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Abstract

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PHYSICS

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DEPOLARIZATIONS AND INTENSITIES IN THE RAMAN SPECTRA OF BENZENE AND HEXADEUTEROBENZENE

(Presented by Academician G. S. Landsberg, 27 IX 1956)

In the present work we use the method for calculating depolarizations and intensities developed in ([1]) and detailed in ([2]). The method is applied to non-limiting compounds for the first time.

1. Totally symmetric vibrations (A_{1g})

The CH bonds in benzene are formed by carbon atoms with trigonal hybridization and need not possess cylindrical symmetry; it may be assumed that $\alpha_{q1} \neq \alpha_{q2} \neq \alpha_{q3}$ and $\alpha'_{q1} \neq \alpha'_{q2} \neq \alpha'_{q3}$. The derivatives of the polarizability tensor of the molecule with respect to the normal coordinates K_i are as follows:

$$\begin{aligned} &\frac{\partial a_{\xi\xi}}{\partial K_i} = \frac{\partial a_{\eta\eta}}{\partial K_i} = \frac{3}{\sqrt{6}} N_i \left[C_{1i}(\alpha'_{Q1} + \alpha'_{Q2}) + C_{2i}(\alpha'_{q1} + \alpha'_{q2}) \right]; \\ &\frac{\partial a_{\zeta\zeta}}{\partial K_i} = \sqrt{6} N_i \left(C_{1i}\alpha'_{Q3} + C_{2i}\alpha'_{q3} \right) \quad (i = 1, 2, 3, 4). \end{aligned} \tag{1}$$

The coefficients C_{1i}, C_{2i} and the normalizing factors N_i are known from the solution of the mechanical problem ([3]):

$$\begin{aligned} \mathrm{C_6H_6}: \quad &\nu_1 = 992\ \mathrm{cm^{-1}}; \quad N_1^2 = 0.083; \quad C_{11} = 1; \quad C_{21} = 0.037; \\ &\nu_2 = 3062\ \mathrm{cm^{-1}}; \quad N_2^2 = 1.091; \quad C_{12} = -0.085; \quad C_{22} = 1; \\ \mathrm{C_6D_6}: \quad &\nu_3 = 945\ \mathrm{cm^{-1}}; \quad N_3^2 = 0.074; \quad C_{13} = 1 \quad \cdot \quad C_{23} = 0.151; \\ &\nu_4 = 2292\ \mathrm{cm^{-1}}; \quad N_4^2 = 0.601; \quad C_{14} = -0.168; \quad C_{24} = 1. \end{aligned} \tag{2}$$

Introducing the notation

$$\begin{aligned} \alpha'_{Q1}+\alpha'_{Q2}+\alpha'_{Q3}=v; \quad \alpha'_{Q1}+\alpha'_{Q2}-2\alpha'_{Q3}=u; \\ \alpha'_{q1}+\alpha'_{q2}+\alpha'_{q3}=d; \quad \alpha'_{q1}+\alpha'_{q2}-2\alpha'_{q3}=c, \end{aligned} \tag{3}$$

we represent the squares of the traces $b^2_{i'}$ and the anisotropies $g^2_{i'}$ of the derivative polarizability tensors in the form

$$\begin{aligned} b^2_{i'} &= 6N_i^2(C_{1i}v+C_{2i}d)^2, \\ g^2_{i'} &= \frac{3}{2}N_i^2(C_{1i}u+C_{2i}c)^2. \end{aligned} \tag{4}$$

