

On the Fundamental Frequencies of CH₂, CHD, CD₂, CHCl, CDCl, and Cis and Trans C₂H₂D₂ and C₂H₂Cl₂

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result that the analytical spread is too small to permit sufficient accuracy to be attained. Obviously combinations of the gases studied in this research can be analyzed for by the thermal conductivity method described and several such analyses have been made by the author.¹³ It is planned to use this method of analysis in general on the isotopic isomers of neon, oxygen and carbon. Simple calculation shows that $C^{13}H_4$ and $C^{12}H_4$ could be determined with an accuracy of about 0.5 percent since in this case no marked specific heat differences appear possible. The important features which the compound to be used for thermal analysis must have are relatively small "dead" mass and either very large or

negligible specific heat differences for the isotopic isomers.

That this type of thermal conductivity gauge has proved a powerful tool in the investigation of a wide variety of researches concerned with the kinetics of general aliphatic hydrocarbons is amply indicated by several of the papers referred to above. Its most notable feature is its easy adaptation to carrying out analyses on *both* the hydrogens and the hydrocarbons permitting therefore a very complete study to be made of both the kinetics and the equilibria in any hydrogen isotope-lower aliphatic hydrocarbon system, provided only a correct separational procedure is adopted.

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On the Fundamental Frequencies of CH_2 , CHD , CD_2 , $CHCl$, $CDCl$, and *Cis* and *Trans* $C_2H_2D_2$ and $C_2H_2Cl_2$

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A valence force treatment of the groups CH_2 , CHD , CD_2 , $CHCl$, $CDCl$ is given. The relative dependence of the three fundamental frequencies calculated for each group on the deformation force constant is used as a guide in correlating these frequencies with the three individual modes of vibration of the group. On the basis of this calculation, an assignment of the fundamental frequencies of *cis*, *trans* and

asymmetric $C_2H_2D_2$ calculated by Manneback and Verleysen is given. Also from the data on the degrees of depolarization of the Raman lines of *cis* $C_2H_2Cl_2$ and *trans* $C_2H_2Cl_2$, intensity and selection rules in Raman effect and infrared absorption, an assignment of the fundamental frequencies of these isomers is suggested.

I. INTRODUCTION

THE molecules C_2H_4 , C_2D_4 , C_2Cl_4 belong to the symmetry type V_h , the *cis* $C_2H_2D_2$ or $C_2H_2Cl_2$ to the type C_{2v} , and the *trans* $C_2H_2D_2$ or $C_2H_2Cl_2$ to the type C_{2h} . Each molecule possesses twelve fundamental vibrations, nine of which take place in the plane of the molecule, and two in directions perpendicular to the plane. One is the torsional vibration. The symmetrical properties and the selection rules in the infrared and the Raman effect can be summarized in Table I.¹

In C_2H_4 , except for the torsional vibration which is inactive in both the infrared and the Raman effect, there is little doubt concerning the other eleven frequencies. These frequencies are given in Table II. For the vibrations S_1 and A_1 ,

Sutherland and Dennison² obtained a potential function with four constants. For the nine vibrations in the plane of the molecule, Bonner³ obtained a potential function containing eight constants, while Manneback and Verleysen² determined one with eleven constants. With this potential function and on the assumption that it is invariant under a substitution by an isotope, Manneback and Verleysen calculated the nine frequencies of the vibrations in the molecular plane of each of the *cis*, *trans* and asymmetric $C_2H_2D_2$. The determinantal equation in each case separates into two; one of the 5th degree for the five π' , S , π vibrations in the case of the *cis*, *trans* and asymmetric $C_2H_2D_2$, respectively, and one

¹ See, for example, Placzek, *Leipziger Vorträge* (1931).

² G. Sutherland and D. M. Dennison, Proc. Roy. Soc. A148, 250 (1935).

³ Bonner, J. Am. Chem. Soc. 58, 34 (1936).

TABLE I. Fundamental vibrations of C_2H_4 , *cis*, *trans* and asymmetric $C_2H_2X_2$. The notation of the symmetry character is that of Manneback and Verleysen.⁴

