The Normal Vibrations of Ethylene Halides.

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In the preceding article⁽¹⁾ it was established that the Raman lines observed in the solid state correspond to the symmetric vibrations of the *trans*-form of $C_2H_4X_2$, while those disappearing upon solidification to the antisymmetric vibrations, etc. This fact is very useful for the assignment of the fundamental frequencies of ethylene halides.

In our previous paper⁽²⁾ we calculated the normal frequencies of $C_2H_4X_2$ considering CH_2-group as one particle, because it was chiefly in the lower frequency region that we were interested. To treat mathematically C-H vibrations as well as their effects on chain frequencies, we must consider the molecule as a system of eight particles having eighteen

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(1) S. Mizushima and Y. Morino, this Bulletin, **13** (1938), 182. See also S. Mizushima, Y. Morino, and S. Noziri, *Nature*, **137** (1936), 945; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **29** (1936), 63.

(2) S. Mizushima and Y. Morino, *Sci. Papers Inst. Chem. Phys. Research* (Tokyo), **26** (1934), 1.

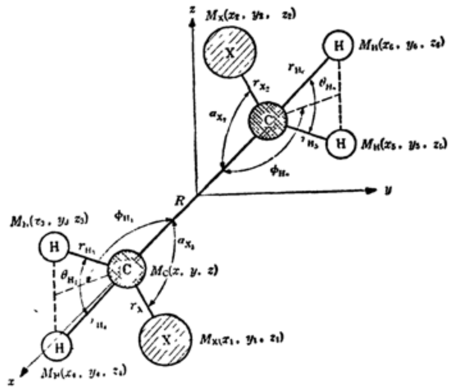

Fig. 1.

normal modes of vibrations. The equilibrium position of this system is the *trans*-form as shown in Fig. 1. It has the symmetry of C_{2h}, viz. one plane of symmetry and one centre of symmetry. The system makes a small vibration about this configuration. Let M_C, M_X, and M_H be the masses of carbon, halogen, and hydrogen atoms respectively, and x_i, y_i, z_i be their coordinates. The kinetic energy of this system T is easily separated as follows:

$$T = T_1 + T_2 + T_3 + T_4$$

where

$$\begin{aligned} T_1 = {} & \frac{1}{4}M_C\Big[(\dot{x}-\dot{x}')^2+(\dot{y}-\dot{y}')^2\Big]+\frac{1}{4}M_X\Big[(\dot{x}_1-\dot{x}_2)^2+(\dot{y}_1-\dot{y}_2)^2\Big] \\ & +\frac{1}{8}M_H\Big[(\dot{x}_3+\dot{x}_4-\dot{x}_5-\dot{x}_6)^2+(\dot{y}_3+\dot{y}_4-\dot{y}_5-\dot{y}_6)^2+(\dot{z}_3-\dot{z}_4-\dot{z}_5+\dot{z}_6)^2\Big], \end{aligned}$$

$$\begin{aligned} T_2 = {} & \frac{1}{4}M_C\Big[(\dot{x}+\dot{x}')^2+(\dot{y}+\dot{y}')^2\Big]+\frac{1}{4}M_X\Big[(\dot{x}_1+\dot{x}_2)^2+(\dot{y}_1+\dot{y}_2)^2\Big] \\ & +\frac{1}{8}M_H\Big[(\dot{x}_3+\dot{x}_4+\dot{x}_5+\dot{x}_6)^2+(\dot{y}_3+\dot{y}_4+\dot{y}_5+\dot{y}_6)^2+(\dot{z}_3-\dot{z}_4+\dot{z}_5-\dot{z}_6)^2\Big], \end{aligned}$$

$$\begin{aligned} T_3 = {} & \frac{1}{4}M_C(\dot{z}-\dot{z}')^2+\frac{1}{4}M_X(\dot{z}_1-\dot{z}_2)^2 \\ & +\frac{1}{8}M_H\Big[(\dot{x}_3-\dot{x}_4-\dot{x}_5+\dot{x}_6)^2+(\dot{y}_3-\dot{y}_4-\dot{y}_5+\dot{y}_6)^2+(\dot{z}_3+\dot{z}_4-\dot{z}_5-\dot{z}_6)^2\Big], \end{aligned}$$