In (4), the experimental values of the quantities are given

$$S_i=\frac{5b'^2_i+7g'^2_i}{(5b'^2+7g'^2)_{458}}, \tag{5}$$

where the denominator refers to the 458 cm^{-1} line of CCl_4, and its numerical value is not indicated in (4). Therefore, only the ratios $u:v:d:c$ are determined on the basis of the experimental values of the quantities

$$\rho_i=\frac{6g'^2_i}{5b'^2_i+7g'^2_i} \quad (i=1,2,3,4) \tag{6}$$

and, for example, of the ratios $S_1/S_2,\ S_3/S_2,\ S_4/S_2$. Substituting (2) into (4), (5), (6) and assuming, according to (4), $\rho_1=0.11;\ \rho_2=0.21;\ S_1/S_2=0.267$, we find:

$$d=1.090c; \quad u=1.180c; \quad v=1.837c, \tag{7}$$

whereas in paraffinic hydrocarbons [(1)] $d=1.95c$. The signs in solving the equations were chosen so that u,v,c,d would have the same sign, since all these quantities are positive by their physical meaning. Substitution of (7) into (4), (5), (6) makes it possible to find ρ_3,ρ_4 and $S_3/S_2,\ S_4/S_2$ (see Table 1).

Table 1

	Observed [(4)]	Calculated
ρ_3	0.11	0.11
ρ_4	0.21	0.23
S_3/S_2	0.24	0.27
S_4/S_2	0.47	0.40

The quantities (2) differ somewhat from those found in the article [(3)]. They have been refined so that the quantities (4) exactly satisfy the sum rule [(5)].

2. Nonplanar degenerate vibrations (E_g^-)

Calculation of the projection of the momentum M in Jacobi coordinates [(1)] leads to the formulas:

$$M_\xi = \sqrt{3}\,[m_{\mathrm{H(D)}}(a+b)^2\dot{\varphi}_{\mathrm{H(D)}} + m_{Ca}^2\dot{\varphi}_C]; \quad M_\zeta = 0; \tag{8}$$

$$\varphi_{\mathrm{H(D)}} = \frac{1}{\sqrt{3}}\left(-\varphi_1 - \frac{\varphi_2}{2} + \frac{\varphi_3}{2} + \varphi_4 + \frac{\varphi_5}{2} - \frac{\varphi_6}{2}\right); \tag{9}$$

$$\varphi_C = \frac{1}{\sqrt{3}}\left(-\varphi_7 - \frac{\varphi_8}{2} + \frac{\varphi_9}{2} + \varphi_{10} + \frac{\varphi_{11}}{2} - \frac{\varphi_{12}}{2}\right), \tag{10}$$

where a, b are the lengths of the CC and CH(D) bonds; $a = 1.39$ Å; $b = 1.08$ Å; $\varphi_1, \ldots, \varphi_6$; $\varphi_7, \ldots, \varphi_{12}$ are angles characterizing the displacement of the H and C atoms out of the plane of the ring. From the geometric picture of nonplanar vibrations [(1)] it follows that

$$\varphi_{\mathrm{H(D)}} = \frac{b}{a+b}\Phi_{\mathrm{H(D)}} + \frac{a}{a+b}\Phi_C; \quad \varphi_C = \Phi_C; \tag{11}$$

$$\Phi_{\mathrm{H(D)}} = \frac{1}{\sqrt{3}}\left(-\Phi_1 - \frac{\Phi_2}{2} + \frac{\Phi_3}{2} + \Phi_4 + \frac{\Phi_5}{2} - \frac{\Phi_6}{2}\right) \tag{12}$$

$$\Phi_C = \frac{1}{\sqrt{3}}\left(-\frac{\Phi_7}{2} - \Phi_8 - \frac{\Phi_9}{2} + \frac{\Phi_{10}}{2} + \Phi_{11} - \frac{\Phi_{12}}{2}\right), \tag{13}$$

where $\Phi_1, \ldots, \Phi_6$; $\Phi_7, \ldots, \Phi_{12}$ are angles characterizing the displacement of the CH(D) and CC bonds out of the plane of the ring. The symmetry coordinate of the nonplanar vibrations is:

$$\rho = \rho_{E_g\text{–II}} = \frac{1}{\sqrt{3}}\left(-\rho_1 - \frac{\rho_2}{2} + \frac{\rho_3}{2} + \rho_4 + \frac{\rho_5}{2} - \frac{\rho_6}{2}\right) = \Phi_H - \Phi_C, \tag{14}$$

