

## A Normal Coordinate Analysis of the Planar Vibrations of Substituted Ethylenes. I. CH Bending Modes

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# A Normal Coordinate Analysis of the Planar Vibrations of Substituted Ethylenes.

## I. CH Bending Modes

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(Received April 29, 1949)

A normal coordinate analysis of the planar vibrations of some substituted ethylenes is carried out. Thirteen compounds are studied, including mono-substituted and 1:1- and *cis*- and *trans*-1:2-disubstituted ethylenes. Various solutions for the CH bending force constants are obtained and correlated. Some attempt is made to study the range of allowed solutions, and to examine the coupling of the different coordinates in the potential function.

### I. INTRODUCTION

SATISFACTORY vibrational assignments are now available for a number of substituted ethylenes. In the present work, it is proposed to carry out a normal coordinate analysis of the planar vibrations, with the object of finding sets of force constants for the various coordinates occurring in the valence-force potential functions, having particular regard to the possibility of there being small variations in the value of a force constant going with any particular coordinate common to a series of related molecules as the substituents change. This type of analysis has been developed because of inconsistencies which have arisen through the carrying-over of force constants between related molecules, which suggest that some formal investigation should be made into the allowed variations in the force constants of a given molecule. A somewhat similar treatment of the non-planar vibrations of substituted ethylenes has already been carried out;<sup>1</sup> the balance of evidence is in favor of detectable variations in force constants, which can be correlated with the electro-negativities and powers of conjugation of the substituents. In the present investigation, use is made of recent developments in the theory of the secular equation,<sup>2</sup> which facilitate comparatively rapid handling of quite high order matrix equations.

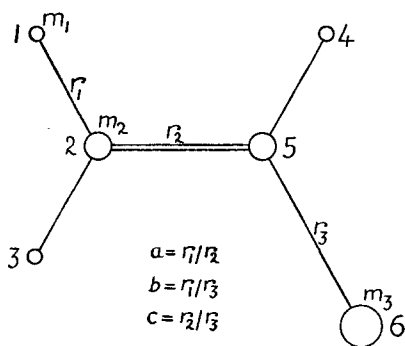


FIG. 1. Numbering of coordinates for mono-substituted ethylenes.

<sup>1</sup> P. Torkington, Proc. Roy. Soc. London (in press); Nature **163**, 96 (1949).

<sup>2</sup> P. Torkington, J. Chem. Phys. **17**, 1026 (1949); Nature **162**, 370, 607 (1948).

### II. THE SECULAR EQUATIONS

The notation used in previous papers<sup>2,3</sup> is adopted here; for an  $n$ th-order symmetry-factor, the  $n$  valence-type symmetry coordinates  $\Delta_1$  to  $\Delta_n$  are defined in terms of  $N$  Cartesian displacement coordinates  $z_1$  to  $z_N$ :

$$\Delta_i = \sum_{j=1}^N a_{ij} z_j \quad (1)$$

and the secular equation is written in matrix form:

$$|\mathbf{dA} - \lambda \mathbf{I}| = 0, \quad (2)$$

where the elements of  $\mathbf{d}$  are the force constants in the potential function defined below:

$$2V = \sum_{i=1}^n \sum_{j=1}^n d_{ij} \Delta_i \Delta_j \quad (3)$$

and the elements of  $\mathbf{A}$  (related to the inverse kinetic energy matrix  $\mathbf{G}$  of Wilson),<sup>4,5</sup> are as follows:

$$A_{ij} = \sum_{k=1}^N a_{ik} a_{jk} (M/m_k) \quad (4)$$

where  $m_k$  is the mass of the atom whose Cartesian dis-

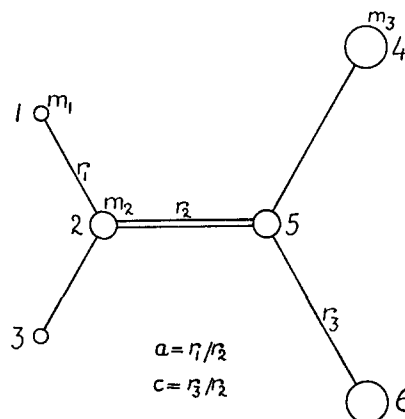
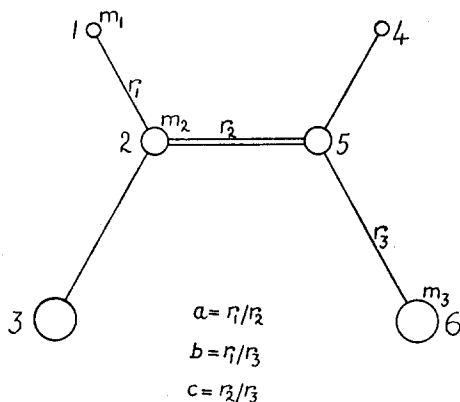
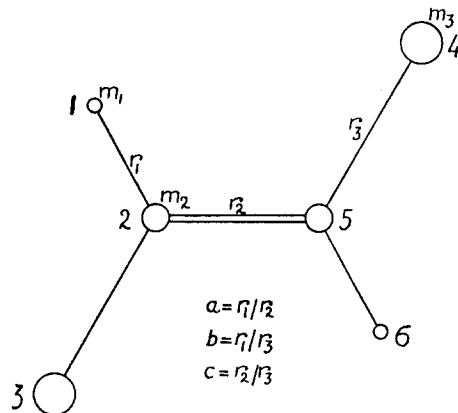


FIG. 2. Numbering of coordinates for 1:1-disubstituted ethylenes.

<sup>3</sup> P. Torkington, J. Chem. Phys. **17**, 357 (1949).

<sup>4</sup> E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939).

<sup>5</sup> E. B. Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).

FIG. 3. Numbering of coordinates for *cis*-1:2-disubstituted ethylenes.FIG. 4. Numbering of coordinates for *trans*-1:2-disubstituted ethylenes.

placement coordinate is  $z_k$ , and  $M$  is an arbitrary mass (conveniently chosen to be one of the  $m_k$ 's), introduced in order that the  $A_{ij}$  shall be dimensionless quantities of convenient magnitude. Both  $\mathbf{d}$  and  $\mathbf{A}$  are symmetric; only half the matrix will be given whenever they are introduced explicitly.  $\mathbf{I}$  is the unit matrix, and the quantity  $\lambda$  is defined as follows:

$$\lambda = 4\pi^2 \sigma^2 c^2 M, \quad (5)$$

$\sigma$  being a fundamental vibration frequency in  $\text{cm}^{-1}$  and  $c$  the velocity of light in  $\text{cm sec}^{-1}$ . In the numerical calculations, the force constants and related quantities are usually given to four significant figures, as this is sometimes necessary to illustrate small differences between various solutions for the same constant. No absolute significance is to be attached to the fourth figure.