and

$$\begin{aligned} T_4 = {} & \frac{1}{4}M_C(\dot{z}+\dot{z}')^2+\frac{1}{4}M_X(\dot{z}_1+\dot{z}_2)^2 \\ & +\frac{1}{8}M_H\Big[(\dot{x}_3-\dot{x}_4+\dot{x}_5-\dot{x}_6)^2+(\dot{y}_3-\dot{y}_4+\dot{y}_5-\dot{y}_6)^2+(\dot{z}_3+\dot{z}_4+\dot{z}_5+\dot{z}_6)^2\Big]. \end{aligned}$$

The coordinates $x-x'$, $y-y'$, etc. belonging to the first part T_1 are totally symmetric, i.e. symmetric to the centre of symmetry as well as to the plane of symmetry. The coordinates $x+x'$, $y+y'$, etc. belonging to the second part T_2 are antisymmetric to the centre and symmetric to the plane. The coordinates of the third part T_3 are symmetric to the centre and antisymmetric to the plane. The coordinates of the last part T_4 are antisymmetric both to the centre and to the plane. (See Table 1). It can be shown that the expression of the potential energy is also splitted into these four groups, although we assume the general quadratic form for it. The fundamental frequencies are thus separated into the four classes.

Table 1.

		Class I	Class II	Class III	Class IV
Centre of symmetry		sym.	antisym.	sym.	antisym.
Plane of symmetry		sym.	sym.	antisym.	antisym.
Coordinates of	carbon atoms	$x-x'$ $y-y'$	$x+x'$ $y+y'$	$z-z'$	$z+z'$
	halogen atoms	x_1-x_2 y_1-y_2	x_1+x_2 y_1+y_2	z_1-z_2	z_1+z_2
	hydrogen atoms	$x_3+x_4-x_5-x_6$ $y_3+y_4-y_5-y_6$ $z_3-z_4-z_5+z_6$	$x_3+x_4+x_5+x_6$ $y_3+y_4+y_5+y_6$ $z_3-z_4+z_5-z_6$	$x_3-x_4-x_5+x_6$ $y_3-y_4-y_5+y_6$ $z_3+z_4-z_5-z_6$	$x_3-x_4+x_5-x_6$ $y_3-y_4+y_5-y_6$ $z_3+z_4+z_5+z_6$
Total number of coordinates		7	7	5	5
Conditions for translational motions			2		1
Conditions for rotational motions		1		2	
Number of normal coordinates		6	5	3	4
Selection rules for	Raman-spectra	active	inactive	active	inactive
	Infrared	inactive	active	inactive	active

The condition that the x-coordinate of the centre of gravity of the whole system is fixed, can be expressed by means of the coordinates belonging to Class II only:

$$M_C(\dot{x}+\dot{x}')+M_X(\dot{x}_1+\dot{x}_2)+M_H(\dot{x}_3+\dot{x}_5+\dot{x}_4+\dot{x}_6) = 0\,.$$

The same holds for the y- and z-coordinates, thus we have

$$M_C(\dot{y}+\dot{y}')+M_X(\dot{y}_1+\dot{y}_2)+M_H(\dot{y}_3+\dot{y}_4+\dot{y}_5+\dot{y}_6) = 0\,,$$

$$M_C(\dot{z}+\dot{z}')+M_X(\dot{z}_1+\dot{z}_2)+M_H(\dot{z}_3+\dot{z}_4+\dot{z}_5+\dot{z}_6) = 0\,.$$

The conditions that the system is devoid of rotation are also given in a similar way. The number of the normal modes of vibrations belonging to each class is given by the difference between the number of the coordinates mentioned above and that of the conditions of this class. The vibrations of Classes I and III are active in the Raman effect, but inactive in the infrared. The vibrations of Classes II and IV are inactive in the Raman effect, but active in the infrared. These relations are summarized in Table 1.