NOTATION	C_2H_4			<i>cis</i> $C_2H_2X_2$			<i>trans</i> $C_2H_2X_2$			asym. $C_2H_2X_2$		
	Sym.	Infra.	Raman	Sym.	Infra.	Raman	Sym.	Infra.	Raman	Sym.	Infra.	Raman
$\nu_{\pi s}$	S_1	—	<i>s.p.</i>	π'	<i>M</i>	<i>s.p.</i>	<i>S</i>	—	<i>s.p.</i>	π	<i>L</i>	<i>p.</i>
$\nu_{\pi a}$	A_1	<i>L</i>	—	σ'	<i>L</i>	<i>d.</i>	<i>A</i>	—	—	π	<i>L</i>	<i>p.</i>
$\delta_{\pi s}$	S_1	—	<i>s.p.</i>	π'	<i>M</i>	<i>s.p.</i>	<i>S</i>	—	<i>s.p.</i>	π	<i>L</i>	<i>p.</i>
$\delta_{\pi a}$	A_1	<i>L</i>	—	σ'	<i>L</i>	<i>d.</i>	<i>A</i>	—	—	π	<i>L</i>	<i>p.</i>
$\nu_{2\pi s}$	S_1	—	<i>s.p.</i>	π'	<i>M</i>	<i>s.p.</i>	<i>S</i>	—	<i>s.p.</i>	π	<i>L</i>	<i>p.</i>
$\nu_{\sigma s}$	S_2	—	<i>w.d.</i>	σ'	<i>L</i>	<i>d.</i>	<i>S</i>	—	<i>s.p.</i>	σ	<i>M</i>	<i>d.</i>
$\nu_{\sigma a}$	A_2	<i>M</i>	—	π'	<i>M</i>	<i>s.p.</i>	<i>A</i>	—	—	σ	<i>M</i>	<i>d.</i>
$\delta_{\sigma' s}$	S_2	—	<i>w.d.</i>	σ'	<i>L</i>	<i>d.</i>	<i>S</i>	—	<i>s.p.</i>	σ	<i>M</i>	<i>d.</i>
$\delta_{\sigma' a}$	A_2	<i>M</i>	—	π'	<i>M</i>	<i>s.p.</i>	<i>A</i>	—	—	σ	<i>M</i>	<i>d.</i>
$\delta_{\sigma'' s}$	—	—	<i>w.d.</i>	—	—	<i>d.</i>	S'	—	<i>d.</i>	—	<i>G</i>	<i>d.</i>
$\delta_{\sigma'' a}$	—	<i>G</i>	—	—	<i>G</i>	<i>d.</i>	A'	—	—	—	<i>G</i>	<i>d.</i>
Torsion	—	—	—	—	—	<i>d.</i>	A'	—	—	—	—	<i>d.</i>

 π, σ = sym. or antisym. with respect to the C=C axis, π', σ' = sym. or antisym. with respect to an axis perpendicular to the C=C axis in the plane of the molecule, S, A = sym. or antisym. with respect to the center of symmetry, $S_1 = (\pi\pi'), S_2 = (\sigma\sigma'), A_1 = (\pi\sigma'), A_2 = (\pi'\sigma')$.For the Raman effect, *s* = strong, *w* = weak, *p* = polarized ($\rho < \frac{1}{2}$), *d* = depolarized ($\rho = \frac{1}{2}$).For the infrared, *L, M, G* signify change of electric moment along axis of least, middle, and greatest moment of inertia, respectively.

A dash signifies inactive frequency.

of the 4th degree for the corresponding four σ' , A , σ vibrations. There is no question as to the accuracy of these calculated frequencies; but the way in which these frequencies are obtained and tabulated does not make it clear which frequency should be assigned to a particular one of the vibrations of the same symmetry group. This can be done in general only by considering the transformation equations between the generalized coordinates used and the normal coordinates. We attempt, however, in this note to give a very plausible assignment by considering the fundamental frequencies of the groups CH_2 , CHD , CD_2 from which the three isomers of $C_2H_2D_2$ are formed.

There has been considerable work on the Raman spectra of these isomers.⁵ The degrees of depolarization of the Raman lines have been studied by Heidenreich,⁶ Paulsen⁷ and Trumpy.⁸ The Raman spectra of the two isomers of $C_2D_2Cl_2$ have also been studied by Trumpy.⁸ The infrared absorption spectra of these isomers have been investigated by Wu⁹ in the region between 2 and 23μ . A classification of the Raman frequencies

⁴ C. Manneback and A. Verleysen, *Nature* **138**, 367 (1936).⁵ Kohlrausch, *Smekal-Raman Effekt*.⁶ Heidenreich, *Zeits. f. Physik* **97**, 277 (1935).⁷ Paulsen, *Zeits. f. physik. Chemie* **B28**, 123 (1935).⁸ B. Trumpy, *Zeits. f. Physik* **98**, 672 (1935).⁹ T. Y. Wu, *Phys. Rev.* **46**, 465 (1934).

has been given by Trumpy. But from considerations of the vibrations of $CHCl$, it seems to need modification. It seems possible to give also a reasonable assignment of the infrared frequencies, although the present data are still not sufficient for a definite assignment of some of the fundamental frequencies of these isomers.

II. FUNDAMENTAL VIBRATIONS OF CH_2 , CHD , CD_2

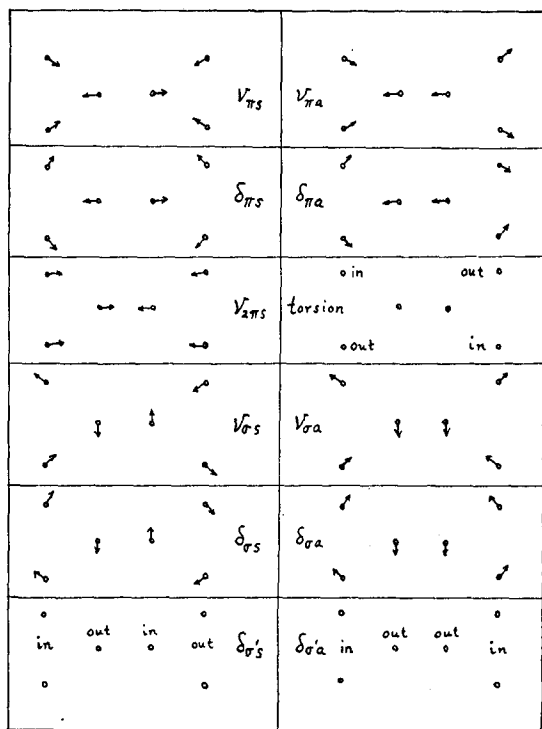
The fundamental frequencies of these groups can be treated either by a valence force system or by a noncentral force system. We shall give here a valence force treatment, as the non-central force treatment leads to similar results.