The symmetry coordinates and the derived  $\mathbf{A}$  matrices are given in Tables I to IV; for the coordinates  $z_j$  and other quantities, see Figs. 1 to 4. The same matrices are

TABLE I. Symmetry coordinates for substituted ethylenes.

(a) *Mono-Substituted ethylenes*,  $\text{CH}_2=\text{CHX}^a$

$\Delta_1 = \Delta r_{12} - \Delta r_{23}$ $\Delta_2 = \Delta r_{45}$ $\Delta_3 = \Delta r_{12} + \Delta r_{23}$ $\Delta_4 = \Delta r_{25}$ $\Delta_5 = r_1(\Delta\theta_{12} - \Delta\theta_{15} - \Delta\theta_{25})$	$\Delta_6 = r_1(\Delta\theta_{46} - \Delta\theta_{24})$ $\Delta_7 = r_1(\Delta\theta_{15} - \Delta\theta_{35})$ $\Delta_8 = \Delta r_{56}$ $\Delta_9 = r_2\Delta\theta_{26}$
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(b) *1:1-disubstituted ethylenes*,  $\text{CH}_2=\text{CX}_2^b$

$\Delta_1 = \Delta r_{12} + \Delta r_{23}$ $\Delta_2 = \Delta r_{25}$ $\Delta_3 = r_1(\Delta\theta_{12} - \Delta\theta_{15} - \Delta\theta_{25})$ $\Delta_4 = \Delta r_{45} + \Delta r_{56}$ $\Delta_5 = r_2(\Delta\theta_{46} - \Delta\theta_{24} - \Delta\theta_{26})$	$\Delta_6 = \Delta r_{12} - \Delta r_{23}$ $\Delta_7 = r_1(\Delta\theta_{15} - \Delta\theta_{25})$ $\Delta_8 = \Delta r_{45} - \Delta r_{56}$ $\Delta_9 = r_2(\Delta\theta_{24} - \Delta\theta_{26})$
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(c) *Cis*-1:2-disubstituted ethylenes<sup>c</sup>

$\Delta_1 = \Delta r_{12} + \Delta r_{45}$ $\Delta_2 = \Delta r_{25}$ $\Delta_3 = r_1(\Delta\theta_{12} + \Delta\theta_{24} - \Delta\theta_{13} - \Delta\theta_{46})$ $\Delta_4 = \Delta r_{23} + \Delta r_{56}$ $\Delta_5 = r_2(\Delta\theta_{24} + \Delta\theta_{26})$	$\Delta_6 = \Delta r_{12} - \Delta r_{45}$ $\Delta_7 = r_1(\Delta\theta_{15} - \Delta\theta_{24} - \Delta\theta_{13} + \Delta\theta_{46})$ $\Delta_8 = \Delta r_{23} - \Delta r_{56}$ $\Delta_9 = r_2(\Delta\theta_{25} - \Delta\theta_{26})$
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(d) *Trans*-1:2-disubstituted ethylenes<sup>d</sup>

$\Delta_1 = \Delta r_{12} + \Delta r_{56}$ $\Delta_2 = \Delta r_{25}$ $\Delta_3 = r_1(\Delta\theta_{12} + \Delta\theta_{26} - \Delta\theta_{13} - \Delta\theta_{46})$ $\Delta_4 = \Delta r_{23} + \Delta r_{45}$ $\Delta_5 = r_2(\Delta\theta_{24} + \Delta\theta_{25})$	$\Delta_6 = \Delta r_{12} - \Delta r_{56}$ $\Delta_7 = r_1(\Delta\theta_{15} - \Delta\theta_{26} - \Delta\theta_{13} + \Delta\theta_{46})$ $\Delta_8 = \Delta r_{23} - \Delta r_{45}$ $\Delta_9 = r_2(\Delta\theta_{25} - \Delta\theta_{24})$
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<sup>a</sup> See Fig. 1.

<sup>b</sup> See Fig. 2.

<sup>c</sup> See Fig. 3.

<sup>d</sup> See Fig. 4.

used for the unsaturated hydrocarbons dealt with, treating the methyl groups as single masses; it will be shown that this approximation does not affect the values of the force constants seriously. Angles of  $120^\circ$  are used throughout; the order of the corrections to be applied for variations from this angle will be estimated. The degree of the equations is in all cases reduced before solving for the constants by factoring out the C—H valence modes, using the method introduced by Wilson.<sup>5</sup> The small corrections to be applied may be assumed constant for force constants going with coordinates common to a series of molecules.

### III. THE VIBRATIONAL ASSIGNMENTS

For the four vinyl halides and for vinylidene fluoride and chloride the assignments of Thompson and Torkington<sup>6</sup> are used, with the following minor alterations. In vinyl fluoride, the infra-red absorption maxima at 1363 and  $1393 \text{ cm}^{-1}$  are now taken for the *P* and *R* branches of a parallel band,  $\delta\text{CH}_2^8$  then having the value  $1378 \text{ cm}^{-1}$  in place of  $1393 \text{ cm}^{-1}$ . In vinylidene chloride, the Raman line at  $375 \text{ cm}^{-1}$  previously assigned to (non-planar)  $B_1$  rocking, is now taken for planar  $B_2$  rocking. In vinylidene fluoride, for which Raman data are not available, 559 and  $680 \text{ cm}^{-1}$  are accepted for  $A_1$   $\text{CF}_2$  deformation and  $B_2$  CCF rocking respectively, though these values seem rather high; there are infra-red-Raman coincidences at 570 and  $650 \text{ cm}^{-1}$  in  $\text{CF}_2=\text{CCl}_2$ ,<sup>6</sup> though the strong Raman line<sup>7</sup> at  $435 \text{ cm}^{-1}$  seems likely to be  $\delta\text{CF}_2$ .<sup>(a)</sup> For *cis*- and *trans*-1:2-dichloro-<sup>\*</sup> and 1:2-dibromo-ethylenes

<sup>6</sup> H. W. Thompson and P. Torkington, Proc. Roy. Soc. London A184, 21 (1945); Trans. Faraday Soc. 41, 236 (1945); J. Chem. Soc. 303 (1944).

