{iA}^0$, and make in (3) the substitution

$$\mathbf{s}_i = \sum_j \frac{\partial \mathbf{s}_i}{\partial Q_j} Q_j; \tag{4}$$

Then the matrix element of the transition $n_j \to n_j - 1$ (n_j is the quantum number of oscillator Q_j) is

$$H'_{n_j \to n_j - 1} = -\alpha V_0 \sum_{i,A} \exp(-\alpha R_{iA}^0)(\mathbf{n}_{iA} \partial \mathbf{s}_i / \partial Q_j)(\hbar n_j / 2\mu_j \omega_j)^{1/2}. \tag{5}$$

Here μ_j and ω_j are the mass and frequency of the oscillator Q_j.

The time dependence of (5) is contained in $\mathbf{R}_{iA}$ and $\mathbf{n}_{iA}$, which vary at random as the molecules are displaced relative to one another. $\mathbf{R}_{iA}$, $\mathbf{n}_{iA}$ are coordinates that describe the translational and rotational degrees of freedom of the molecules; in the transition $n_j \rightarrow n_j - 1$, the energy is transferred from the oscillator Q_j to the indicated degrees of freedom.

To calculate the transition probability we use the perturbation-theory formula

$$w_{n_j \rightarrow n_j - 1} = \hbar^{-2} \, \overline{|H_{n_j \rightarrow n_j - 1}|^2} \, \rho(\omega_j), \tag{6}$$

where $\rho(\omega_j)$ is the spectral density, calculated in terms of the normalized correlation function $g(\tau)$ of the random quantity H′:[4]

$$\rho(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega\tau} g(\tau)\, d\tau, \qquad g(\tau) = \overline{H'(0)\, H'(\tau)} / \overline{|H'(0)|^2}. \tag{7}$$

The interaction energy H′ is greatly changed as the distance between the particles is changed by an amount on the order of the atomic diameter. We shall therefore use, as the time during which the values of H′ are correlated, the time of the "sedentary" life of the molecule between the two jumps[5]

$$\tau_c = \tau_0 e^{E/RT}, \tag{8}$$

and the correlation function will be taken in the form $g(\tau) = \exp(-\tau/\tau_c)$. Then

$$\rho(\omega_j) = 2\tau_c / (1 + \omega_j^2 \tau_c^2). \tag{9}$$

The probability of the transition $n_j \rightarrow n_j - 1$ will be found with the aid of (5), (6), and (9):

$$w_{n_j \rightarrow n_j - 1} = \hbar^{-2} \frac{4\pi N V_0^2}{3} \sum_i \left| \frac{\partial s_i}{\partial Q_j} \right|^2 \frac{\hbar n_j}{2\mu_j \omega_j} e^{-2\alpha\Delta} \left(\frac{1}{4\alpha} + \frac{\Delta}{2} + \frac{\alpha\Delta^2}{2} \right) \rho(\omega_j). \tag{10}$$

Here N is the number of particles per cm^3 and Δ the shortest approach distance between the atoms i and A. In averaging the square of | H′ |, the summation over A is replaced by integration over the volume.

A numerical estimate of (10), assuming the values $V_0 = 500$ ev, $1/\alpha = 0.4$ A, $\Delta = 3$ A, $N = 3 \times 10^{22}$, $\tau_c = 5 \times 10^{-12}$ sec, $\mu_j = 2 \times 10^{-24}$ g, $\omega_j = 2 \times 10^{14}$ sec^{-1}, and $\Sigma_i | \partial S_i / \partial Q_j |^2 = 1$, we get $w_{n_j \rightarrow n - 1} \approx 25$ cm^{-1}.