The valence force treatment of the motion of a three-particle system has been given by Lechner.¹⁰

TABLE II. Assignment of fundamental frequencies of *cis*, *trans* and asym. $C_2H_2D_2$ calculated by Manneback and Verleysen.

NOTATION	C_2H_4	<i>cis</i> $C_2H_2D_2$	<i>trans</i> $C_2H_2D_2$	asym. $C_2H_2D_2$	C_2D_4
$\nu_{\pi s}$	3019.0	π' 2304	<i>S</i> 2291	π 3004	2283.9
$\nu_{\pi a}$	2988.0	σ' 2229	<i>A</i> 2233	π 2221	2152.5
$\delta_{\pi s}$	1343.9	π' 1248	<i>S</i> 1240	π 1043	1008.9
$\delta_{\pi a}$	1444.0	σ' 1295	<i>A</i> 1308	π 1357.8	1072.8
$\nu_{2\pi s}$	1621.3	π' 1516.5	<i>S</i> 1514.2	π 1555	1428.8
$\nu_{\sigma s}$	3069	σ' 3031	<i>S</i> 3049	σ 3088	2308.0
$\nu_{\sigma a}$	3170	π' 3065	<i>A</i> 3053	σ 2316	2325.0
$\delta_{\sigma' s}$	950	σ' 820	<i>S</i> 808	σ 945.6	758.3
$\delta_{\sigma' a}$	949.7	π' 752.7	<i>A</i> 765.3	σ 725	678.1

¹⁰ F. Lechner, *Graz Dissertation*; *Monatsh. f. Chem.* **61**, 385 (1932).

FIG. 1. Modes of vibrations of $C_2H_2X_2$ type molecules.

Let the potential energy of the system be

$$2V = K_1(\Delta r_{12})^2 + K_2(\Delta r_{23})^2 + \delta(S\Delta\alpha)^2$$

where S is a length. The fundamental frequencies are then given by the three equations

$$\begin{aligned} \nu_1^2 + \nu_2^2 + \nu_3^2 &= K_1/\mu_1 + K_2/\mu_2 + \delta/\mu_4, \\ \nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2 &= K_1K_2/\mu_1\mu_2 \cdot (1 - \mu_1\mu_2 \cos^2 \alpha/r_{12}^2) \\ &\quad + (K_1/\mu_1 + K_2/\mu_2)\delta/\mu_4 \\ &\quad - (K_1/r_{23}^2 + K_2/r_{12}^2)\delta S^2 \sin^2 \alpha/m_2^2, \\ \nu_1^2\nu_2^2\nu_3^2 &= K_1K_2\delta/\mu_1\mu_2\mu_4 \cdot (1 - \mu_1\mu_2/m_2^2), \end{aligned} \quad (1)$$

where $1/\mu_1 = 1/m_1 + 1/m_2$, $1/\mu_2 = 1/m_3 + 1/m_2$, $1/\mu_4 = S^2(1/\mu_1 r_{12}^2 + 1/\mu_2 r_{23}^2 - 2 \cos \alpha/m_2 r_{12} r_{23})$. For symmetric molecules, $K_1 = K_2$, $m_1 = m_3$, $m_2 = M$, $r_{12} = r_{23} = s$, the Eqs. (1) become¹¹

$$\begin{aligned} \nu_3^2 &= K_1(1/\mu - \cos \alpha/M), \\ \nu_3^2(M + 2m)K_\alpha &= m^2 M \nu_1^2 \nu_2^2 (1/\mu - \cos \alpha/M), \\ \nu_1^2 + \nu_2^2 &= K_1(1/\mu + \cos \alpha/M) \\ &\quad + K_\alpha(1/\mu - \cos \alpha/M)/S^2, \end{aligned} \quad (2)$$

where $K_\alpha = 2\delta S^2$, $1/\mu = 1/m + 1/M$.

For CH_2 , the constants K_1 and K_α can be determined from the values of its three funda-

¹¹ W. Penney and G. Sutherland, Proc. Roy. Soc. A156, 654 (1936).

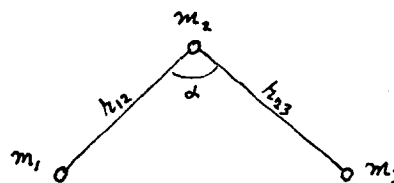


FIG. 2.

mental frequencies.¹² In C_2H_4 , the vibrations $\nu_{\pi a}$, $\delta_{\pi a}$ correspond to the vibrations ν_1 , ν_2 , respectively, of the two groups of CH_2 (see Fig. 3). In the approximation of Sutherland and Dennison,³ $\nu_{\pi a}$ and $\delta_{\pi a}$ are independent of the force constant of the two carbon atoms. Hence the frequencies $\nu_{\pi a}$, $\delta_{\pi a}$ of C_2H_4 are essentially equal to ν_1 and ν_2 , respectively, of CH_2 . The vibration $\nu_{\sigma a}$ of C_2H_4 consists of two CH_2 groups vibrating in ν_3 with no relative displacement of the carbon atoms. Hence we may take $\nu_3 = \nu_{\sigma a}(C_2H_4)$. Thus $\nu_3 \cong 3100$, $\nu_2 \cong 1440$, $\nu_1 \cong 2988$. On substituting $m_1 = m_3 = 1$, $M = 12$, $\alpha = 115^\circ$, $r_{12} = r_{23} = s = 1.08 \times 10^{-8}$, Eqs. (2) give

$$\begin{aligned} K_1 &= 5.0 \times 10^5 \text{ dynes/cm}, \\ K_\alpha &= 1.28 \times 10^{-11} \text{ dyne cm/radian}. \end{aligned} \quad (3)$$

For CD_2 , with the use of K_1 and K_α for CH_2 (Eqs. (3)), Eqs. (2) give

$$\nu_1 = 2164, \quad \nu_2 = 1065, \quad \nu_3 = 2292,$$

which are comparable with the values A_1 2152.5, A_1 1072.8 and A_2 2325 of C_2D_4 obtained by Manneback and Verleysen.