<sup>7</sup> J. B. Hatcher and D. M. Yost, J. Chem. Phys. 5, 992 (1937).  
<sup>a</sup> But there is an A type band at  $559 \text{ cm}^{-1}$  in  $\text{C}_2\text{F}_4$  (see reference 6) which could be assigned to  $B_{3u}$   $\text{CF}_2$  deformation.

<sup>\*</sup> Note added in proof.—The infra-red spectra of *cis*- and *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{D}_2\text{Cl}_2$ , have recently been measured, (H. J. Bernstein and D. A. Ramsay, J. Chem. Phys. 17, 556 (1949)); the suggested assignments for the H compounds are essentially the same as used here, except that  $B_1$  CCl bending is given as  $571 \text{ cm}^{-1}$ , which is almost certainly too high for such a mode. It is of interest

TABLE II. The A matrix for mono-substituted ethylenes.\*

$\begin{bmatrix} (3+2\mu_1) & 0 & 0 & 0 & 0 & -a\sqrt{3} & -\sqrt{3}(1+2a) & 0 & -\sqrt{3} \\ & (1+\mu_1) & 0 & -(1/2) & 0 & \sqrt{3}(a-b)/2 & a\sqrt{3} & -(1/2) & \sqrt{3}(c+1)/2 \\ & & (1+2\mu_1) & -1 & -2\sqrt{3} & 0 & 0 & 0 & 0 \\ & & & 2 & 2\sqrt{3} & \sqrt{3}(b+2)/2 & 0 & -(1/2) & -c\sqrt{3}/2 \\ & & & & 4(3+2\mu_1) & 0 & 0 & 0 & 0 \\ & & & & & (P_1+4\mu_1+b^2\mu_3) & a(3+4a-b) & -\sqrt{3}(a+2)/2 & (P_4-bc\mu_3) \\ & & & & & & (P_2+2\mu_1) & -a\sqrt{3} & (1+4a+b) \\ & & & & & & & (1+\mu_3) & -\sqrt{3}/2 \\ & & & & & & & & (P_3+c^2\mu_3) \end{bmatrix}$	$\begin{bmatrix} \cdots \nu_{CH_2^a} \\ \cdots \nu_{CH} \\ \cdots \nu_{CH_2^b} \\ \cdots \nu_{C=C} \\ \cdots \delta_{CH_2^b} \\ \cdots \delta_{CH} \\ \cdots \delta_{CH_2} \\ \cdots \nu_{C-X} \\ \cdots \delta_{CCX} \end{bmatrix}$
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\*  $\mu_1 = (m_2/m_1)$  throughout  $P_1 = 2(2+a+b+a^2) - b(a-b)$   
 $\mu_3 = (m_2/m_3)$   $P_2 = 1+4a+8a^2$   
 $P_3 = 2+c+c^2$   
 $P_4 = 1+2a-c(1+b).$

TABLE III. A matrices for 1:1-disubstituted ethylenes.

Class A <sub>1</sub>	
$\begin{bmatrix} (1+2\mu_1) & -1 & -2\sqrt{3} & 0 & 0 \\ & 2 & 2\sqrt{3} & -1 & 2\sqrt{3} \\ & & 4(3+2\mu_1) & 0 & 0 \\ & & & (1+2\mu_3) & -2\sqrt{3} \\ & & & & 4(3+2\mu_3) \end{bmatrix}$	$\begin{bmatrix} \cdots \nu_{CH_2^a} \\ \cdots \nu_{C=C} \\ \cdots \delta_{CH_2^a} \\ \cdots \nu_{CX_2^a} \\ \cdots \delta_{CX_2^a} \end{bmatrix}$
Class B <sub>2</sub>	
$\begin{bmatrix} (3+2\mu_1) & -(2a+1)\sqrt{3} & 0 & 2c\sqrt{3} \\ & (1+4a+8a^2+2\mu_1) & 2a\sqrt{3} & -2(a+c+4ac) \\ & & (3+2\mu_3) & -(2c+1)\sqrt{3} \\ & & & (1+4c+8c^2+2\mu_3) \end{bmatrix}$	$\begin{bmatrix} \cdots \nu_{CH_2^a} \\ \cdots \delta_{CH_2} \\ \cdots \nu_{CX_2^a} \\ \cdots \delta_{CCX} \end{bmatrix}$

TABLE IV. A matrices for *cis*-1:2-disubstituted ethylenes.\*

Class A <sub>1</sub>	
$\begin{bmatrix} 2(1+\mu_1) & -1 & b\sqrt{3} & -1 & c\sqrt{3} \\ & 2 & -(b+2)\sqrt{3} & -1 & -c\sqrt{3} \\ & & (4A_{11}+a^2A_{55}+4b) & 2\sqrt{3} & (2c+aA_{55}) \\ & & & 2(1+\mu_3) & 0 \\ & & & & 2c^2(1+\mu_3) \end{bmatrix}$	$\begin{bmatrix} \cdots \nu_{CH} \\ \cdots \nu_{C=C} \\ \cdots \delta_{CH} \\ \cdots \nu_{C-X} \\ \cdots \delta_{CCX} \end{bmatrix}$
Class B <sub>1</sub>	
$\begin{bmatrix} 2(1+\mu_1) & -(2a-b)\sqrt{3} & -1 & (c+2)\sqrt{3} \\ & \{A_{33}+4a(2+2a-b)\} & 2(1+a)\sqrt{3} & \{A_{55}-4(1+2a)\} \\ & & 2(1+\mu_3) & -2\sqrt{3} \\ & & & \{A_{55}+4(c+2)\} \end{bmatrix}$	$\begin{bmatrix} \cdots \nu_{CH} \\ \cdots \delta_{CH} \\ \cdots \nu_{C-X} \\ \cdots \delta_{CCX} \end{bmatrix}$

\* The subsidiary quantities  $A_{11}$ ,  $A_{55}$  etc., are the elements of the class A<sub>1</sub> factor of **A**. The matrices for the *trans*-1:2-disubstituted ethylenes are obtained from the above for the *cis*-compounds by striking out the second row and column and inserting them to form the second row and column of the class B<sub>1</sub> factor; the residue of the former is then the class B<sub>u</sub> factor of the *trans*-compound, and the latter has become the class A<sub>g</sub> factor.

the assignments given in Wu<sup>8</sup> and Herzberg<sup>9</sup> are accepted, with the alteration that the strong depolarised Raman lines at 406 and 372 cm<sup>-1</sup> in the *cis*-compounds are assigned to B<sub>1</sub> CCl and CBr bending respectively, instead of to the twisting modes. (See CH<sub>2</sub>=CHCl (395), CH<sub>2</sub>=CCl<sub>2</sub> (375); CH<sub>2</sub>=CHBr (345), CH<sub>2</sub>=CBr<sub>2</sub>

that B<sub>u</sub> CCl bending is predicted from combination bands to be at 265 cm<sup>-1</sup>, in excellent agreement with the predicted value here.