3. DISSIPATION OF VIBRATIONAL ENERGY OF MOLECULES. ELECTROSTATIC INTERACTIONS

Let us consider the probability of dissipation of the vibrational energy of the molecules, due to electrostatic interactions between dipoles and a dipole liquid. The part of the dipole-dipole interaction dependent on the coordinates $Q_j^{(i)}$ of the vibrations of the molecule i is equal to

$$H' = \sum_j Q_j^{(i)} \sum_A R_{iA}^{-5} [R_{iA}^2 (\mathbf{d}_A \mathbf{D}_i^{(j)}) - 3 (\mathbf{d}_A \mathbf{R}_A)(\mathbf{D}_i^{(j)} \mathbf{R}_A)]. \tag{11}$$

Here $\mathbf{D}_i^{(j)} = \partial \mathbf{d}_i / \partial Q_j$; $\mathbf{d}_i$ and $\mathbf{d}_A$ are the dipole moments of the molecules i and A.

The time dependence of the energy H′ is due to the rotational and translational diffusion of the particles. These motions will be regarded as independent, and their corresponding contributions to dissipation will be assumed additive. To calculate the correlation function $g(\tau)$ and the spectral density $\rho(\omega)$, we use the solutions (Green's functions) $u(q_0, 0; q, \tau)$ of the corresponding equations of free diffusion. For the rotational motion we find

$$g_{rot}(\tau) = \exp(-|\tau|/\tau_{rot}), \tag{12}$$

$$\rho_{rot}(\omega) = 2\tau_{rot}/(1 + \omega^2 \tau_{rot}^2), \qquad \tau_{rot} = 4(\pi\eta a^3/kT) = 4\tau_0. \tag{13}$$

Analogously we obtain for the translational motion[6]

$$\rho_t(\omega) = 36\tau_0 [(z^{-3} - 2z^{-5}) + e^{-z} \cos z \, (z^{-3} + 4z^{-4} + 2z^{-5}) + e^{-z} \sin z \, (z^{-3} - 2z^{-5})], \qquad z = \sqrt{24\omega\tau_0}. \tag{14}$$

It is easy to find the limiting expressions for (14):

$$\rho_t(\omega) = 3/(4\sqrt{6}\,\omega^{3/2}\tau_0^{1/2}) \quad \text{for} \quad \omega\tau_0 \gg 1,$$

$$\rho_t(\omega) = (24/5)\tau_0 \quad \text{for} \quad \omega\tau_0 \ll 1. \tag{15}$$

After averaging $|H'|^2$ over the angles and the distances, using (13) and (15), we obtain the probability of the transition $n_j \rightarrow n_j - 1$ for $\omega_j \tau_0 \gg 1$:

$$w_{n_j \rightarrow n_j - 1} = \frac{8\pi N}{9} \frac{n_j \hbar^{-1}}{2\mu_j \omega_j} \frac{d^2 (D^{(j)})^2}{(2a)^3} \left[\frac{1}{2\omega_j^2 \tau_0} + \frac{\sqrt{3}}{4\omega_j^{3/2} \tau_0^{1/2}} \right]. \tag{16}$$

Here a is the radius of the molecule. A numerical estimate of the probability $w_{n_j \rightarrow n_j - 1}$, assuming the following values,

$N = 3 \cdot 10^{22}$, $d = 1.5\,D$, $D^{(j)} = 5 \cdot 10^{-10}$ cgs esu,[7]

$\tau_0 = 5 \cdot 10^{-12}$ sec,

$\omega_j = 10^{14}$ sec^{-1}, $2a = 4$Å, $\mu_j = 2 \cdot 10^{-24}$;

yields $w_{1 \rightarrow 0} = 4 \times 10^{11}$ sec^{-1}.

We have also calculated the probability of dissipation of the vibrational energy of ionic complexes formed in the solutions of metal-ion salts. To be specific, we consider octahedral complexes. The electric moments of the complex vanish under equilibrium. The internal vibrations disturb the symmetry of the complex, which acquires a quadrupole moment. The five independent components of the quadrupole moment, introduced in accordance with the formulas

$$D_0 = \frac{\sqrt{6}}{2} D_{zz},$$

$$D_{\pm 1} = \pm D_{xz} - i D_{yz}, \qquad 2D_{\pm 2} = D_{xx} - D_{yy} \mp 2D_{xy}, \tag{17}$$

are expressed in terms of the normal coordinates Q_j of the vibrations of the complex in the following manner:

$$D_0 = 6\sqrt{2}\, d\, Q_3,\ D_{\pm 1} = \pm 6d\,[Q_5 \mp i Q_6],$$
$$D_{\pm 2} = 2d\,[6 Q_2 \mp 3i Q_4 - 2\sqrt{3} Q_3]. \qquad (18)$$