For CHD , $K_1 = K_2$, $r_{12} = r_{23} = s$, $m_1 = 1$, $m_3 = 2$, $m_2 = 12$, $\alpha = 115^\circ$, Eqs. (1) give

$$\begin{aligned} \nu_1^2 + \nu_2^2 + \nu_3^2 &= 5/3 \cdot K_1 + 1.575 K_\alpha / 2s^2, \\ \nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2 &= 0.630 K_1^2 + 2.614 K_1 K_\alpha / 2s^2, \\ \nu_1^2\nu_2^2\nu_3^2 &= 0.985 K_1^2 K_\alpha / 2s^2, \end{aligned} \quad (4)$$

where the ν 's are expressed in units of 1000 cm^{-1} and the K_1 , $K_\alpha / 2s^2$ in units of 0.5875×10^{-5} dynes/cm. Using the values of K_1 , K_α in (3), we have

$$\begin{aligned} \nu_1^2 + \nu_2^2 + \nu_3^2 &= 15.65, \\ \nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2 &= 66.50, \\ \nu_1^2\nu_2^2\nu_3^2 &= 66.60. \end{aligned} \quad (4')$$

¹² These are taken by Sutherland and Dennison from OCH_2 to be $\nu_1 = 2970$, $\nu_2 = 1444$, $\nu_3 = 3000$. We prefer, however, to obtain them from C_2H_4 , although the difference in the values of the force constants determined from the two sets of values of $\nu_1 \nu_2 \nu_3$ is small and would not affect greatly our result below.

Solution of (4') gives

$\nu_1 = 2240 \text{ cm}^{-1}$, $\nu_2 = 1204 \text{ cm}^{-1}$, $\nu_3 = 3034 \text{ cm}^{-1}$ approximately. To show that 2240, 1204 and 3034 correspond, respectively, to the modes of vibration ν_1 , ν_2 , ν_3 , let us consider the dependence of ν_1 , ν_2 , ν_3 on the deformation constant K_α or $\delta = K_\alpha/2s^2$. For symmetric molecules, it is seen from Eqs. (2) that ν_3 is independent of K_α , while ν_1 and ν_2 depend on K_α . For CHD, the motions are no longer symmetric, but one would still expect ν_3 to depend on K_α not so strongly as ν_1 and ν_2 . Writing Eqs. (4) in the form

$$\begin{aligned}\nu_i^2 + \nu_j^2 + \nu_k^2 &= 5/3 \cdot K_1 + \alpha\delta, \\ \nu_i^2\nu_j^2 + \nu_j^2\nu_k^2 + \nu_k^2\nu_i^2 &= 0.630K_1^2 + \beta\delta, \\ \nu_i^2\nu_j^2\nu_k^2 &= \gamma\delta,\end{aligned}$$

where $\alpha = 1.575$, $\beta = 22.2$, $\gamma = 71.3$, one readily obtains

$$\begin{aligned}d\nu_i/d\delta &= -\nu_i[\nu_i^2\alpha + \nu_j^2\nu_k^2/\delta - \beta] \\ &\quad /2(\nu_i^2 - \nu_j^2)(\nu_k^2 - \nu_i^2), \\ d\nu_j/d\delta &= -\nu_j[\nu_j^2\alpha + \nu_k^2\nu_i^2/\delta - \beta] \\ &\quad /2(\nu_j^2 - \nu_k^2)(\nu_i^2 - \nu_j^2), \\ d\nu_k/d\delta &= -\nu_k[\nu_k^2\alpha + \nu_i^2\nu_j^2/\delta - \beta] \\ &\quad /2(\nu_k^2 - \nu_i^2)(\nu_j^2 - \nu_k^2).\end{aligned}\quad (5)$$

Expressing ν 's in units of 1000 cm^{-1} , δ in units of $0.5875 \times 10^5 \text{ dynes/cm}$, we have

$$\begin{aligned}\nu_i &= 2.240, & d\nu_i/d\delta &= 0.011, & \text{or} & & 19 \text{ cm}^{-1}/10^5 \text{ dynes/cm.} \\ \nu_j &= 1.204, & d\nu_j/d\delta &= 0.054, & \text{or} & & 92 \text{ cm}^{-1}/10^5 \text{ dynes/cm.} \\ \nu_k &= 3.100, & d\nu_k/d\delta &< 0.00145, & \text{or} & & < 2.5 \text{ cm}^{-1}/10^5 \text{ dynes/cm.}\end{aligned}$$

The strong dependence of the frequency 1204 cm^{-1} on the deformation force constant and the exceedingly slight dependence of 3034 cm^{-1} on it leave no doubt as to the correctness of the assignment $\nu_1 = 2240 \text{ cm}^{-1}$, $\nu_2 = 1204 \text{ cm}^{-1}$, $\nu_3 = 3100 \text{ cm}^{-1}$.