<sup>8</sup> T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, 1946).

<sup>9</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. van Nostrand Company, Inc., New York, 1945).

(322).) The unobservable B<sub>u</sub> skeletal bendings in the *trans*-compounds are predicted here by making the sum of the A<sub>g</sub> and B<sub>u</sub> bending constants the same as the sum of the A<sub>1</sub> and B<sub>1</sub> bending constants in the corresponding *cis*-compound. For vinylidene bromide, the infra-red data of Thompson and Torkington<sup>6</sup> and the Raman data of de Hemptinne, Velghe, and van Riet<sup>10</sup> are used; the latter have also measured the Raman spectra of the deuterated vinyl and vinylidene bromides. For propy-

<sup>10</sup> M. de Hemptinne and C. Velghe, *Bull. Class. Sci. Acad. Roy. Belgium* 30, 75 (1944); de Hemptinne, Velghe, and van Riet, *Bull. Class. Sci. Acad. Roy. Belgium* 30, 40 (1944).

lene<sup>b</sup> and isobutene, the assignments given by Kilpatrick and Pitzer<sup>11</sup> are accepted, with the alteration that 1062 cm<sup>-1</sup>, assigned by them to B<sub>1</sub> CH<sub>3</sub> rocking in the latter, is taken for planar CH<sub>2</sub> bending;<sup>c</sup> 1280 cm<sup>-1</sup> is too high for this mode. Their assignments for the 2-butenes are not thought sufficiently certain to justify detailed calculations; thus, there is no infra-red band, (or only a very weak one), at 1267 cm<sup>-1</sup> in the *cis*-compound, where there is a Raman line which they assign to A<sub>1</sub> CH wagging; it seems peculiar that this mode should be so weakly-active in the infra-red. And there is some confusion between methyl rocking and C—C stretching modes.

The assignments are summarized in Tables V to VIII.

#### IV. SOLUTIONS FOR THE FORCE CONSTANTS

In the substituted ethylenes, the fundamental modes of vibration can be conveniently grouped into four types, as follows:

- (a) C—H stretching,
- (b) C=C stretching,
- (c) C—H bending,
- (d) Skeletal stretching and bending other than (b).

Type (a) is factored off before solving for the constants for types (b), (c), and (d). For the latter, the procedure developed in a previous paper<sup>2</sup> is used. For each molecule, a standard solution for the force constants is obtained, (together with the matrix of components in the displacements and the percentage of potential energy in the principal square terms). This standard solution corresponds to the fundamental vibrations factoring off in the order in which the corresponding coordinates occur in the matrix **A** (see Tables II to IV). The standard force field can thus be regarded as subjecting the molecule to a graded rigidity; in passing from  $\nu_1$  to  $\nu_n$  each fundamental mode involves one fewer coordinate. With the order adopted here, the C=C stretching coordinate takes no part in the displacements for modes other than  $\nu_{C=C}$ . It is reasonable to assume that the error introduced by this step in a constant going with any given coordinate will be the same for all members of a series of molecules for which this is a common coordinate. This means that a constant correction can be applied for, for example,  $\Delta r_{C=C} \cdot \Delta \theta_{CCH}$  interaction. The standard force constant matrix **d**<sup>0</sup> having been obtained, small off-diagonal elements are then removed as described previously;<sup>2</sup> the relevant quantities ( $\partial \lambda_k / \partial d_{ij}$ ) are readily calculated from the matrix determining the components in the displacements. This

<sup>b</sup> 1042 cm<sup>-1</sup> is assigned to CH<sub>2</sub> wagging in the text; this is accepted in the present work. In their table it is assigned to CH<sub>3</sub> wagging, and CH<sub>2</sub> wagging given as 1172 cm<sup>-1</sup>. The assignments for non-planar CH wagging and twisting also appear to have become transposed.

<sup>11</sup> J. E. Kilpatrick and K. S. Pitzer, J. Research Nat. Bur. of Stand. 38, 191 (1947).

<sup>c</sup> The value given by Kilpatrick and Pitzer is 1066; the present value is taken from the Catalog of Infra-red Spectrograms, American Petroleum Institute Research Project 44.

removal of small interaction constants smooths off the step-like graded rigidity, since in the standard solution the interaction constants take such values that coordinates  $\Delta_1$  to  $\Delta_{i-1}$  are prevented from taking part in  $\nu_i$ . With **d**<sup>0</sup> and the partially diagonalized matrix **d'** the coordinates  $\Delta_{i+1}$  to  $\Delta_n$  are represented in the displacement for  $\nu_i$ ; these solutions can be regarded as allowing a natural coupling, (determined by the off-diagonal elements of the matrix **A**), between the C—H bending modes and the lower-frequency skeletal vibrations (d). For comparison, the solution for the C—H bending constants in which all coordinates other than  $\Delta_i$  remain rigid in  $\nu_i$  is found. These constants,<sup>12</sup> which will be referred to as the Wilson-Pitzer constants, are given by the following formula:

$$d_{ii}'' = (|A|_{ii}/|A|)\lambda_i \quad (6)$$

where  $|A|_{ii}$  is the minor of  $|A|$  obtained by striking out the *i*th row and column. Pitzer has developed a semi-rigid-molecule approximation for dealing with large symmetry factors.<sup>13</sup> In his method, the fundamentals are grouped into classes, (e.g., skeletal vibrations and vibrations of attached groups), and the matrix **A**, (or **G**), reduced to a series of matrices of lower order, one for each class, that for any given class being obtained by applying the conditions that all coordinates of other classes shall remain rigid. The method is an extension of Wilson's treatment of C—H stretching vibrations.<sup>5</sup> Each reduced matrix gives rise to a reduced secular equation, which can then be solved for vibrations of that class. It should be remembered that these reduced equations are not factors of the complete secular equation; constants which satisfy the reduced equation will not satisfy the complete symmetry factor from which it is derived, the error depending on the degree of coupling between coordinates allocated to different classes. The Wilson-Pitzer constants given here go with linear reduced equations;  $d_{ii}''$  is identical with  $d_{ii}^0$  when  $\nu_i$  and  $\nu_n$  are transposed. They are therefore associated with  $(n-1)$  interaction constants, required to maintain the remaining coordinates rigid.