where ρ_i are natural vibrational coordinates. Taking $\rho = NK$, $\varphi_H = E_1K$, $\varphi_C = E_2K$, where K is the normal coordinate, and using (8)–(14), we find:

$$E_{1\mathrm{H(D)}} = \frac{b}{a+b}N_{\mathrm{H(D)}}\frac{I_C}{I_C + I_{\mathrm{H(D)}}}, \quad E_{2\mathrm{H(D)}} = -\frac{b}{a+b}N_{\mathrm{H(D)}}\frac{I_{\mathrm{H(D)}}}{I_C + I_{\mathrm{H(D)}}}; \tag{15}$$

$$I_C = 3m_{Ca}^2; \quad I_{\mathrm{H(D)}} = 3m_{\mathrm{H(D)}}(a+b)^2. \tag{16}$$

Here N_H, N_D are normalization factors for C_6H_6 and C_6D_6.

The derivative of the polarizability tensor with respect to the normal coordinate is

$$\left(\frac{\partial a_{\eta\zeta}}{\partial K}\right)_{\mathrm{H(D)}} = \frac{\partial a_{\eta\zeta}}{\partial \varphi_{\mathrm{H(D)}}} E_{1\mathrm{H(D)}} + \frac{\partial a_{\eta\zeta}}{\partial \varphi_C} E_{2\mathrm{H(D)}} = g'_{\mathrm{H(D)}}. \tag{17}$$

From the theory of Wolkenstein and Eliashevich one can find ([1]):

$$\frac{\partial a_{\eta\zeta}}{\partial \Phi_{\mathrm{H(D)}}} = \sqrt{3}\, x; \qquad \frac{\partial a_{\eta\zeta}}{\partial \Phi_C} = \sqrt{3}\, y, \tag{18}$$

where

$$x = \alpha_{q1} + \alpha_{q2} - 2\alpha_{q3}; \quad y = \alpha_{Q1} + \alpha_{Q2} - 2\alpha_{Q3}. \tag{19}$$

The anisotropy of the polarizability tensor of the molecule ([7]) is equal to

$$g = 3(x + y) = 5.96\,\text{Å}^3. \tag{20}$$

Substitution of expressions (11), (15), (18), (19) into (17) gives:

$$g'_{\mathrm{H(D)}} = N_{\mathrm{H(D)}} z_{\mathrm{H(D)}}; \quad z_{\mathrm{H(D)}} = \sqrt{3}\, x - \frac{b}{a+b}\frac{g}{\sqrt{3}}\frac{I_{\mathrm{H(D)}}}{I_C + I_{\mathrm{H(D)}}}. \tag{21}$$

The theoretical ratio of the intensities J of the E_g^- lines of C_6D_6 and C_6H_6 is

$$\tau = \frac{J_D}{J_H} = \frac{\nu_D}{\nu_H}\frac{z_D^2}{z_H^2}\frac{1-\exp(-h\nu_H/kT)}{1-\exp(-h\nu_D/kT)}\left(\frac{\nu_0 - \nu_D}{\nu_0 - \nu_H}\right)^4, \tag{22}$$

where ν_0 is the frequency of the undisplaced line, $\nu_D = 661$ cm^{-1} and $\nu_H = 849$ cm^{-1}. Formula (22) was obtained using the relations:

$$\frac{\nu_H}{\nu_D} = \sqrt{\frac{\mu_D}{\mu_H}} = \frac{N_H}{N_D} = \sqrt{\frac{A_H}{A_D}}, \tag{23}$$

where A_H, A_D are the kinematic coefficients of C_6H_6 and C_6D_6, and μ are the reduced moments of inertia:

$$\mu_{\mathrm{H(D)}} = \frac{I_{\mathrm{H(D)}} I_C}{I_C + I_{\mathrm{H(D)}}}. \tag{24}$$