IIIa. *Cis* C₂H₂D₂

From Table I, it is seen that the five π' vibrations correspond to the S_1 and A_2 vibrations of C₂H₄, and the four σ' vibrations correspond to the A_1 and S_2 vibrations of C₂H₄. There is little doubt that the frequency 1516.5 corresponds to $\nu_{2\pi s}$ of C₂H₄. In the following we shall for convenience denote a vibration by the notation

of the corresponding vibration of C₂H₄. The vibrations $\delta_{\pi s}$, $\delta_{\pi a}$ are essentially the deformation vibration ν_2 of CHD, and should not be greatly different from each other. From the calculation above, $\nu_2 = 1204$. Hence the π' 1247.9 and the σ' 1295.4 must be the frequencies $\delta_{\pi s}$ and $\delta_{\pi a}$. The vibrations $\delta_{\sigma s}$ and $\delta_{\sigma a}$ in C₂H₄ consist essentially in a relative vibration of the two CH₂ groups and have low frequencies. It is apparent that in *cis* C₂H₂D₂, $\delta_{\sigma s} = \sigma'$ 820.2, $\delta_{\sigma a} = \pi'$ 750.7. Of the vibrations $\nu_{\pi s}\nu_{\pi a}$, $\nu_{\sigma s}\nu_{\sigma a}$, one expects for mechanical reasons that $\nu_{\pi s}$ and $\nu_{\pi a}$ would not be greatly different from each other, nor would $\nu_{\sigma s}$ and $\nu_{\sigma a}$. Since $\nu_{\sigma s}$, $\nu_{\sigma a}$ are essentially the ν_3 vibration of CHD, and $\nu_{\pi s}$, $\nu_{\pi a}$ the ν_1 vibration of CHD, it is seen from our calculation of CHD that $\nu_{\pi s} = \pi'$ 2304.2, $\nu_{\pi a} = \sigma'$ 2228.9, $\nu_{\sigma s} = \sigma'$ 3031, $\nu_{\sigma a} = \pi'$ 3065. This assignment is given in Table II.

IIIb. *Trans* C₂H₂D₂

In this molecule, the five S vibrations correspond to the S_1S_2 vibrations, and the four A vibrations to the A_1 , A_2 vibrations of C₂H₄. Similar argument as given above for *cis* C₂H₂D₂ leads to the assignment in Table II.

IIIc. ASYMMETRIC C₂H₂D₂

In this case the five π frequencies correspond to the S_1 , A_1 vibrations, and the four σ frequencies correspond to the S_2 , A_2 vibrations of C₂H₄. That the assignment $\delta_{\pi s} = \pi$ 1043.1, $\delta_{\pi a} = \pi$ 1357.8, $\nu_{2\pi s} = \pi$ 1555.3, $\delta_{\sigma s} = \sigma$ 945.6, $\delta_{\sigma a} = \sigma$ 724.8 is reasonable is evident from the general trend of the corresponding frequencies in C₂H₄, *cis* and *trans* C₂H₂D₂ and C₂D₄. But as the two frequencies π 3004.3 and σ 3088.1 are of different symmetry character and so are π 2221.0 and σ 2316.3, one must now make the assignment

$$\left. \begin{matrix} \nu_{\pi s} \\ \nu_{\pi a} \end{matrix} \right\} = \left\{ \begin{matrix} \pi 3004.3 & \nu_{\sigma s} \\ \pi 2221.0 & \nu_{\sigma a} \end{matrix} \right\} = \left\{ \begin{matrix} \sigma 3088.1 \\ \sigma 2316.3 \end{matrix} \right.$$

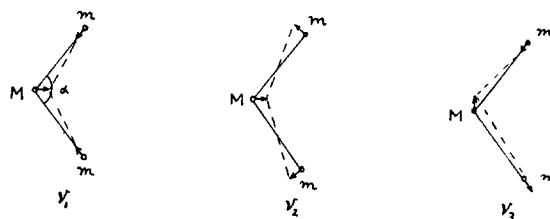


FIG. 3. Fundamental vibrations of CH₂.

and in this case it seems that one cannot distinguish between the two alternative assignments without studying the transformation relations between the generalized coordinates and the normal coordinates.

IV. FUNDAMENTAL VIBRATIONS OF CHCl, CDCl

We may treat the vibrations of CHCl and CDCl by the valence force method as the interaction between the Cl and the H or D atom is smaller than those between C and Cl, and C and H. That this is justified will be seen from the following calculations.