Here d is the dipole moment of the particles forming the complex. Then the particles carry equal charges q, and we must put qb in (18) in lieu of d (b is the distance between the particles in the complex). The components D_r in (18) are defined in a system of coordinates rotating together with the complex. In the laboratory system we write

$$D_p = \sum_{r=-2}^{2} T_{rp}^{(2)}(\theta, \psi, \varphi)\, D_r, \qquad (19)$$

where $T_{rp}^{(2)}(\theta, \psi, \varphi)$ are generalized spherical functions.[8]

It is also easy to find the components of the tensor of the electric field intensity gradient of the dipole $\mathbf{d}_A(d_A, \alpha_A, \beta_A)$ at a distance $\mathbf{R}_A$ $(R_A, \theta_A, \varphi_A)$ from it (near the complex):

$$\sqrt{2/3}\,(\nabla E)_A^0 = (\nabla E)_A^{zz} = d_A R_A^{-4}\Phi_A^0,\ (\nabla E)_A^{\pm 1} = \pm(\nabla E)_A^{xz}$$
$$+ i(\nabla E)_A^{yz} = d_A R_A^{-4}\Phi_A^{\pm 1},$$
$$2(\nabla E)_A^{\pm 2} = (\nabla E)_A^{xz} - (\nabla E)_A^{yy} \pm 2i(\nabla E)_A^{xy} = d_A R_A^{-4}\Phi_A^{\pm 2}; \qquad (20)$$

$$\Phi_A^0 = (4\pi/\sqrt{7})[\sqrt{8}\, Y_3^{-1}(\theta)\, Y_1^1(\alpha) + \sqrt{8}\, Y_3^1(\theta)\, Y_1^{-1}(\alpha)$$
$$- \sqrt{12}\, Y_3^0(\theta)\, Y_1^0(\alpha)],$$
$$\Phi_A^{-1} = (4\pi/\sqrt{7})[\sqrt{20}\, Y_3^{-2}(\theta)\, Y_1^1(\alpha) + \sqrt{6}\, Y_3^0(\theta)\, Y_1^{-1}(\alpha)$$
$$- 4 Y_3^{-1}(\theta)\, Y_1^0(\alpha)],$$
$$\Phi_A^{-2} = (4\pi/\sqrt{7})[\sqrt{2}\, Y_3^{-1}(\theta)\, Y_1^{-1}(\alpha) - \sqrt{10}\, Y_3^{-2}(\theta)\, Y_1^0(\alpha)$$
$$- \sqrt{30}\, Y_3^{-3}(\theta) Y_1^{-1}(\alpha)]. \qquad (21)$$

The energy of interaction between the quadrupole moment of the complex and the electric field of the dipoles surrounding the complex will be written with the aid of (19) and (20):

$$H' = \frac{1}{6}\sum_{r=-2}^{2} D_r \sum_{p=-2}^{2} T_{rp}^{(2)}(\theta, \psi, \varphi) \sum_A (\nabla E)_A^p. \qquad (22)$$

We give the calculated spectral density of H′:

$$\rho_{rot}(\omega) = 2\tau_r/(1 + \omega^2\tau_r^2),\ 1/\tau_r = 1/\tau_1 + 1/\tau_2,$$
$$\tau_1 = 4\pi\eta a_1^3/kT,\ \tau_2 = {}^4\!/_3\, \pi\eta a_2^3/kT; \qquad (23)$$

a_1 and a_2 are the radii of the complex and of the solvent molecule. If H′ is disturbed by translational diffusion,

$$\rho_t(\omega) = 480\,\tau_0\,[({}^1\!/_4 z^{-3} - {}^3\!/_2 z^{-5} - 9z^{-7})$$
$$+ e^{-z}\cos z\,(-{}^1\!/_4 z^{-3} - 3z^{-4} - {}^{15}\!/_2 z^{-5} + 9z^{-7})$$
$$+ e^{-z}\sin z\,(-{}^1\!/_4 z^{-3} + {}^{15}\!/_2 z^{-5} + 18z^{-6} + 9z^{-7})]. \qquad (24)$$

