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Trans-Gauche Equilibrium of 1,2-Dibromoethane and Dipole-interactions in Solutions

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The relative absorption intensities of the scissoring vibration bands of *trans*- and *gauche*-1,2-dibromoethanes were measured in pure liquid and in solutions of *cis*-1,2-dichloroethylene or tetrachloroethylene at various concentrations. The relative populations of the rotational isomers were determined from the intensity data. An attempt was made to describe quantitatively the observed concentration-dependence of the relative population on the basis of a semi-molecular theory of dipole-interaction. An equation is proposed for the averaged interaction energy of a molecule with its surrounding molecules, which is expressed in terms of the dipole moments and the polarizabilities of the solute and the solvent molecules.

The problem of rotational isomerism has been one of the major subjects in the field of physical chemistry.[1–3] Many investigations have been concerned with the determination of the energy difference, ΔE, between rotational isomers. In doing so, one uses the van't Hoff's relation and plots the logarithms of the relative intensities (either absorption or scattering) of two isomers against $1/T$, where T is the absolute temperature, and obtains ΔE from the slope of the plot. There remain two problems, however. One is that a straight-line relation is assumed in the plot. This means that ΔE is assumed to be independent of the temperature or, more generally, of intermolecular interactions. Although the assumption holds effectively in many cases, the present authors[4] recently showed that ΔE depends on the temperature in the case of liquid 1,2-dibromoethane. The other problem is that, in general, only the relative intensities, and not the relative populations, can be known from spectroscopic measurements. If one wants to discuss the equilibrium properties of rotational isomers, however, the relative populations must be known experimentally. Fortunately, the present authors[4] succeeded in obtaining the relative populations at several temperatures from the relative intensities of Raman lines in the case of liquid 1,2-dibromoethane. This permits one to discuss the equilibrium property of liquid 1,2-dibromoethane in some detail.

The present investigation concerns the quantitative description of the concentration-dependence of the relative populations of *trans*- and *gauche*-1,2-dibromoethanes. The solvents used were *cis*-1,2-dichloroethylene and tetrachloroethylene: they were chosen because the former is strongly polar, while the latter is nonpolar. *gauche*-1,2-Dibromoethanes and *trans*-1,2-dibromoethanes are also characterized by their dipole moments; the former is strongly polar, while the latter is nonpolar. The effects of intermolecular dipole-interactions on ΔE are estimated in this paper; a good agreement is obtained between the calculated and observed concentration-dependencies of the relative populations of *trans*- and *gauche*-1,2-dibromoethanes.

Experimental

All the chemicals used in the present study were commercial products. Purchased samples showed no trace of impurity in the infrared spectra covering the range of 400—4000 cm^{-1} and were used without further purification. Solutions of 1,2-dibromoethane in *cis*-1,2-dichloroethylene or in tetrachloroethylene were prepared just before the observations so as to obtain the appropriate concentrations by measuring the weight of each component. On determining the mole percents and the molar concentrations, the density data from a standard table[5] were used. The additivity of the volumes of the components was assumed in this process.

The infrared absorption spectra were measured for the scissoring vibration of 1,2-dibromoethane (ν_{15} of the *trans* form, and ν_3 and ν_{13} of the *gauche* form) in pure liquid and in solutions by the use of a Perkin-Elmer 112G single-beam infrared spectrometer. The spectrometer was operated under a resolution of about 1 cm^{-1} and at room temperature (25 °C). The effects of a finite slit-width on the observed band shapes and on the intensities were ascertained to be very small. The observed spectra were reduced to the absorption-index curves, $k(\nu)$'s.[6] It is known that the effects of the refractive index often spoil the observed relative intensity data when the absorption bands are strong.[7] In the present case, however, all the absorption bands observed was very weak, so no special correction for the observed intensity data was made.

The observed spectra, as is shown in Figs. 1 through 3, contain two absorption bands arising from the *trans* and the *gauche* isomers of 1,2-dibromoethane. We separated the two slightly overlapping bands by the method of least-squares,

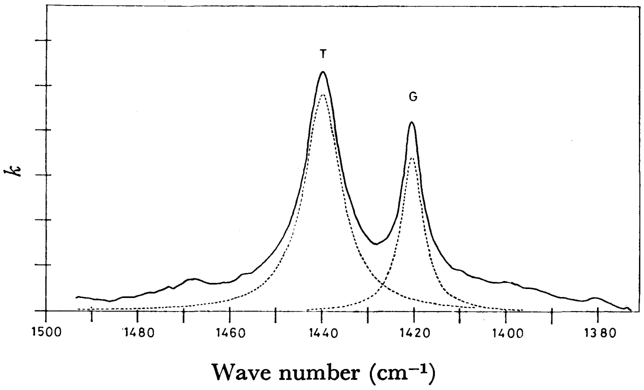

Fig. 1. Absorption index curve for the scissoring vibration bands of liquid 1,2-dibromoethane. Solid line; observed curve, broken line; calculated Lorentzian curve.