For CHCl, let $m_1=1$, $m_3=36$, $m_2=12$, $r_{12}=1.08 \times 10^{-8}$ cm, $r_{23}=1.8 \times 10^{-8}$ cm, $\alpha=110^\circ$. Denoting the force constant between C and H by K_1 , that between C and Cl by K_2 , we have, from Eqs. (1),

$$\begin{aligned} \nu_1^2 + \nu_2^2 + \nu_3^2 &= 13/12 \cdot K_1 + K_2/9 + 0.496K_\alpha, \\ \nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2 &= 0.1195K_1K_2 + 0.536K_1K_\alpha + 0.526K_2K_\alpha, \\ \nu_1^2\nu_2^2\nu_3^2 &= 0.05625K_1K_2K_\alpha. \end{aligned} \quad (6)$$

Let us consider the Raman lines and the infrared data of *trans* C₂H₂Cl₂ in Table III. The selection rules require that frequencies active in Raman effect should be inactive in infrared and *vice versa*. As the frequencies of two vibrations of C₂H₂Cl₂ that differ only in the phase relation in the two CHCl groups should not be greatly different from each other, we can pick out the three pairs

$$\begin{Bmatrix} 3072 \text{ (Ra.)} \\ 3090 \text{ (Inf.)} \end{Bmatrix}, \begin{Bmatrix} 1271 \text{ (Ra.)} \\ 1200 \text{ (Inf.)} \end{Bmatrix}, \begin{Bmatrix} 840 \text{ (Ra.)} \\ 820 \text{ (Inf.)} \end{Bmatrix}$$

as the only ones that can be reasonably ascribed to

$$\begin{Bmatrix} \nu_{\sigma s} \\ \nu_{\sigma a} \end{Bmatrix}, \begin{Bmatrix} \delta_{\pi s} \\ \delta_{\pi a} \end{Bmatrix}, \begin{Bmatrix} \nu_{\pi s} \\ \nu_{\pi a} \end{Bmatrix}.$$

The differences between the two frequencies in each pair are due to the interaction between the two CHCl groups. Hence as an approximation we shall take the mean of the Raman and the infrared frequencies, namely, 3080, 1230, 830, as the three fundamental frequencies of CHCl. For the determination of the constants K_1 , K_2 , K_α , an exact assignment is immaterial, as ν_1 , ν_2 , ν_3 enter symmetrically in the above three equations.

Solution of Eqs. (6) with $(\nu_1, \nu_2, \nu_3) = (3080, 1230, 830)$ gives

$$\begin{aligned} K_1 &= 5.17 \times 10^5 \text{ dynes/cm}, \\ K_2 &= 4.01 \times 10^5 \text{ dynes/cm}, \\ K_\alpha &= 1.71 \times 10^{11} \text{ dyne cm/radian}. \end{aligned} \quad (7)$$

The closeness of the value K_1 (CH) to that obtained from CH₂, namely 5.0×10^5 , and the order of magnitude of K_α as compared with the deformation constants of all known triatomic systems¹¹ justified the valence force treatment.

To find the correspondence between the frequencies 3080, 1230, 830 and the three modes of vibrations ν_1 , ν_2 , ν_3 (Fig. 4), let us again study the relative dependence of these frequencies on K_α . One would expect ν_2 to depend most strongly on K , while ν_3 should be practically independent of K_α . From Eqs. (5), we have

$$\begin{aligned} dv_i/dK_\alpha &= 14 \text{ cm}^{-1}/10^5 \text{ dynes/cm}, \quad \nu_i = 830, \\ dv_j/dK_\alpha &= 338 \text{ cm}^{-1}/10^5 \text{ dynes/cm}, \quad \nu_j = 1230, \\ dv_k/dK_\alpha &= 1 \text{ cm}^{-1}/10^5 \text{ dynes/cm}, \quad \nu_k = 3080. \end{aligned}$$

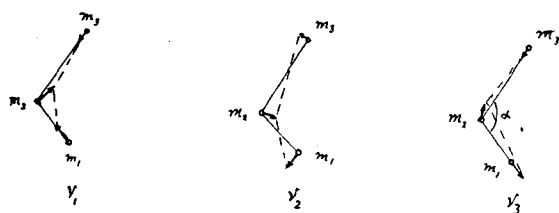
The slight dependence of the frequency 3080 and the great dependence of the frequency 1230 show that $\nu_1=830$, $\nu_2=1230$, $\nu_3=3080$.

For CDCl, $m_3=2$ and the other data are the same as for CHCl. Eqs. (1) give

$$\begin{aligned} \nu_1^2 + \nu_2^2 + \nu_3^2 &= 7/12 \cdot K_1 + K_2/9 + 0.2815K_\alpha, \\ \nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2 &= 0.064K_1K_2 + 0.163K_1K_\alpha + 0.310K_2K_\alpha, \\ \nu_1^2\nu_2^2\nu_3^2 &= 0.01627K_1K_2K_\alpha. \end{aligned}$$

TABLE III. Raman and infrared data of *trans* C₂H₂Cl₂, C₂D₂Cl₂.

C ₂ H ₂ Cl ₂						C ₂ D ₂ Cl ₂	
Infrared	Raman			Assignment		Raman	
cm ⁻¹	cm ⁻¹	Int.	ρ	Trumpy	Wu	cm ⁻¹	Int.
620	350	(10)	0.29	$\delta_{\sigma s}$	$\delta_{\sigma s}$	346	(4)
820	752	($\frac{3}{2}$)	0.70	$\delta_{\sigma'a}$	$\delta_{\sigma'a}$	657	(1)
917	840	(3)	0.08	$\nu_{\sigma s}$	$\nu_{\pi a}$	765	(2)
1200					torsion		
	1271	(7)	0.20	$\delta_{\pi s}$	$\delta_{\pi s}$	992	(6)
	1575	(5)	0.08	$\nu_{2\pi s}$	$\nu_{2\pi s}$	1570	(6)
	1625	($\frac{1}{2}$)	p	$\delta_{\sigma s} + \delta_{\pi s}$	$\delta_{\sigma s} + \delta_{\pi s}$	1323	(0)
	1690	($\frac{1}{2}$)	p	$2\nu_{\sigma s}$	$2\nu_{\pi s}$	1540	(3)
3090	3072	(5)	0.20	$\nu_{\pi s}$	$\nu_{\sigma a}$	2325	(4)
	3140	($\frac{1}{2}$)	p	$2\nu_{2\pi s}$	$2\nu_{2\pi s}$	3150	(0)

FIG. 4. Fundamental vibrations of CHCl_3 .