The following values, given in angstrom units, are used here for the bond lengths.

$$\begin{aligned} r_{C-H} &= 1.071,^{14} r_{C=C} = 1.353^{14} \text{ throughout;} \\ r_{C-Cl} &= 1.69,^{15} r_{C-Br} = 1.83,^d r_{C-I} = 2.03;^{16} \\ r_{C-F} &= 1.36^d,^{17} \text{ in } CH_2=CHF, 1.33^d \text{ in } CH_2=CF_2; \\ \text{Effective } r_{C-C} &= 1.60_3.^e \end{aligned}$$

<sup>12</sup> P. Torkington, Nature 164, 113 (1949).

<sup>13</sup> W. J. Taylor and K. S. Pitzer, J. Research Nat. Bur. of Stand. 38, 1 (1947).

<sup>14</sup> W. S. Gallaway and E. F. Barker, J. Chem. Phys. 10, 88 (1942).

<sup>15</sup> Brockway, Beach, and Pauling, J. Am. Chem. Soc. 57, 2693 (1935).

<sup>16</sup> Huggill, Coop, and Sutton, Trans. Faraday Soc. 34, 1518 (1938).

<sup>d</sup> Estimated from comparison of data for C<sub>2</sub>H<sub>3</sub>Cl, CH<sub>3</sub>Cl and CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub> (see reference 17).

<sup>17</sup> L. O. Brockway, J. Phys. Chem. 41, 747 (1937).

<sup>e</sup> Assuming a mass ( $m_C + 3m_H$ ) at the center of gravity of the

TABLE V. Vibration frequencies of planar modes of  $\text{CH}_2=\text{CHX}$ , in  $\text{cm}^{-1}$ .

X	$\nu_{\text{C}=\text{C}}$	$\delta\text{CH}_2^a$	$\delta\text{CH}$	$\delta\text{CH}_2$	$\nu_{\text{C}-\text{X}}$	$\delta\text{CCX}$
$\text{CH}_3$	1649	1415	1297	1042	920	417
$\text{F}^a$	1650	1378	1306	924	1153	500
Cl	1610	1370	1280	1030	724	395
Br	1605	1377	1262	1008	615	345
I	1593	1376	1242	990	550	309

<sup>a</sup> Numbering from the left, in vinyl fluoride  $\nu_6 > \nu_4$  and in vinylidene fluoride  $\nu_6 > \nu_5$ ; the order here is retained for consistency.

TABLE VI. Vibration frequencies of planar modes of  $\text{CH}_2=\text{CX}_2$ , in  $\text{cm}^{-1}$ .

X	$A_1$				$B_2$		
	$\nu_{\text{C}=\text{C}}$	$\delta\text{CH}_2^a$	$\nu_{\text{CX}_2^a}$	$\delta\text{CX}_2^a$	$\delta\text{CH}_2$	$\nu_{\text{CX}_2^a}$	$\delta\text{CCX}$
$\text{CH}_3$	1664	1390	800	378	1062	986	431
$\text{F}^a$	1730	1386	921	559	945	1295	680
Cl	1620	1395	605	295	1094	794	375
Br	1593	1379	467	184	1085	696	322

<sup>a</sup> Numbering from the left, in vinyl fluoride  $\nu_6 > \nu_4$  and in vinylidene fluoride  $\nu_6 > \nu_5$ ; the order here is retained for consistency.

All ethylenic angles are assumed  $120^\circ$  throughout; deviations from this value will not affect the C—H bending constants; their effect on the skeletal constants will be estimated when these are dealt with.

The results for C—H bending modes are summarized in Tables IX to XI. Force constants are given in units of  $10^5$  dynes  $\text{cm}^{-1}$  and the energy fractions  $V_{ii}(\nu_i)$ , referring to the standard solutions, as percentages. The subscripts are ordered to go with the reduced matrices  $\mathbf{A}$ , and with the assignments given in Tables V to VIII. Thus  $d_{22}$  in the vinyl compounds is here the constant going with the coordinate for  $\text{CH}_2$  deformation, given as  $\Delta_5$  in Table I (a).

## V. DISCUSSION OF THE RESULTS

We have obtained three solutions for each of the C—H bending constants occurring in the potential functions for substituted ethylenes. From the results summarized in Tables IX to XI it is seen that, with the coordinates used, the  $\text{CH}_2$  deformation constant lies between 0.130 and 0.145, the C—H bending constant between 0.18 and 0.24, and the  $\text{CH}_2$  rocking constant between 0.20 and 0.35, in units of  $10^5$  dynes  $\text{cm}^{-1}$ . In every case, the elimination of the small interaction constants from  $\mathbf{d}^0$  produces negative increments in the CH bending constants, and the Wilson-Pitzer constant is greater than either of the other two\*; i.e.,  $d_{ii}'' > d_{ii}^0 > d_{ii}'$ .  $d_{ii}''$  is associated with a pure vibration  $\nu_i$  in which the

methyl group, taking  $r_{\text{C}-\text{C}}$  in propylene as 1.53, (allowing for a small degree of shortening from the value 1.57<sub>3</sub> found in ethane (see reference 9))  $r_{\text{C}-\text{H}}=1.093_6$ , as in methane (see reference 9), and assuming tetrahedral angles.

\* It can be shown that inclusion of  $\Delta_j$  in the displacement for  $\nu_i$  decreases or increases  $d_{ii}$  from the value  $d_{ii}''$  for the pure mode, according as  $\nu_i$  is greater than or less than  $\nu_j$ ; similarly, that  $d_{ii}^0$  is always greater than  $d_{ii}'$ .

TABLE VII. Vibration frequencies of planar modes of  $\text{cis-CHX}=\text{CHX}$ , in  $\text{cm}^{-1}$ .

X	$A_1$				$B_1$		
	$\nu_{\text{C}=\text{C}}$	$\delta\text{CH}$	$\nu_{\text{CX}}$	$\delta\text{CCX}$	$\delta\text{CH}$	$\nu_{\text{CX}}$	$\delta\text{CCX}$
Cl	1587	1179	711	173	1303	857	406
Br	1584	1150	580	109	1229	673	372

TABLE VIII. Vibration frequencies of planar modes of  $\text{trans-CHX}=\text{CHX}$ , in  $\text{cm}^{-1}$ .