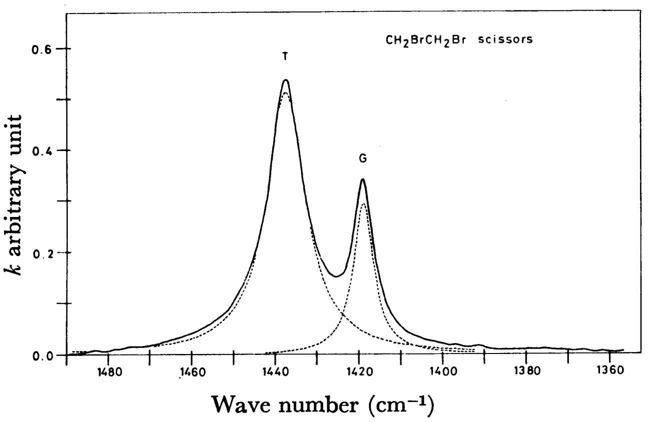

Fig. 2. Absorption index curve for the scissoring vibration bands of 20 mol% solution of 1,2-dibromoethane in *cis*-1,2-dichloroethylene. The unit of the ordinate is arbitrary. Meanings of the lines are the same as in Fig. 1.

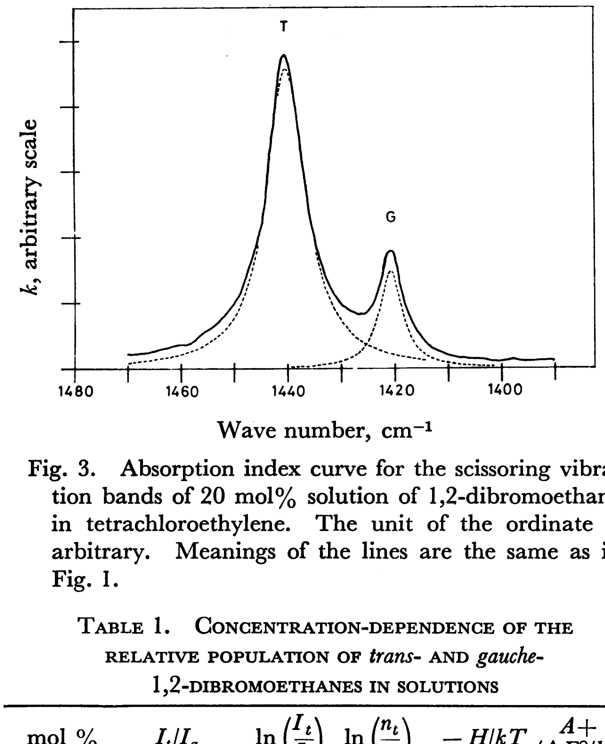

Fig. 3. Absorption index curve for the scissoring vibration bands of 20 mol% solution of 1,2-dibromoethane in tetrachloroethylene. The unit of the ordinate is arbitrary. Meanings of the lines are the same as in Fig. 1.

Table 1. Concentration-dependence of the relative population of *trans*- and *gauche*-1,2-dibromoethanes in solutions

mol %	I_t/I_g	$\ln\left(\frac{I_t}{I_g}\right)$	$\ln\left(\frac{n_t}{n_g}\right)$	$-H/kT$	$A+(\Delta E°/kT)$
— Solutions in *cis*-1,2-dichloroethylene —					
100.00	3.37(0.13)	1.215	0.300$^{a)}$	0.508	0.808
79.76	3.16(0.16)	1.151	0.236	0.605	0.841
59.89	2.82(0.14)	1.037	0.122	0.705	0.827
39.59	2.55(0.14)	0.936	0.021	0.800	0.821
20.22	2.35(0.23)	0.854	−0.061	0.884	0.823
— Solutions in tetrachloroethylene —					
79.84	3.64(0.18)	1.292	0.377	0.395	0.772
59.98	4.12(0.22)	1.416	0.501	0.291	0.792
40.21	4.47(0.20)	1.497	0.582	0.209	0.791
21.75	5.17(0.32)	1.643	0.728	0.136	0.864