With the values K_1 , K_2 and K_α determined above for CHCl_3 (Eq. (7)), solution of these equations gives

$$\nu_1 = 755, \quad \nu_2 = 960, \quad \nu_3 = 2320.$$

The closeness between these values and the Raman lines of *trans* $\text{C}_2\text{D}_2\text{Cl}_2$ found by Trumphy,⁸ namely,

$$765, \quad 992, \quad 2325,$$

again show that the assignment of these frequencies is essentially correct, and that the valence force treatment of these CHCl_3 , CDCl_3 groups is satisfactory.

Va. *Trans* $\text{C}_2\text{H}_2\text{Cl}_2$

Let us consider the *trans* $\text{C}_2\text{H}_2\text{Cl}_2$. According to the selection rules in Table I, there should be five strong and polarized, one weak and depolarized Raman lines. These six Raman effect active frequencies are inactive in the infrared, while the other six Raman effect inactive frequencies are active in the infrared. The Raman spectra and infrared absorption data are summarized in Table III.

The classification of the Raman lines by Trumphy⁸ is shown in the fifth column. In view of our calculations on CHCl_3 and CDCl_3 , the lines 3072 and 840 should be $\nu_{\sigma s}$ and $\nu_{\pi s}$, respectively. The Raman line 752 is probably $\delta_{\sigma' s}$ which should be completely depolarized and comparatively weak, although the value $\rho = 0.70$ is a little too low for a completely depolarized line ($\rho = 6/7$). The infrared bands at 820, 1200 and 3090 cm^{-1} have already been assigned to $\nu_{\pi a}$, $\delta_{\pi a}$ and $\nu_{\sigma a}$ in the above calculations. $\delta_{\sigma a}$, which one expects to be of the same order of, and in fact lower than $\delta_{\sigma s}$, lies in a region not covered in the work of Wu.⁹ The vibration $\delta_{\sigma' a}$ and the torsional vibration are infrared active and there are two infrared bands at 620 and 917 cm^{-1} . If one assumes $\delta_{\sigma' s} > \delta_{\sigma' a}$ as in C_2H_4 , then $\delta_{\sigma' a} = 620$,

torsional frequency = 917. As the torsional frequency in C_2H_4 has been estimated at 745–800 cm^{-1} from specific heat data,¹³ and as in *cis* $\text{C}_2\text{H}_2\text{Cl}_2$ $\delta_{\sigma' a} = 694$, the assignment here is not unreasonable.

Vb. *Cis* $\text{C}_2\text{H}_2\text{Cl}_2$

In the case of *cis* $\text{C}_2\text{H}_2\text{Cl}_2$, there should be five strong and polarized ($\rho < 6/7$) lines and seven weaker, completely depolarized ($\rho = 6/7$) lines. The five strong Raman frequencies are active in infrared; the direction of the change of electric moment is along the axis of middle moment of inertia, and according to the consideration of Dennison¹⁴ for the vibration-rotational band of an asymmetrical rotator, the band should possess no zero branch (type *M*). The four σ' vibrations, however, have their change of electric moment along the axis of least moment of inertia, and the vibration-rotational bands should possess a zero branch (type *L*). The vibration $\delta_{\sigma' a}$ corresponds to a change of electric moment along the axis of greatest moment of inertia and the band should also possess a zero branch (type *G*). Investigation, however, of the infrared spectrum⁹ reveals only six intense absorptions at 570 (*M*), 694 (*L* or *G*), 857 (*L*), 1303 (*L*), 1591 (*M*) and 3087 (*M*). The band 3087 (*M*) has the corresponding strong, polarized Raman line at 3078; and according to our calculations on CHCl_3 , it is $\nu_{\sigma s}$. The band

TABLE IV. Raman and infrared data of *cis* $\text{C}_2\text{H}_2\text{Cl}_2$, $\text{C}_2\text{D}_2\text{Cl}_2$.

$\text{C}_2\text{H}_2\text{Cl}_2$				Assignment		$\text{C}_2\text{D}_2\text{Cl}_2$	
Infrared	Raman					Raman	
cm^{-1}	cm^{-1}	Int.	ρ	Trumphy	Wu	cm^{-1}	Int.
	171 (9)	0.5		$\delta_{\sigma a}$	$\delta_{\sigma a}$	171 (6)	
	407 (5)	0.84		$\delta_{\sigma s}$	$\delta_{\sigma s}$	368 (3)	
570 <i>M</i>	560 ($\frac{5}{2}$)	0.88		$\delta_{\pi s}$?	515 ($\frac{3}{2}$)	
694 <i>G</i>					$\delta_{\sigma' a}$		
710	711 (7)	0.07		$\nu_{\sigma a}$	$\nu_{\pi s}$	689 (6)	
	806 ($\frac{1}{2}$)	d		$\nu_{\sigma s}$	$\delta_{\sigma' s}$		
857 <i>L</i>					$\nu_{\pi a}$		
	880 ($\frac{1}{2}$)	p		$\nu_{\sigma a} + \delta_{\sigma a}$	torsion		
	1180 (5)	0.70		$\delta_{\pi s}$	$\delta_{\pi s}$	850 (3)	
1303 <i>L</i>					$\delta_{\pi a}$		
1591 <i>M</i>	1586 (7)	0.08		$\nu_{2\pi s}$	$\nu_{2\pi s}$	1575 (6)	
	1688 (2)	p		?	?	1507 (2)	
3087 <i>M</i>	3078 (10)	0.31		$\nu_{\pi s}$	$\nu_{\sigma a}$	2325 (6)	
	3158 ($\frac{1}{2}$)	p		$2\nu_{2\pi s}$	$2\nu_{2\pi s}$	3150 (0)	

