

Contribution of interatomic repulsion forces to the broadening of vibration bands of planar XY_3 molecules

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The effect of short-range repulsion forces on shape of A_1 vibration bands of planar XY_3 molecules in liquid phase is described. The repulsion forces are described by the Born—Mayer potential. Application of the perturbation theory and stochastic models of reorientation and translation of molecules gives results which for a simple model of radial distribution function agree semiquantitatively with experiment.

В работе описывается влияние отталкивающих сил ближнего порядка на форму колебательных полос A_1 плоских молекул типа XY_3 в жидкостях. Отталкивающие силы описываются потенциалом Борна—Майэра. При помощи теории возмущения и стохастических моделей переориентировки молекул и поступательного движения были получены результаты, которые находятся в полуколичественном согласии простой модели радиальной функции состояний с экспериментом.

The effect of short-range repulsion forces on the bandwidths of vibrational spectra of liquids was first explained by Valiev [1]. His theory was later modified and applied to spherical top molecules [2]. Recently, several papers [2—7] appeared, where vibrational bandwidths were studied. This paper is an extension of theory to planar XY_3 molecules with D_{3h} symmetry. Since the theory of the effect of repulsion forces on bandwidths was already described elsewhere [2], we shall only briefly review the basic ideas.

Theory

It follows from the perturbation theory that the probability p of transition $v_k \rightarrow v_k - 1$, where v_k is vibrational quantum number of k -th vibration, is given by the following expression

$$p(v_k \rightarrow v_k - 1) = \hbar^{-2} \int_{-\infty}^{\infty} \overline{H'^*(0)H'(t)} \exp(-2\pi i \omega_k t) dt \quad (1)$$

where $H' = \langle v_k | H | v_k - 1 \rangle$, ω_k is the wavenumber in cm^{-1} . The studied liquid is formed by only one type of molecule and repulsion between the i -th atom of studied molecule and j -th atom of molecule μ is given by the Born—Mayer potential

$$H(R_{i,j\mu}) = V_{ij} \exp(-\alpha_{ij} R_{i,j\mu}) \quad (2)$$

$$\mathbf{R}_{i,j\mu} = \mathbf{R}_\mu + \mathbf{A}_{j\mu} - \mathbf{A}_i \quad (3)$$

\mathbf{R}_μ is a vector connecting centres of mass of the studied molecule and molecule μ , vectors $\mathbf{A}_{j\mu}$, \mathbf{A}_i determine the positions of atom j in molecule μ and atom i in the studied molecule. It follows then

$$H' = (\hbar v_k)^{1/2} (4\pi c \omega_k)^{-1/2} \sum_{i,j,\mu} \alpha_{ij} V_{ij} \exp(-\alpha_{ij} R_{i,j\mu}) (\mathbf{N}_{i,j\mu} \mathbf{C}_{ik}) \quad (4)$$

where $\mathbf{N}_{i,j\mu} = \mathbf{R}_{i,j\mu} / R_{i,j\mu}$.

Vectors \mathbf{C}_{ik} are defined by the following transformation

$$\mathbf{S}_i = \sum_k \mathbf{C}_{ik} Q_k \quad (5)$$

Q_k is the k -th normal coordinate and \mathbf{S}_i is the displacement of atom i in this vibration (for vectors we shall use small letters if they are expressed in molecule-fixed system of coordinates and capital letters if they are expressed in laboratory system of coordinates). Averaging in eqn (1) is carried out in the following way

$$\overline{H'^*(0)H'(t)} = \int H'^*(0)H'(t) W(q_0, 0; q, t) dq_0 dq \quad (6)$$

where $W(q_0, 0; q, t) dq_0 dq$ is the probability that at time $t=0$ the values of variables are within the interval $(q_0, q_0 + dq_0)$ while at time t they are within the interval $(q, q + dq)$. It follows from eqns (3) and (4) that H' is a function of nine variables — three components of vector \mathbf{R}_μ , three Eulerian angles of molecule μ (vector $\mathbf{A}_{j\mu}$ is their function), and three Eulerian angles of the studied molecule (vector \mathbf{A}_i is their function). Therefore integration in eqn (6) must be carried out over 18 variables (9 at $t=0$ and 9 at time t). Unfortunately the integral cannot be evaluated analytically. Thus in order to evaluate the integral (6) we expand the expression $H'^*(0)H'(t)$ into the Taylor series with respect to powers of components of vector $\mathbf{A}_{j\mu} - \mathbf{A}_i$ and neglect all powers higher than the second.

We shall further assume that probability density $W(\Omega_0, 0; \Omega, t)$ for Eulerian angles Ω (which define the orientation of molecule) is given according to Ivanov's jump model [8] by the following expression

$$W(\Omega_0, 0; \Omega, t) = \sum_{L,m,n} (2L+1) (8\pi^2)^{-1} \mathbf{D}_{mn}^{L*}(\Omega_0) \mathbf{D}_{mn}^L(\Omega) \exp(-t/t_{Lm}) \quad (7)$$

where \mathbf{D}_{mn}^L are well-known rotation matrices [9] satisfying the following orthogonality relations

$$\int \mathbf{D}_{mn}^{L*}(\Omega) \mathbf{D}_{m'n'}^L(\Omega) d\Omega = 8\pi^2 / (2L+1)^{-1} \delta_{LL'} \delta_{mm'} \delta_{nn'} \quad (8)$$

If atoms Y in planar XY_3 molecule are given numbers 1—3 and atom X is given number 4 then for A_1 vibration

$$\mathbf{c}_{ik} = (3m_Y)^{-1/2} \mathbf{e}_i \quad i = 1, 2, 3 \quad (9)$$

$$\mathbf{c}_{ik} = 0 \quad i = 4 \quad (9a)$$

where \mathbf{e}_i is unit vector directed from the centre of mass to atom i .