It is very difficult to solve the secular equation for all the 18 frequencies. For the vibrations of Classes I and II, however, the solution can be obtained in the following way: For the potential energy of these classes we assume the following expression corresponding to a valence force system:

$$V = \frac{1}{2}k\overline{\Delta R}^2+\frac{1}{2}k_X(\overline{\Delta r}^2_{X_1}+\overline{\Delta r}^2_{X_2})+\frac{1}{2}\delta_X r_X^2(\overline{\Delta\alpha}^2_{X_1}+\overline{\Delta\alpha}^2_{X_2})$$

$$+\frac{1}{2}k_H(\overline{\Delta r}^2_{H_3}+\overline{\Delta r}^2_{H_4}+\overline{\Delta r}^2_{H_5}+\overline{\Delta r}^2_{H_6})+\delta_H r_H^2(\overline{\Delta\phi}^2_{H_1}+\overline{\Delta\phi}_{H_2})+\frac{1}{2}\beta_H r_H^2(\overline{\Delta\theta}^2_{H_1}+\Delta\theta^2_{H_2}),$$

where the notations are shown in Fig. 1.

In Class I, we have $\dot{x}=-\dot{x}'$, $\dot{y}=-\dot{y}'$, $\dot{x}_1=-\dot{x}_2$, $\dot{y}_1=-\dot{y}_2$, $\dot{x}_3=\dot{x}_4=-\dot{x}_5=-\dot{x}_6$, $\dot{y}_3=\dot{y}_4=-\dot{y}_5=-\dot{y}_6$, $\dot{z}_3=-\dot{z}_4=-\dot{z}_5=\dot{z}_6$, and $\Delta r_{X_1}=\Delta r_{X_2}$, $\Delta\alpha_{X_1}=\Delta\alpha_{X_2}$, $\Delta r_{H_3}=\Delta r_{H_4}=\Delta r_{H_5}=\Delta r_{H_6}$, $\Delta\phi_{H_1}=\Delta\phi_{H_2}$, $\Delta\theta_{H_1}=\Delta\theta_{H_2}$. Through complicated calculations similar to those given in our previous paper,(2) the secular equation which designates the six totally symmetric vibrations is found to be

$$\begin{vmatrix} A_{11}\lambda^2-k, & A_{12}\lambda^2, & A_{13}\lambda^2, & A_{14}\lambda^2, & A_{15}\lambda^2, & A_{16}\lambda^2, \\ 2A_{12}\lambda^2, & A_{22}\lambda^2-k_X, & A_{23}\lambda^2, & A_{24}\lambda^2, & A_{25}\lambda^2, & A_{26}\lambda^2, \\ 2A_{13}\lambda^2, & A_{23}\lambda^2, & A_{33}\lambda^2-\delta_X r_X^2, & A_{34}\lambda^2, & A_{35}\lambda^2, & A_{36}\lambda^2, \\ 2A_{14}\lambda^2, & A_{24}\lambda^2, & A_{34}\lambda^2, & A_{44}\lambda^2-2k_H, & A_{45}\lambda^4, & A_{46}\lambda^2, \\ 2A_{15}\lambda^2, & A_{25}\lambda^2, & A_{35}\lambda^2, & A_{45}\lambda^2, & A_{55}\lambda^2-4\beta_H r_H^2, & A_{56}\lambda^2, \\ 2A_{16}\lambda^2, & A_{26}\lambda^2, & A_{36}\lambda_2, & A_{46}\lambda^2, & A_{56}\lambda^2, & A_{66}\lambda^2-2\delta_H r_H^2, \end{vmatrix} = 0,$$

where A_{ij} are the coefficients defined by the masses of the atoms and the geometrical form of the molecule by means of the following relations:

$$\left\{\begin{aligned}
A_{11} &= \frac{1}{2}M+2a^2\rho\,,\\
A_{22} &= M_{\mathrm{X}}+b_1^2\rho\,,\\
A_{33} &= M_{\mathrm{X}}r_{\mathrm{X}}^2+c_1^2\rho\,,\\
A_{44} &= 2M_{\mathrm{H}}+b_2^2\rho\,,\\
A_{55} &= 2M_{\mathrm{H}}r_{\mathrm{H}}^2+d^2\rho\,,\\
A_{66} &= 2M_{\mathrm{H}}r_{\mathrm{H}}^2\cos^2\frac{\theta_{\mathrm{H}}}{2}+c_2^2\rho\,,
\end{aligned}\right.$$