I_t/I_g is the relative intensity of the scissoring vibration bands. Numbers in parentheses indicate the standard deviations. n_t/n_g is the relative population obtained from $\ln(I_t/I_g)$ (see the text). H is calculated through Eq. (15). The sixth column is the sum of the fourth and the fifth columns. a) See Ref. 4.

assuming a Lorentzian band shape, and estimated the relative values of the integrated intensities. The separated bands are illustrated by the broken lines in Figs. 1 through 3. Table 1 contains the relative intensity at each concentration thus obtained. The standard deviations attached to the relative intensities in Table 1 were estimated from the deviation between the observed and the calculated absorption curves.

The logarithmic relative population, $\ln(n_t/n_g)$, differs from the corresponding logarithmic relative intensity, $\ln(I_t/I_g)$, only by a constant which is independent of the concentration, if the absolute intensities of the *trans* and the *gauche* isomers do not change in the concentration-variation.[8] The constant was determined so as to make $\ln(n_t/n_g)$ in pure liquid equal to

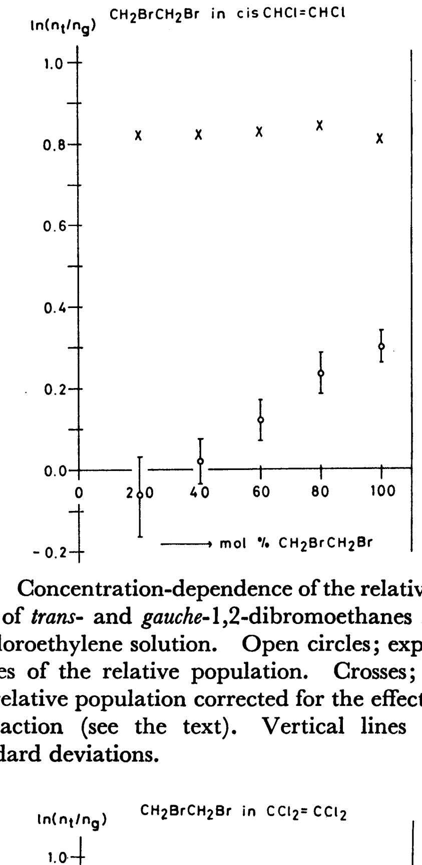

Fig. 4. Concentration-dependence of the relative population of *trans*- and *gauche*-1,2-dibromoethanes in *cis*-1,2-dichloroethylene solution. Open circles; experimental values of the relative population. Crosses; values of the relative population corrected for the effect of dipole interaction (see the text). Vertical lines show the standard deviations.

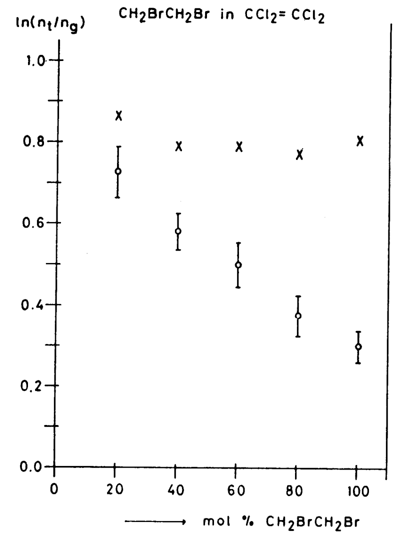

Fig. 5. Concentration-dependence of the relative population of *trans*- and *gauche*-1,2-dibromoethanes in tetrachloroethylene solution. Meanings of the symbols are the same as in Fig. 4.

0.300, the value of which had previously been determined by the present authors.[4] The value of $\ln(n_t/n_g)$ was determined at each concentration from the corresponding $\ln(I_t/I_g)$ by substracting the constant. The results are shown in Table 1 and Figs. 4 and 5.