¹³ A. Eucken and A. Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

¹⁴ D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

TABLE V. Fundamental frequencies of *cis* and *trans* C₂H₂Cl₂.

NOTATION	<i>cis</i> C ₂ H ₂ Cl ₂						<i>trans</i> C ₂ H ₂ Cl ₂				
	Sym.	Infrared		Raman			Sym.	Infrared	Raman		
		cm ⁻¹	envel. obs.	cm ⁻¹	int.	ρ			cm ⁻¹	int.	ρ
<i>ν</i> _{πs}	π'	711	<i>M</i> ?	711	(7)	0.07	<i>S</i>	—	840	(3)	0.08
<i>ν</i> _{πa}	σ'	857	<i>L</i>				<i>A</i>	820	—		
<i>δ</i> _{πs}	π'			1180	(5)	0.7	<i>S</i>	—	1270	(5)	0.20
<i>δ</i> _{πa}	σ'	1300	<i>L</i>				<i>A</i>	1200	—		
<i>ν</i> _{2πs}	π'	1591	<i>M</i>	1586	(7)	0.08	<i>S</i>	—	1575	(5)	0.08
<i>ν</i> _{σs}	σ'						<i>S</i>	—	3072	(5)	0.20
<i>ν</i> _{σa}	π'	3087	<i>M</i>	3078	(10)	0.31	<i>A</i>	3090	—		
<i>δ</i> _{σs}	σ'			407	(5)	0.84	<i>S</i>	—	350	(10)	0.29
<i>δ</i> _{σa}	π'			171	(9)	0.5	<i>A</i>		—		
<i>δ</i> _{σ's}		—		806	(½)	depol.		—	752	(¾)	0.70
<i>δ</i> _{σ'a}		694	<i>G</i>					620	—		
Torsion		—		878	(½)	pol.		917	—		

1591 (M) and the corresponding Raman line 1586 are evidently $\nu_{2\pi s}$. One expects to have a pair of frequencies at about 1200–1300 corresponding to the $\delta_{\pi s}$ 1270 (Ra), $\delta_{\pi a}$ 1200 (Inf.) of *trans* C₂H₂Cl₂. The infrared band 1303 (L) is probably the frequency $\delta_{\pi a}$ whose symmetry type is σ' and whose corresponding Raman line might have been too weak to be observed. The strong line 1180 cm⁻¹ must then be ascribed to $\delta_{\pi s}$ although the degree of depolarization ($\rho=0.70$) seems rather high. The line 711 cm⁻¹, being the only strong and polarized line in the neighborhood of 800 cm⁻¹, can be ascribed to $\nu_{\pi s}$. Its corresponding infrared band is not explicitly given in the paper, but the asymmetry and the great width of the absorption region at 694 cm⁻¹⁹ compared with other bands suggest the existence of a band at about 710 cm⁻¹. The infrared band at 857 cm⁻¹ has a zero branch and is most probably $\nu_{\pi a}$. The larger differences between $\nu_{\pi s}$ (711) and $\nu_{\pi a}$ (857), and between $\delta_{\pi s}$ (1180) and $\delta_{\pi a}$ (1303) than in the case of *trans* C₂H₂Cl₂ may be due to the larger interaction between the two CHCl groups in *cis* C₂H₂Cl₂. The completely depolarized line 407 is $\delta_{\sigma s}$ as Trumpy assumed, and the polarized line 171 ($\rho=0.5$) is then probably $\delta_{\sigma a}$. The infrared

band 694 cm⁻¹ with a strong zero branch may be ascribed to $\delta_{\sigma' a}$, and the weak and depolarized line 806 can be ascribed to $\delta_{\sigma' s}$ as it is the only one near the corresponding frequency 752 in *trans* C₂H₂Cl₂. The torsional vibration should be active in Raman effect. If the assignment of the infrared band 917 in *trans* C₂H₂Cl₂ to its torsional vibration is correct, then it is reasonable to ascribe the weak line 878 to it, although its polarization character does not fit with the rule very well. It seems that all the observed strong Raman lines and infrared bands can be accounted for except the strong, completely depolarized line 561 and the infrared band at 570 cm⁻¹ with no zero branch. The closeness between these two values shows that they are probably due to one single vibration. The theory requires that in *cis* C₂H₂Cl₂, an infrared band of the M type must appear as a strong and polarized Raman line, and a completely depolarized line must appear in the infrared with a zero branch. Thus these rules provide no place for the frequency in *cis* C₂H₂Cl₂, and hence the difficulty cannot be removed by changing the assignment alone.

The assignment of the fundamental frequencies is given in Tables IV and V.