X	$A_g$				$B_u$		
	$\nu_{\text{C}=\text{C}}$	$\delta\text{CH}$	$\nu_{\text{CX}}$	$\delta\text{CCX}$	$\delta\text{CH}$	$\nu_{\text{CX}}$	$\delta\text{CCX}$
Cl	1576	1270	844	349	1200	820	270(calc.)
Br	1578	1246	748	218	1145	746	247(calc.)

potential energy is a function of only the one coordinate  $\Delta_i$ , (i.e.,  $V_{ii}''(\nu_i)=1$ ,  $V_{ij}''(\nu_i)=0$  for  $i \neq j$ ). With  $d_{ii}^0$ ,  $V_{ii}(\nu_i)$  is greater than unity, there being negative contributions from the various cross-terms  $d_{ij}\Delta_i\Delta_j$ , ( $j > i$ ). With  $d_{ii}'$ ,  $V_{ii}(\nu_i)$  is in general less than unity, and terms involving  $\Delta_j$ , ( $j < i$ ), take non-zero values. (See Appendix II.) The range of values covered by the three solutions can be taken as representative of the range physically possible, the standard constants  $d_{ii}^0$  being convenient mean values. Change of sign of all the small off-diagonal elements of  $\mathbf{d}^0$  reduced to zero in  $\mathbf{d}'$  would give a fourth solution  $\mathbf{d}^m$  such that  $(d_{ii}^0 - d_{ii}') \approx (d_{ii}' - d_{ii}^m)$ .  $\mathbf{d}^m$  could be regarded as a conventional minimum solution, but since the small off-diagonal elements of  $\mathbf{d}^0$  have no physical significance when their sign is changed, we will not go beyond  $\mathbf{d}'$  here. The absolute values of the constants have still to be corrected for coupling with C=C stretching; as already stated, it is justifiable to assume that, for a given type of C—H bending, this interaction will remain constant throughout the series of substituted ethylenes. Variations deduced from the values in Tables IX to XI can therefore be taken as absolute.

Consider first the  $\text{CH}_2$  deformation constant. For the vinyl halides, a value lying between 0.132 and 0.134 will fit all four compounds; for propylene, however, a value greater than 0.139 is required, which will not fit any of the other halides. In the vinylidene compounds, a value within the range 0.135 to 0.139 fits all four molecules. The analogous constants, ( $d^0=d''$ ), in ethylene, with  $\nu_{A_g}=1342.4$ ,  $\nu_{B_{3u}}=1443.5$ ,<sup>9,14</sup> have the following values: 0.1337( $A_g$ ), 0.1380( $B_{3u}$ ). The constant for the  $A_g$  mode is probably better chosen as a standard, since the  $B_{3u}$  mode does not interact with C=C stretching. Thus, the value 0.134–0.135 will fit all ethylenic molecules studied here, with the exception of propylene. This anomaly of propylene is rather obscure. In the series  $\text{CH}_2=\text{CHX}$ ,  $\text{CH}_2=\text{CX}_2$ ,  $\delta\text{CH}_2^a$  is higher in the di-substituted than in the mono-substituted compounds in all cases except  $\text{X}=\text{CH}_3$ , which suggests that the observed frequency

TABLE IX. Solutions for mono-substitutes ethylenes  $\text{CH}_2=\text{CHX}$ .

X	$\text{CH}_3$			F		
<i>i</i>	2	3	4	2	3	4
$d_{ii}^0$	0.1407	0.2290	0.2532	0.1338	0.2339	0.2077
$d_{ii}'$	0.1393	0.2183	0.2297	0.1317	0.2184	0.1718
$d_{ii}''$	0.1424	0.2333	0.2886	0.1355	0.2368	0.2252
$\Delta_j^0(\nu_i)$	$\begin{bmatrix} 1 \\ -0.0393 & 1 \\ -0.0009 & 0.0762 & 1 \\ 0.0088 & -0.0331 & -0.0368 \\ 0.0113 & 0.0276 & 0.1347 \end{bmatrix}$			$\begin{bmatrix} 1 \\ -0.0409 & 1 \\ -0.0009 & 0.0744 & 1 \\ 0.0088 & -0.0326 & -0.0369 \\ 0.0135 & 0.0238 & 0.1387 \end{bmatrix}$		
$V_{ii}^0(\nu_i)$	100.496	102.231	104.868	100.748	103.178	109.472
X	Cl			Br		
<i>i</i>	2	3	4	2	3	4
$d_{ii}^0$	0.1320	0.2238	0.2470	0.1333	0.2177	0.2352
$d_{ii}'$	0.1305	0.2139	0.2249	0.1320	0.2087	0.2168
$d_{ii}''$	0.1343	0.2314	0.2887	0.1364	0.2275	0.2807
$\Delta_j^0(\nu_i)$	$\begin{bmatrix} 1 \\ -0.0388 & 1 \\ -0.0009 & 0.0770 & 1 \\ 0.0088 & -0.0334 & -0.0367 \\ 0.0107 & 0.0338 & 0.1330 \end{bmatrix}$			$\begin{bmatrix} 1 \\ -0.0381 & 1 \\ -0.0009 & 0.0778 & 1 \\ 0.0088 & -0.0337 & -0.0367 \\ 0.0099 & 0.0369 & 0.1311 \end{bmatrix}$		
$V_{ii}^0(\nu_i)$	100.527	102.110	104.671	100.481	101.986	104.070
X	I					
<i>i</i>	2	3	4			
$d_{ii}^0$	0.1330	0.2108	0.2258			
$d_{ii}'$	0.1318	0.2026	0.2103			
$d_{ii}''$	0.1363	0.2218	0.2734			
$\Delta_j^0(\nu_i)$	$\begin{bmatrix} 1 \\ -0.0373 & 1 \\ -0.0009 & 0.0787 & 1 \\ 0.0088 & -0.0339 & -0.0366 \\ 0.0088 & 0.0387 & 0.1292 \end{bmatrix}$					
$V_{ii}^0(\nu_i)$	100.429	101.859	103.563			

for propylene and/or isobutene is not the true one. The symmetrical methyl deformation lies close, at 1370 to 1380  $\text{cm}^{-1}$ ; it is possible that Fermi resonance between these two modes occurs, for which a correction should be applied.<sup>f, 18</sup> Resonance is also possible between  $\nu_{\text{C}=\text{C}}$  and CH bending modes, but it seems reasonable to assume that for a given mode this would take place to the same extent for all related molecules.