Theory

Usually the enrgy difference, ΔE, and the relative population, n_t/n_g, are related by the van't Hoff equation:

$$\ln(n_t/n_g) = A + (\Delta E/kT) \tag{1}$$

where A is a constant, k is the Boltzmann's constant, and T is the absolute temperature. Let us consider the effect of intermolecular interaction on the magnitude of ΔE. The effect is, in principle, a function of the temperature, the concentration, and other parameters characterizing the system. We may write:

$$\Delta E = \Delta E^\circ + H \tag{2}$$

and

$$\ln(n_t/n_g) = A + (\Delta E^\circ/kT) + (H/kT) \tag{3}$$

where ΔE^0 means the intrinsic energy difference or the energy difference of the rotational isomers when they are well isolated from other molecules, and where H is the effect of intermolecular interactions.

From the microscopic point of view, the *gauche* and the *trans* isomers are considered to differ only in that the former possesses a dipole moment, while the latter does not. The other physical properties may be regarded as almost identical for the two isomers. H, then, arises from the dipole-interaction of a *gauche* isomer with other molecules. In the following, we will focus our attention on a special *gauche* isomer, which will be designated as "central", and try to find the energy of its dipole interaction with the surrounding molecules. It may be expedient to distinguish here the following four types of dipoles which interact with the central *gauche*-dipole; (1) the dipole moments of other *gauche* molecules, (2) the dipole moments of solvent molecules (if any), (3) the dipole moments of other molecules of 1,2-dibromoethane (*gauche*+*trans*) induced by the central *gauche*-dipole, and (4) the dipole moments of solvent molecules induced by the central *gauche*-dipole. The reason why we do not distinguish the *trans* and the *gauche* isomer in (3) is that the refractive index, and hence the polarizability, is known only for the equilibrium mixture of the *trans* and the *gauche* isomers.

Let the polar coordinates of the central *gauche*-dipole, $\boldsymbol{\mu}_g$, of another dipole, $\boldsymbol{\mu}$, and of the radius vector, $\boldsymbol{r}$, pointing from $\boldsymbol{\mu}_g$ to $\boldsymbol{\mu}'$, be (θ_g, φ_g), (θ', φ'), and (θ_r, φ_r) respectively. $\boldsymbol{\mu}'$ can be any one of the aforementioned four types of interacting dipoles. The dipole, $\boldsymbol{\mu}'$, induces an electric field at the point of $\boldsymbol{\mu}_g$. The component of the field along the direction of $\boldsymbol{\mu}_g$ is written as:[11]

$$F = -\frac{\mu'}{r^3}(A+B+C+D+E+F) = -\frac{\mu'}{r^3}\Omega \tag{4}$$

where A, B, C, D, E, and F are expressed in terms of the spherical harmonic with respect to polar coordinates, (θ_g, φ_g), (θ', φ'), and (θ_r, φ_r),[11] and where Ω means the sum of these six terms. Similarly, $\boldsymbol{\mu}_g$ induces an electric field in the surroundings and produces an induced moment, $\boldsymbol{\mu}_i$:

$$\mu_i = -\frac{\alpha\mu_g}{r'^3}\Omega' \tag{5}$$

where α is the polarizability of the molecule in the surroundings. The primes on r and Ω in Eq. (5) show that r Ω of Eq. (5) are not necessarily the same as those in Eq. (4). The induced moment, $\boldsymbol{\mu}_i$, in turn induces and electric field on the position of $\boldsymbol{\mu}_g$. The component of the field along the direction of $\boldsymbol{\mu}_g$ is, according to Eq. (4):

$$F = \frac{\alpha\mu_g}{r'^6}\Omega'^2 \tag{6}$$

Now we can write the induced field at the position and along the direction of the central $\boldsymbol{\mu}_g$:

$$F_1 = -\frac{\mu_g}{r_g^3}\Omega_g \tag{7a}$$

$$F_2 = -\frac{\mu_s}{r_s^3}\Omega_s \tag{7b}$$

$$F_3 = \frac{\alpha_m\mu_g}{r_m^6}\Omega_m^2 \tag{7c}$$

$$F_4 = \frac{\alpha_s\mu_g}{r_s^6}\Omega_s^2 \tag{7d}$$

where all the quantities suffixed with g, s, or m, except for the μ_g in Eq. (7c) or (7d), which stands for the dipole moment of the central *gauche* isomer, are related with the surrounding *gauche* isomers. the solvent molecules, or the mixture of the *trans* and the *gauche* isomers, respectively. The total interaction energy, $\mathscr{H}$, of the central *gauche* isomer is, then:

$$\mathscr{H} = \mu_g(F_1+F_2+F_3+F_4) \tag{8}$$

To obtain H of Eq. (2) or (3), one must average Eq. (8) over all the possible orientations and distances of the interacting pair. In doing so, it must be considered that the relative orientation of two dipole moments is distributed according to their interaction energy; that is, energetically more stable configurations are distributed more than the less stable configurations. This concept is considered in the averaging process by introducing the Boltzmann distribution function:

$$W = w\exp(-\mathscr{H}/kT) \tag{9}$$

where w is a constant which is to be determined by the normalization condition:[12]

$$w\int_v \mathrm{d}\tau = n \tag{10}$$

where v indicates a sphere of the unit volume, at the center of which the central *gauche*-dipole is situated, where $\mathrm{d}\tau$ is the volume element:

$$\mathrm{d}\tau = r^2\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\,\mathrm{d}r \tag{11}$$

and where n is the number of molecules in v. Now, the average way be expressed in terms of an integral:

$$H = \sum_i w_i\int \mu_g F_i\exp(-\mu_g F_i/kT)\,\mathrm{d}\tau \tag{12}$$

where the suffix i corresponds to the four terms of Eq. (7). In Eq. (12), it is assumed that the averages of the four terms of Eq. (8) can be taken independently. In other words, the orientational correlation between neighbour dipoles is assumed to have no effect on the interaction of the dipoles with the central *gauche*-dipole.

To calculate the integral in Eq. (12), we expand the exponential and neglect the higher terms than the second:[13]

$$H=\sum_i w_i\int\mu_g F_i[1-(\mu_g F_i/kT)]\mathrm{d}\tau \tag{13}$$

Integration over orientations is performed by the use of the orthonormality of the spherical harmonics, which results in:[13]

$$\int\Omega\mathrm{d}\tau'=\int\Omega^3\mathrm{d}\tau'=0$$

and

$$\int\Omega^2\mathrm{d}\tau'=\frac{128}{3}\pi^3 \tag{14}$$

where $\mathrm{d}\tau'$ is the angular part of the volume element. A lower limit, a_0, must exist for the integration over the distance; the meaning of this is that two molecules can not come closer than a_0. We estimated the a_0 from the density and the molecular weight, assuming a rigid sphere for each molecule.[14] The result is:

$$\begin{aligned}H=&-\frac{4\pi^2}{27}\frac{\mu_g{}^4}{kT}\frac{\rho}{W_m}c_m\frac{N_a{}^2}{1+(n_t/n_g)}\\&-\frac{4\pi^2}{27}\alpha_m\mu_g{}^2\frac{\rho}{W_m}c_mN_a{}^2\\&-\frac{32\pi^2}{27}\left(\frac{\mu_g{}^2\mu_s{}^2}{kT}+\alpha_s\mu_g{}^2\right)\frac{c_{ms}N_a{}^2}{\left[\left(\frac{W_m}{\rho}\right)^{1/3}+\left(\frac{W_{ms}}{\rho_s}\right)^{1/3}\right]^3}\end{aligned} \tag{15}$$

where N_a is Avogardo's number, where W_m, ρ, and c_m are the molecular weight, the density, and the molar concentration (mol/cm^3) respectively of the solute, and where the same symbols suffixed with s refer to those of the solvent molecule.

Results and Discussion

Figures 4 and 5 show the experimental values of the relative populations of *trans*- and *gauche*-1,2-dibromoethanes in solutions. It may be seen from the figures that the population varies on going from pure liquid to dilute solutions: it increases in a tetrachloroethylene solution. In other words, the numbers of the *gauche* isomer increase as the polarity of the environment increases.

To see whether or not the model of dipole interaction, developed in the last section, is appropriate, we calculate H/kT from Eq. (15) at each concentration and subtract it from the observed value of $\ln(n_t/n_g)$. The resultant value should be $A+(\Delta E^0/kT)$, as may be seen from Eq. (2), and should remain constant over all concentrations. In the calculation, α_m and α_s were estimated from the values of the refractive indices[5] using the Lorentz-Lorenz formula, the densities were taken from a standard table,[5] and μ_g and μ_s (of *cis*-1,2-dichloroethylene) were taken to be 2.20 D[15] and 1.89 D[16] respectively. The results of the subtraction are shown in Table 1 and in Figs. 4 and 5. It may be seen from the table and the figures that the resultant value remains almost constant for all the concentrations; this indicates the validity of the model used in the calculation. Thus, it may be concluded that the equilibrium properties of the *trans*- and *gauche*-1,2-dibromoethanes in solutions are fully described by the model of dipole-interaction, Eq. (15).