Rather lengthy but straightforward calculation using eqns (6—9) and the Taylor expansion of expression $H'^*(0)H'(t)$ gives the following result

$$\begin{aligned} \langle H'^*(0)H'(t) \rangle_{OR} = a^2 (30m_Y)^{-1} \sum_{\mu} \{ 10\gamma_{\mu}(0)\gamma_{\mu}(t) + \delta_{\mu}(0)\delta_{\mu}(t) \cdot \\ \cdot [3(\mathbf{N}_{\mu}(0)\mathbf{N}_{\mu}(t)) - 1] \exp(-t/t_{20}) \} \end{aligned} \quad (10)$$

$\langle \rangle_{OR}$ denotes averaging over Eulerian angles, $\mathbf{N}_{\mu} = \mathbf{R}_{\mu}/R_{\mu}$, a is X—Y bond length, and t_{20} is a correlation time of the corresponding rotation matrix. The symbols γ and δ are defined as follows

$$\gamma_{\mu} = 3\beta_{YY\mu}(\alpha_{YY} - 2/R_{\mu}) + \beta_{YX\mu}(\alpha_{YX} - 2/R_{\mu}) \quad (11)$$

$$\delta_{\mu} = 3\beta_{YY\mu}(\alpha_{YY} + 1/R_{\mu}) + \beta_{YX\mu}(\alpha_{YX} + 1/R_{\mu}) \quad (12)$$

where $\beta_{ij\mu} = (\hbar v_k)^{1/2} (4\pi c \omega_k)^{-1/2} \alpha_{ij} V_{ij} \exp(-\alpha_{ij} R_{\mu})$.

In eqns (11) and (12) time-independent terms were omitted. The next step is averaging over translational coordinates with probability density given in papers [10, 11]. However, this averaging cannot be done analytically. Therefore expressions (11) and (12) will be averaged at $t=0$ and normalized time correlation function for translation is taken to be

$$g_{tr} = \exp(-t/t_{tr}) \quad (13)$$

When averaging at $t=0$ we shall use radical distribution function $\Phi(r) = 4\pi r^2 u(r)$, where $N\Phi(r) dr$ is a number of molecules in spherical layer between radii $r, r+dr$ and origin is at the centre of the studied molecule (N is a number density). Averaging gives the following result

$$\overline{H'^*(0)H'(t)} = a^2 N (15m_Y)^{-1} \{ 5G \exp(-t/t_{tr}) + D \exp[-t(t_{tr}^{-1} + t_{20}^{-1})] \} \quad (14)$$

where

$$G = 4\pi \int_0^{\infty} \gamma^2(r) r^2 u(r) dr \quad (15)$$

$$D = 4\pi \int_0^\infty \delta^2(r) r^2 u(r) dr \quad (16)$$

and after substituting to eqn (1) we obtain the final result

$$(2\pi c)^{-1} P(1 \rightarrow 0) = (60m_Y)^{-1} a^2 N (\pi c)^{-3} \hbar^{-2} \omega^{-2} [5Gt_{tr}^{-1} + D(t_{tr}^{-1} + t_{20}^{-1})] \quad (17)$$

which gives the contribution of repulsion forces to the bandwidth of fundamental A_1 in a liquid composed of planar XY_3 molecules. For evaluation of expressions G , D the knowledge of radial distribution function is required. If we use the simplest model, where $u(r) = 0$ for $0 < r < d$ and $u(r) = \text{const}$ for $r > d$ and assume that constants α_{ij} , V_{ij} are universal (α , V), then G , D are given by the following expressions

$$G = C_0(2d^2\alpha - 6d + 5/\alpha) \quad (18)$$

$$D = C_0(2d^2\alpha + 6d + 5/\alpha) \quad (19)$$

$$C_0 = 4\hbar\alpha^2 V^2 (c\omega_k)^{-1} \exp(-2ad) \quad (20)$$

If the following typical values are substituted to eqns (17—20), $a = 150$ pm, $d = 300$ pm, $\alpha = 0.03$ pm⁻¹, $V = 3.2 \times 10^{-16}$ J, $t_{tr} = 2$ psec, $t_{20} = 1$ psec, $m_Y = 2.5 \times 10^{-22}$ g, $\omega = 1000$ cm⁻¹ and $N = 2.5 \times 10^{22}$ cm⁻³, then the contribution of studied effect to the bandwidth is 1.5 cm⁻¹. Since the observed bandwidths of A_1 fundamentals are usually in the interval 6—20 cm⁻¹ and other effects also contribute, the theory outlined in this paper gives at least semiquantitative agreement with experiment.

Discussion

There are two interesting points which concern the extension of theory to symmetric top molecules. It is interesting that lowering of symmetry from spherical to axial one did not bring about significant complication and final equations are only a little more complex than those for XY_4 molecule [2]. It is also worth mentioning that while for XY_4 molecule the contribution to bandwidth depends only on translational correlation function, for planar XY_3 molecule this contribution depends on both the translational and rotational correlation function.

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