The  $\text{CH}_2$  bending constant varies much more in passing from  $d'$  to  $d''$  than does the symmetrical  $\text{CH}_2$  deformation constant; the coupling with coordinates other than  $\text{C}=\text{C}$  stretching is of more importance. A value of 0.225 can satisfy all the vinyl halides; if we

<sup>f</sup> On the other hand,  $\delta\text{CH}_2^s$  in the allyl halides (see reference 18) lies at 1405 to 1410  $\text{cm}^{-1}$ ; any resonance would involve the saturated  $\text{CH}_2$  deformation at 1440 to 1450  $\text{cm}^{-1}$ , leading to a positive correction.

<sup>18</sup> H. W. Thompson and P. Torkington, Trans. Faraday Soc. 42, 432 (1946).

omit the fluoride, a range of 0.225 to 0.27 is allowed, nearly the whole being also available for propylene. Passing to the vinylidene compounds, the minimum allowed value becomes raised to 0.245, which is also the maximum for vinylidene fluoride. The value 0.245 could thus be a common solution for all the molecules studied, except vinyl fluoride. Since this compound falls outside the range, it seems probable that this is also the case for vinylidene fluoride. 0.245 is the value of the Wilson-Pitzer constant for  $\text{CH}_2=\text{CF}_2$ ; it seems most unlikely that there should be less kinetic coupling in the fluoride, where  $\nu_{\text{C}-\text{X}}$  and  $\delta_{\text{CCX}}$  are higher, than in the other halides. The values of the comparable  $\text{CH}_2$  rocking constants in ethylene, ( $d^0=d''$ ), with  $\nu_{\text{B}_{1g}}=1050$ ,  $\nu_{\text{B}_{2u}}=995$   $\text{cm}^{-1}$ <sup>19, 14</sup> and with accepted molecular dimensions,<sup>14</sup> are as follows: 0.1987( $\text{B}_{1g}$ ), 0.2833( $\text{B}_{2u}$ ); (mean: 0.2410).

The range of values for CH wagging constants is less than for  $\text{CH}_2$  rocking constants, though rather more

TABLE X. Solutions for 1:1-disubstituted ethylenes  $\text{CH}_2=\text{CX}_2$ .

X i	$\text{CH}_2$		F		Cl		Br	
	2	5	2	5	2	5	2	5
$d_{ii}^0$	0.1359	0.2671	0.1357	0.2369	0.1368	0.2788	0.1335	0.2718
$d_{ii}'$	0.1342	0.2274	0.1329	0.1546	0.1353	0.2443	0.1319	0.2443
$d_{ii}''$	0.1395	0.3119	0.1392	0.2455	0.1421	0.3407	0.1400	0.3421
$\Delta_j^0(\nu_i)$	$\begin{bmatrix} 1 \\ 0.0168 \\ -0.0581 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0168 \\ -0.0581 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0168 \\ -0.0581 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0168 \\ -0.0581 \end{bmatrix}$	
	$\begin{bmatrix} 1 \\ 0.0850 \\ -0.3340 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0850 \\ -0.2855 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0850 \\ -0.3495 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0850 \\ -0.3744 \end{bmatrix}$	
$V_{ii}^0(\nu_i)$	100.599	108.031	101.055	121.025	100.557	106.272	100.455	105.322

TABLE XI.\* Solutions for *cis*- and *trans*-1:2-disubstituted ethylenes  $\text{CHX}=\text{CHX}$ .

X i	<i>Cis</i> -		<i>Trans</i> -	
	2	5	2	5
$d_{ii}^0$	0.2044	0.2192	0.1946	0.1938
$d_{ii}'$	0.2034	0.1942	0.1938	0.1752
$d_{ii}''$	0.2052	0.2358	0.1958	0.2160
$\Delta_j^0(\nu_i)$	$\begin{bmatrix} 1 \\ 0.0115 \\ -0.0017 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0120 \\ -0.0037 \end{bmatrix}$	
	$\begin{bmatrix} 1 \\ 0.0529 \\ -0.0608 \end{bmatrix}$		$\begin{bmatrix} 1 \\ 0.0530 \\ -0.0651 \end{bmatrix}$	
$V_{ii}^0(\nu_i)$	100.225	106.057	100.206	105.063

\* The constants here are obtained from those going with the coordinates in Table I by multiplying by a factor of two, (this being equivalent to there being a normalizing factor of  $(1/\sqrt{2})$  included in the coordinates), to be comparable with those in Table IX.

than for  $\text{CH}_2$  deformation constants. A value of about 0.22 will satisfy all the vinyl compounds, including propylene. With the *cis*- and *trans*-di-substituted compounds it is likely that the constants comparable with the  $d_{33}$  of the vinyl compounds will be those for the symmetrical ( $A_1$  and  $A_g$ ) modes, (i.e., the  $d_{22}$  of Table XI) since the  $B_1$  and  $B_u$  vibrations do not interact with  $\nu_{\text{C}=\text{C}}$ . These are rather lower than the corresponding constants in the vinyl compounds, except for the *trans*-Wilson-Pitzer constants. The value 0.22 can be fitted to both *trans*-compounds, but this has to be lowered to about 0.20 for the *cis*-isomers; and, in addition, there is for the latter no overlapping of the allowed ranges of values in the chloride and bromide. There is thus some evidence for the constant in the *trans*-compounds being greater than in the *cis*-isomers, and also for there being a variation in the CH bending constant with change in the substituent X. This latter is to be expected, since the coordinate used involves the angle HXC. (See Table I.) For the *cis*-compounds, the  $B_1$  constants overlap with the  $A_1$  constants, but for the *trans*-compounds there is no such overlap, the  $B_u$  constants taking the lower range of values. However, no absolute significance is to be

attached to this difference, since the correction for coupling with  $\text{C}=\text{C}$  stretching is not known.\*

Recapitulating, it has been shown that it is possible to use the same value for the  $\text{CH}_2$  deformation constant as in ethylene for all the vinyl and vinylidene compounds studied here, with the possible exception of propylene. And that the ethylenic  $\text{CH}_2$  wagging constant (taking the mean for  $B_{1g}$  and  $B_{2u}$  modes), can also be carried over except to the fluorides, for which a lower value must be used. For CH bending there is definite evidence that the constant varies with the substituent.