Determining the average of $|H'|^2$, we obtain for the probability that the energy of one of the oscillators of the complex (Q_2) will change by an amount $\hbar\omega_2$

$$w_{n_2 \to n_2 - 1} = \frac{1024\pi}{25}\,\frac{d^2 d_A^2 N}{\hbar^2 (2a)^5}\,\frac{\hbar n_2}{2\mu_2\omega_2}\left(\frac{16}{7}\tau_0 + 2\tau_r\right),\quad \omega\tau_0 \ll 1, \qquad (25)$$

$$w_{n_2 \to n_2 - 1} = \frac{1024\pi}{25}\,\frac{d^2 d_A^2 N}{\hbar^2 (2a)^5}\,\frac{\hbar n_2}{2\mu_2\omega_2}\left(\frac{2}{\omega_2^2\tau_r} + \frac{5}{4\sqrt{6}\,\omega_2^{3/2}\tau_0^{1/2}}\right),\quad \omega\tau_0 \gg 1. \qquad (26)$$

A numerical estimate of the probability by means of (26), using values typical of aqueous solutions, namely $d = d_A = 1.85$ D, $N = 3 \times 10^{22}$ cm^{-3}, $\mu_2 = 3.6 \times 10^{-22}$ g, $\omega_2 = 5 \times 10^{13}$ sec^{-1}, $2a = 4$ A, and $\tau_0 = \tau_r = 5 \times 10^{-12}$ sec yields $w_{1 \to 0}$,$= 1.1 \times 10^{10}$ sec^{-1}. If the complex is made up of charged particles, we must replace d by the quantity qb $\approx 10^{-17}$ cgs esu; in this case $w_{1 \to 0} = 10^{12}$ sec^{-1} $= 5$ cm^{-1}.

We must note that the calculation given here is approximate, owing to the use of an expansion of the energy of electrostatic interaction between molecules in powers of the multipoles, an expansion which is correct only for large distances between molecules.

CONCLUSION

The experimental material on the line widths of the Raman and infrared spectra of molecules in liquids is scanty. The most systematic investigations of the line widths of Raman scattering in dipole organic liquids was carried out by Rakov.[2] He observed an exponential increase in the line width with increasing temperature: $\delta(T) = \Delta_0 + A\exp(-E/RT)$, and the values he obtained for the parameter E agreed closely with the viscosity barrier for the investigated liquid. In addition, a correlation was observed between the degree of depolarization ρ and the width of the line: the greater ρ, the broader the lines. These facts can be explained by assuming that one of the principal causes of Raman line broadening is Brownian rotation of the molecules with an anisotropic tensor of the derivative of the polarizability with respect to the normal coordinates of the vibrations. This source of broadening, however, is lacking in oscillations which have an isotropic tensor of the derivative of the polarizability.

It appears to us that the experimental data can be explained better by taking into account the dissipative broadening of the lines considered in the present paper. The temperature dependence predicted by (10), as well as the calculated order of magnitude of the line width, coincide with those observed. The width of the polarized lines in dipole-free liquids is determined obviously essentially by the dissipation of the vibrational energy through exchange interactions. For depolarized lines, the dissipative broadening and the broadening due to Brownian rotation of the molecules will be additive; as a result, the greater ρ the greater the width.

We note that the contribution made by dissipation of the vibrational energy through exchange interactions to the line width depends greatly on the distance between molecules; in this connection, it would be interesting to observe the dependence of the line width on the pressure in the liquid. In addition, steric effects can be important; in complex molecules protected against external influences, vibrations may produce narrower lines.

In dipole liquids there is an additional dissipative broadening due to the presence of electrostatic interactions between molecules; judging from our estimate, this broadening is approximately one order of magnitude smaller than the broadening due to exchange interactions. Only in ionic complexes consisting of charged particles will the electrostatic and exchange interactions yield comparable contributions to the line widths.

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