$$\left\{\begin{aligned}
A_{12} &= -\frac{1}{2}M_{\mathrm{X}}\cos\alpha_{\mathrm{X}}+ab_1\rho\,,\\
A_{13} &= \frac{1}{2}M_{\mathrm{X}}r_{\mathrm{X}}\sin\alpha_{\mathrm{X}}+ac_1\rho\,,\\
A_{14} &= -M_{\mathrm{H}}\cos\frac{\theta_{\mathrm{H}}}{2}\cos\phi_{\mathrm{H}}+ab_2\rho\,,\\
A_{15} &= M_{\mathrm{H}}r_{\mathrm{H}}\sin\frac{\theta_{\mathrm{H}}}{2}\cos\phi_{\mathrm{H}}+ad\rho\,,\\
A_{16} &= M_{\mathrm{H}}r_{\mathrm{H}}\cos\frac{\theta_{\mathrm{H}}}{2}\sin\phi_{\mathrm{H}}+ac_2\rho\,,
\end{aligned}\right.$$

$$\left\{\begin{aligned}
A_{23} &= b_1c_1\rho\,,\\
A_{24} &= b_1b_2\rho\,,\\
A_{25} &= b_1d\rho\,,\\
A_{26} &= b_1c_2\rho\,,\\
A_{34} &= c_1b_2\rho\,,\\
A_{35} &= c_1d\rho\,,\\
A_{36} &= c_1c_2\rho\,,\\
A_{45} &= b_2d\rho\,,\\
A_{46} &= b_2c_2\rho\,,\\
A_{56} &= c_2d\rho\,,
\end{aligned}\right.$$

and

$$\left\{\begin{aligned}
M &= M_{\mathrm{C}}+M_{\mathrm{X}}+2M_{\mathrm{H}}\,,\\
-1/\rho &= MR^2+4\left(M_{\mathrm{X}}r_{\mathrm{X}}^2+2M_{\mathrm{H}}r_{\mathrm{H}}^2\cos^2\frac{\theta_{\mathrm{H}}}{2}\right)\\
&\qquad -4R\left(M_{\mathrm{X}}r_{\mathrm{X}}\cos\alpha_{\mathrm{X}}+2M_{\mathrm{H}}r_{\mathrm{H}}\cos\frac{\theta_{\mathrm{H}}}{2}\cos\phi_{\mathrm{H}}\right),\\
a &= -M_{\mathrm{X}}r_{\mathrm{X}}\sin\alpha_{\mathrm{X}}+2M_{\mathrm{H}}r_{\mathrm{H}}\cos\frac{\theta_{\mathrm{H}}}{2}\sin\phi_{\mathrm{H}}\,,\\
b_1 &= M_{\mathrm{X}}R\sin\alpha_{\mathrm{X}}\,,\\
b_2 &= -2M_{\mathrm{H}}R\cos\frac{\theta_{\mathrm{H}}}{2}\sin\phi_{\mathrm{H}}\,,\\
d &= 2M_{\mathrm{H}}r_{\mathrm{H}}R\sin\frac{\theta_{\mathrm{H}}}{2}\sin\phi_{\mathrm{H}}\,,\\
c_1 &= -M_{\mathrm{X}}r_{\mathrm{X}}(2r_{\mathrm{X}}-R\cos\alpha_{\mathrm{X}})\,,\\
c_2 &= 2M_{\mathrm{H}}r_{\mathrm{H}}\cos\frac{\theta_{\mathrm{H}}}{2}\left(2r_{\mathrm{H}}\cos\frac{\theta_{\mathrm{H}}}{2}-R\cos\phi_{\mathrm{H}}\right).
\end{aligned}\right.$$