Incidentally, Eq. (15) tells us that the energy difference, ΔE, should change in value according to the change in temperature as well as that in concentration. The temperature-effect data of the reference[4] can also be explained by the use of Eq. (15).

It should be noted that, in the present calculation, we are considering the environments to be built up of gas-like molecules dispersed in a vacuum to give the actual density, instead of looking them as continuous dielectrics. The latter model yields the famous reaction field of Onsager.[17] The present approach has a close resemblance to the latter in concept, but it has resulted in a quite different equation which is expressed in terms of the dipole moment and the polarizability instead of the dielectric constant, a very macroscopic quantity. The present theory is not, however, a fully molecular theory in the sense that the polarizability is calculated from such macroscopic quantities as the refractive index and the density through the Lorentz-Lorenz formula, and in that the molecular radius is estimated in the same way as in Onsager.[14,17] A comparison of the numerical results of the present equation with those based on the reaction field shows that the two approaches do not give the same results for the averaged electric field acting on a molecule.[4] It can be said at the same time that the present model can well describe the magnitude of the change in the averaged electric field in the concentration- or temperature-variation. To clarify the difference existing between the two approaches is interesting and may be a problem for the future.

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8) In the discussions of the text, it is assumed that the absolute intensity of a *gauche* or a *trans* isomer does not change in dilution. This assumption, however, is not strictly true. The authors are going to show, in a subsequent paper,[9] tha the absolute intensities of the infrared absorption bands may change, in some cases about a factor of two, on going from a pure liquid to a dilute solution. An equation is to be presented to describe the intensity change: the basic concept is that the transition moment, m_1, differs in liquid media from that of an isolated molecule, μ_1:

$$m_1 = \mu_1 + \alpha_1 \langle \mathscr{F} \rangle_{av}$$

where α_1 is the transition polarizability and where $\langle \mathscr{F} \rangle_{av}$ is the averaged field acting on the absorbing molecule. The most contributing term in $\langle \mathscr{F} \rangle_{av}$ is, in the case of liquid 1,2-dibromoethane;

$$\frac{4\pi^2}{27} N_a{}^2 \frac{\mu_g{}^2}{kT} \left(\frac{\rho}{W_m} \right)^2 \frac{1}{1+(n_t/n_g)}$$

where the notations are the same as in the text. We must remember that, among the two scissoring vibrations of *trans*-1,2-dibromoethane, one (b_u) is Raman-inactive ($\alpha_1=0$) and the other (a_g) is infrared-inactive ($\mu_1=0$). Therefore, one might expect that the absolute intensity of the scissoring vibration of the *trans* isomer does not change. On the other hand, the two scissoring vibrations (a and b) of the *gauche* isomer are active in both the infrared and Raman spectra, so one must consider the intensity-change in this case. The results of the present measurement, combined with the value of the relative population in Table 1, yield 504 cm²/mol for the absolute intensity of the scissoring vibration band (a and b combined) of the *gauche* isomer, after the Polo-Wilson correction.[10] This corresponds to m_1 of 0.0449 D. If α_1 is assumed to be 0.1 Å³, which might be unrealistically large for this vibration, then μ_1 becomes 0.0441 D and the corresponding intensity is 487 cm²/mol. Therefore, the change in the absolute intensity is only about 3.5% even for the large value of α_1, on going from a pure liquid to a very dilute solution in nonpolar solvents. Thus, the intensity-change does not exceed the experimental errors in the present work.

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12) More precisely, Eq. (10) should be written as:

$$w\int_v \exp(-\mathscr{H}/kT)\mathrm{d}\tau = n.$$

However, the higher-order terms than the first, in the expansion of the exponential, yield only very small contributions to the result, and so Eq. (10) is justified.

13) The next nonvanishing term in the expansion of H can be calculated by the use of this relation:

$$\int \Omega^4 \mathrm{d}\tau' = \frac{1536}{25}\pi^3.$$

Calculation showed that the contribution from the next nonvanishing term is, at most, about 1% of Eq. (15) in the case of 1,2-dibromoethane in solutions.

14) In principle, one must use a radial distribution function in the integration of the radial part in Eq. (13). The radial distribution function can not, however, be used for large molecules. The present assumption is identical with putting the radial distribution function equal to unity for $r \geqq a_0$ and to 0 for $r < a_0$.

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