Formula (22) coincides with formula (10) of paper ([6]), if one sets $(1-\delta)^2 = z_D^2/z_H^2$. From (21) it follows that

$$\delta = \frac{1}{\sqrt{3}} \frac{b}{a+b} \frac{g\mu_H}{(I_C + I_D) z_H}. \tag{25}$$

The sign of δ depends on the sign of z_H. The formula for δ in the article mentioned is easily transformed to the form (25). Substituting (20), (23), (24) into (21) and taking, according to the data of ([4]), $g_D^2/g_H^2 = 0.204/0.105$, we find that

$$x = 0.22\,\text{Å}^3, \quad y = 1.76\,\text{Å}^3. \tag{26}$$

In paraffinic hydrocarbons ([1]), $x = 0.21\,\text{Å}^3$, and the values (26) may be considered reasonable. The quantity y includes the increased polarizability of the π-electrons, and therefore $y \gg x$. Substituting further (20) and (26) into (21), and (21) into (25), we obtain $\delta = +2.79$ instead of -0.676 in paper ([6]). Thus, the ratio of the intensity of the undisplaced line J_0 to J_H used in ([6]) needs refinement. We note that for $\nu_0 = 22938\ \text{cm}^{-1}$, $T = 300^\circ\text{K}$ ([4]), and upon substituting (20), (26), (21) into (22), one obtains $\tau = 2.66$. The true value of J_D/J_H may differ appreciably from τ, as is evident from formula (1) of paper ([4]).

3. Planar degenerate vibrations (E_g^+)

The calculation of the valence part of each component of the tensor of polarizability derivatives with respect to the normal coordinates is elementary. To calculate the deformation part we used formula (25) of paper ([2]). Although the latter was derived for bonds with axial symmetry, it is applicable also to the E_g^+ vibrations of benzene, since in these vibrations the angles formed by the perpendiculars to the bonds and to the plane of the molecule with the coordinate axes do not change, and the tensors do not depend on α_{Q3}, α_{q3} ([1]).

The tensors have the form:

$$E_g^{+\text{I}}: \quad \begin{pmatrix} T_l & 0 & 0 \\ 0 & -T_l & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad E_g^{+\text{II}}: \quad \begin{pmatrix} 0 & T_l & 0 \\ -T_l & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{27}$$

Here

$$T_l = N_l \left\{ \frac{\sqrt{3}}{2} \left[(\alpha'_{Q2} - \alpha'_{Q1}) C_{Ql} + (\alpha'_{q2} - \alpha'_{q1}) C_{ql} \right] + \left(\alpha_{Q1} - \alpha_{Q2} - \frac{\alpha_{q1}}{2} + \frac{\alpha_{q2}}{2} \right) C_{\gamma l} - \sqrt{\frac{3}{2}} (\alpha_{q1} - \alpha_{q2}) C_{\beta_b l} \right\}, \tag{28}$$

where l is the number of the frequency E_g^+, and C are coefficients determining the form of the vibrations in the symmetry coordinates E_g^+: Q, q, γ, β_b ([3]).

Analogously to the case of A_{1g}, from the experimental values ([4]) one can find the ratios of the electro-optical parameters entering into (28). However, such a calculation appears insufficiently justified, since for the 1600 cm^{-1} frequency of benzene there is a Fermi resonance splitting, and the influence of the latter on the intensities is not reflected within the framework of the theory under consideration.

The present work had already been completed when we became acquainted with paper ([8]), devoted to the same problem. In that paper x and y are not determined, but from comparison of the formulas of that paper with (21) it follows that

$$x = \frac{b}{\sqrt{3}} \frac{\partial \alpha_{zz}^*}{\partial S_{10}} = 0.03 \text{ Å}.$$

Evidently, the value (26) is closer to the true one.

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Note: Figure translations are in progress. See original paper for figures.