Putting $M_C = 12$, $M_H = 1.008$, $M_X = 79.92$, $r_H = 1.08\,\text{Å}$, $r_X = 2.05\,\text{Å}$, $R = 1.54\,\text{Å}$ and $\alpha = 109°28'$ for ethylene bromide, it is found that the cross terms A_{14}, $A_{15} \cdots A_{35}$, A_{36} are smaller than A_{11}, $A_{12} \cdots$, owing to the fact that the mass of hydrogen is small compared with that of bromine atom. If we neglect these cross terms, we have

$$\begin{vmatrix} A_{11}\lambda^2 - k, & A_{12}\lambda^2, & A_{13}\lambda^2, \\ 2A_{12}\lambda^2, & A_{22}\lambda^2 - k_X, & A_{23}\lambda^2, \\ 2A_{13}\lambda^2, & A_{23}\lambda^2, & A_{33}\lambda^2 - \delta_X r_X^2, \end{vmatrix} = 0 \qquad (1),$$

$$A_{44}\lambda^2 - 2k_H = 0 \qquad (2),$$

$$A_{55}\lambda^2 - 4\beta_H r_H^2 = 0 \qquad (3),$$

$$A_{66}\lambda^2 - 2\delta_H r_H^2 = 0 \qquad (4).$$

Equation (1) gives the chain frequencies of X-(CH_2)-(CH_2)-X. It can be reduced to the solution of the four body problem,⁽²⁾ if $M_C + 2M_H$ is put equal to M and the distance r_H to zero. This shows that our former treatment for the chain frequencies is sufficiently correct in this approximation, even if we take the vibrations of hydrogen atoms into consideration. The latter three equations give the frequencies of CH_2-group, viz. equation (2) gives the C-H valency frequency, equation (3) that of the deformation of H-C-H angle, and equation (4) that of the deformation of CH_2-group relative to C-C axis.

These three hydrogen frequencies as well as the three chain frequencies should be active in the Raman effect in solid ethylene bromide. The higher frequencies of ethylene bromide in the solid state 2968 cm.$^{-1}$, 1436 cm.$^{-1}$, and 1254 cm.$^{-1}$ are assigned to the C-H frequencies, while the lower frequencies 187 cm.$^{-1}$, 656 cm.$^{-1}$, and 1057 cm.$^{-1}$ to the chain frequencies. The line 2968 cm.$^{-1}$ is identified with the C-H valency vibration; the line 1436 cm.$^{-1}$ with the deformation of H-C-H angle, and the line 1254 cm.$^{-1}$ with the deformation of CH_2-group relative to C-C axis. This assignment is in conformity with the results of Ta-You Wu⁽³⁾ for C_2H_4 and of Trumpy⁽⁴⁾ for *trans*-$C_2H_2Cl_2$. Ta-You Wu assigned the line 1440 cm.$^{-1}$ of C_2H_4 to the deformation frequency of CH_2-group. Trumpy observed that the frequency 1260 cm.$^{-1}$ of *trans*-$C_2H_2Cl_2$ decreased to 992 cm.$^{-1}$ on the insertion of D in place of H, showing that this frequency

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(3) Ta-You Wu, *J. Chem. Phys.*, **5** (1937), 392.

(4) B. Trumpy, *Nature*, **135** (1935), 764.

is the deformation frequency of C-H to C-C axis. For ethylene chloride the corresponding three lines 2964 cm.$^{-1}$, 1448 cm.$^{-1}$, and 1301 cm.$^{-1}$, are identified with the totally symmetric vibrations of CH_2-groups. The force constants are thus obtained to be

$$\left\{\begin{array}{lll} k_{\mathrm{H}} = 5.19\ \times 10^5 & \text{dyne/cm.} & \\ \beta_{\mathrm{H}} = 0.607 \times 10^5 & \quad ,, & \text{for ethylene bromide,} \\ \delta_{\mathrm{H}} = 0.308 \times 10^5 & \quad ,, & \end{array}\right.$$

and

$$\left\{\begin{array}{lll} k_{\mathrm{H}} = 5.18\ \times 10^5 & \text{dyne/cm.} & \\ \beta_{\mathrm{H}} = 0.618 \times 10^5 & \quad ,, & \text{for ethylene chloride.} \\ \delta_{\mathrm{H}} = 0.330 \times 10^5 & \quad ,, & \end{array}\right.$$

For the vibrations of Class II, we obtain the following secular equation:

$$\begin{vmatrix} B_{11}\lambda^2 - k_{\mathrm{X}}, & 0, & B_{13}\lambda^2, & B_{14}\lambda^2, & B_{15}\lambda^2, \\ 0, & B_{22}\lambda^2 - \delta_{\mathrm{X}} r_{\mathrm{X}}^2, & B_{23}\lambda^2, & B_{24}\lambda^2, & B_{25}\lambda^2, \\ B_{13}\lambda^2, & B_{23}\lambda^2, & B_{33}\lambda^2 - 2k_{\mathrm{H}}, & B_{34}\lambda^2, & 0, \\ B_{14}\lambda^2, & B_{24}\lambda^2, & B_{34}\lambda^2, & B_{44}\lambda^2 - 4\beta_{\mathrm{H}} r_{\mathrm{H}}^2, & 0, \\ B_{15}\lambda^2, & B_{25}\lambda^2, & 0, & 0, & B_{55}\lambda^2 - 2\delta_{\mathrm{H}} r_{\mathrm{H}}^2, \end{vmatrix} = 0,$$

where

$$\left\{\begin{array}{l} B_{11} = M_{\mathrm{X}}(M_{\mathrm{C}} + 2M_{\mathrm{H}})/M, \\ B_{22} = r_{\mathrm{X}}^2 M_{\mathrm{X}}(M_{\mathrm{C}} + 2M_{\mathrm{H}})/M, \\ B_{33} = 2M_{\mathrm{H}} - 4\cos^2\dfrac{\theta_{\mathrm{H}}}{2} M_{\mathrm{H}}^2/M, \\ B_{44} = 2r_{\mathrm{H}}^2 M_{\mathrm{H}} - 4r_{\mathrm{H}}^2 \sin^2\dfrac{\theta_{\mathrm{H}}}{2} M_{\mathrm{H}}^2/M, \\ B_{55} = 2r_{\mathrm{H}}^2 \cos^2\dfrac{\theta_{\mathrm{H}}}{2} M_{\mathrm{H}}(M_{\mathrm{C}} + M_{\mathrm{X}})/M, \end{array}\right.$$

and

$$\left\{\begin{array}{l} B_{13} = -2\cos\dfrac{\theta_{\mathrm{H}}}{2}(\cos\alpha_{\mathrm{X}}\cos\phi_{\mathrm{H}} - \sin\alpha_{\mathrm{X}}\sin\phi_{\mathrm{H}}) M_{\mathrm{H}} M_{\mathrm{X}}/M, \\ B_{14} = 2r_{\mathrm{H}}\sin\dfrac{\theta_{\mathrm{H}}}{2}(\cos\alpha_{\mathrm{X}}\cos\phi_{\mathrm{H}} - \sin\alpha_{\mathrm{X}}\sin\phi_{\mathrm{H}}) M_{\mathrm{H}} M_{\mathrm{X}}/M, \end{array}\right.$$

$$\begin{cases} B_{15} = 2r_{\mathrm{H}} \cos\dfrac{\theta_{\mathrm{H}}}{2} (\cos\alpha_{\mathrm{X}} \sin\phi_{\mathrm{H}} + \sin\alpha_{\mathrm{X}} \cos\phi_{\mathrm{H}}) M_{\mathrm{H}} M_{\mathrm{X}}/M\,, \\ B_{23} = 2r_{\mathrm{X}} \cos\dfrac{\theta_{\mathrm{H}}}{2} (\cos\alpha_{\mathrm{X}} \sin\phi_{\mathrm{H}} + \sin\alpha_{\mathrm{X}} \cos\phi_{\mathrm{H}}) M_{\mathrm{H}} M_{\mathrm{X}}/M\,, \\ B_{24} = -2r_{\mathrm{X}} r_{\mathrm{H}} \sin\dfrac{\theta_{\mathrm{H}}}{2} (\cos\alpha_{\mathrm{X}} \sin\phi_{\mathrm{H}} + \sin\alpha_{\mathrm{X}} \cos\phi_{\mathrm{H}}) M_{\mathrm{H}} M_{\mathrm{X}}/M\,, \\ B_{25} = 2r_{\mathrm{X}} r_{\mathrm{H}} \cos\dfrac{\theta_{\mathrm{H}}}{2} (\cos\alpha_{\mathrm{X}} \cos\phi_{\mathrm{H}} - \sin\alpha_{\mathrm{X}} \sin\phi_{\mathrm{H}}) M_{\mathrm{H}} M_{\mathrm{X}}/M\,, \\ B_{34} = 4r_{\mathrm{H}} \cos\dfrac{\theta_{\mathrm{H}}}{2} \sin\dfrac{\theta_{\mathrm{H}}}{2} M_{\mathrm{H}}^2/M\,. \end{cases}$$

Neglecting the cross terms, we have

$$B_{11}\lambda^2 - k_{\mathrm{X}} = 0 \qquad (5),$$

$$B_{22}\lambda^2 - \delta_{\mathrm{X}} r_{\mathrm{X}}^2 = 0 \qquad (6),$$

$$B_{33}\lambda^2 - 2k_{\mathrm{H}} = 0 \qquad (7),$$

$$B_{44}\lambda^2 - 4\beta_4 r_{\mathrm{H}}^2 = 0 \qquad (8),$$

$$B_{55}\lambda^2 - 2\delta_{\mathrm{H}} r_{\mathrm{H}}^2 = 0 \qquad (9).$$

Equations (5) and (6) express the antisymmetric valency and deformation frequencies of C-Cl bond and are the same as those derived in the previous paper.(2) Equations (7), (8), and (9) are those of the CH_2-groups. These vibrations are forbidden in the Raman effect for the *trans*-form of the molecule, and can be assigned to the lines disappearing in the solid spectra, for in the solid state the molecules of ethylene halides are in the *trans*-configuration, while in the liquid state it considerably deviates from this stable configuration. From the force constants obtained for the vibrations of Class I, we get the values 2978 cm.$^{-1}$, 1445 cm.$^{-1}$, and 1260 cm.$^{-1}$ for these lines. Actually ethylene bromide has the lines 2953 cm.$^{-1}$, 1419 cm.$^{-1}$, and 1276 cm.$^{-1}$, which disappear in the solid state and are to be assigned to the frequencies calculated. For ethylene chloride the observed lines 1429 cm.$^{-1}$ and 1393 cm.$^{-1}$ must be assigned to the calculated frequencies 1465 cm.$^{-1}$ and 1417 cm.$^{-1}$ respectively. Though in the C-H valency frequency region we have no line which vanishes and is to be assigned to the calculated frequency 2984 cm.$^{-1}$, comparison of its spectra with those of bromide suggests that the line corresponding to this frequency might overlap that of a symmetric vibration. (See Table 2.)

Table 2. Antisymmetric C–H vibrations.

	$C_2H_4Cl_2$		$C_2H_4Br_2$	
	$\nu_{calc.}$ (cm.$^{-1}$)	$\nu_{obs.}$ (cm.$^{-1}$)	$\nu_{calc.}$ (cm.$^{-1}$)	$\nu_{obs.}$ (cm.$^{-1}$)
ν(C—H)	2984	(2957) ?	2978	2953
δ(H–C–H)	1465	1429	1445	1419
δ(CH_2–C)	1417	1393	1260	1276

We have discussed eleven frequencies so far. It is easily seen from Table 1 that the remaining seven frequencies must be C-H vibrations except a vibration corresponding to the internal rotation. Thus we get as much lower frequencies as those of the four body problem X-(CH_2)-(CH_2)-X, even though we take the motion of hydrogen atoms into consideration. The conclusion of the previous paper with regard to these chain frequencies of ethylene halides is, therefore, not essentially modified by the consideration of the motion of hydrogen atoms.

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