Reconsidering the  $\text{CH}_2$  bending constant, it has been shown that this is the most strongly affected by kinetic coupling. (This fact is also very evident from ethylene itself; the difference between the (unnormalized) constants for  $B_{1g}$  and  $B_{2u}$  bending amounts to 17.5 percent of the mean constant, this being equivalent to constants  $+0.0417$ ,  $-0.0417$  for interaction between adjacent angles on the same side of  $\text{C}=\text{C}$ , and between alternate

\* In such a case it is usual to assume the constants the same; this would enable the  $\Delta r_{\text{C}=\text{C}} \cdot \Delta \theta_{\text{CH}}$  interaction here to be determined. But such constants are not necessarily equal. (See the pairs of  $\text{CH}_2$  rocking constants in ethylene:  $B_{1g}$ ,  $B_{2u}$ , (see Appendix I),  $B_{1u}$ ,  $B_{2g}$ , (see reference 1).)



TABLE XII.

	B <sub>1g</sub>	C <sub>2</sub> H <sub>4</sub> B <sub>2u</sub>	B <sub>3u</sub>	B <sub>1g</sub>	C <sub>2</sub> D <sub>4</sub> B <sub>2u</sub>	B <sub>3u</sub>
$\nu_1$ (obs.)	3075	3105.5	2989.5	2304	2345	2200.2
$\nu_2$ (obs.)	1050	995	1443.5	883	723.4	1077.9
$d_{11}^c$	1.237 <sub>4</sub>	1.270 <sub>5</sub>	1.271 <sub>3</sub>	1.229 <sub>1</sub>	1.300 <sub>8</sub>	1.318 <sub>9</sub>
$d_{22}^{c''}$	0.0993 <sub>3</sub>	0.1416 <sub>5</sub>	0.0689 <sub>8</sub>	0.1068 <sub>9</sub>	0.1454 <sub>7</sub>	0.0699 <sub>2</sub>
$\nu''$ (calc.)	3074.5	3105.4	2989.5	2304.5	2344.9	2200.8
$\nu_2''$ (calc.)	1046.6	994.7 <sub>4</sub>	1442.5	872.6 <sub>5</sub>	722.8 <sub>6</sub>	1075.2
$d_{22}^c$	0.1002 <sub>7</sub>	0.1417 <sub>9</sub>	0.0690 <sub>7</sub>	0.1091 <sub>0</sub>	0.1458 <sub>2</sub>	0.0701 <sub>0</sub>
$\nu_1^c$ (calc.)	3074.6	3105.4	2989.5	2305.2	2344.9	2200.8
$\nu_2^c$ (calc.)	1051.4 <sub>5</sub>	995.2 <sub>0</sub>	1443.4 <sub>5</sub>	881.4	723.6 <sub>6</sub>	1076.6
$d_{11}$	1.238 <sub>2</sub>	1.270 <sub>4</sub>	1.271 <sub>2</sub>	1.227 <sub>7</sub>	1.300 <sub>9</sub>	1.318 <sub>1</sub>
$d_{22}$	0.0999 <sub>9</sub>	0.1417 <sub>3</sub>	0.0690 <sub>7</sub>	0.1095 <sub>1</sub>	0.1457 <sub>6</sub>	0.0702 <sub>7</sub>
$V_{11}(\nu_1)$	99.255	99.942	99.820	97.188	99.816	99.338
$V_{11}(\nu_2)$	0.745	0.058	0.180	2.812	0.184	0.662

angles, respectively.) If the results for ethylene are interpreted as meaning that the CH<sub>2</sub> bending constant can vary over the range from the B<sub>1g</sub> to the B<sub>2u</sub> constant, then it can be said to be possible to carry over the ethylenic constant in every case studied here, though the significance of variations would be rather obscure. It seems best to take the mean constant, which occurs as the square-term constant in the expanded valence-force potential function for ethylene, as the significant value. Now this value occupies various positions in the ranges of allowed solutions. In the vinyl compounds, excluding the fluoride,  $d_{44}=0.241$  is associated with decreasing coupling in passing from X=CH<sub>3</sub> to X=I; for the former,  $d^0>0.241>d'$ , and for the latter  $d''>0.241>d^0$ . This seems the likely direction for such variation in degree of coupling. In vinylidene chloride and bromide,  $d'>0.241$ , and unless a higher value of the constant is used, the coupling will be greater than in any of the vinyl compounds. This may be due to the presence of a higher degree of symmetry.<sup>h</sup>

The same decrease in coupling occurs when a constant CH bending constant is fitted into the range of values for the vinyl halides; in the fluoride,  $d^0>0.22>d'$ , and in the iodide  $d''>0.22>d^0$ , propylene lying roughly between fluoride and chloride. Common values for CH and CH<sub>2</sub> rocking constants could therefore be used for all the monosubstituted ethylenes here, with the exception of  $\delta\text{CH}_2$  in the fluoride. However, it has been shown from the results for the disubstituted compounds that there is probably a real variation with X of the CH bending constant.

<sup>h</sup> The assignments for these two molecules may be incorrect. For each there is a close pair of A-type bands in the region of 1100 cm<sup>-1</sup>. The lower frequency member was chosen in the chloride; any correction for Fermi resonance would raise the frequency. The higher frequency member was chosen for the bromide, because it led to a better frequency prediction for the deuterated compound, for which there is only a single Raman line. But there are different anharmonicity corrections for CH and CD bending modes, and it is possible that  $\delta\text{CH}_2(\text{B}_2)$  is the band at 1056 cm<sup>-1</sup>.

## VI. CONCLUSION

The present analysis has given series of values for the force constants for planar CH bending modes in substituted ethylenes. The evidence for a given force constant varying with different substituents is not very definite, but it seems likely that, since there is positive evidence in some cases, there are real variations in the remainder; the effect is more noticeable with two substituents than with one. Variations in a group frequency may be due to any or all of three causes, (a) changes in the force constant going with the coordinate determining the group vibration, (b) changes in the overlapping coordinates, (c) changes in the interaction constants in cross-product terms involving the group coordinate. Some attempt has been made here to determine the relative probabilities of (a) and (b); as regards (c), the interaction constants are in general negligible with the exception of those for interaction with C=C stretching. The non-diagonal elements of  $\mathbf{d}^0$  are a measure of the maximum allowed values of these interaction constants. It is readily shown that in most cases they would have to take improbably large values to produce the same effect as a given small increment in the square-term constant for the group vibration. (See Appendix III.)

It is hoped to treat the skeletal vibrations of substituted ethylenes in a second paper. The author wishes to express his gratitude to Courtaulds Limited for making the present program of work possible, and to Sir Cyril Hinshelwood for granting him facilities at the Physical Chemistry Laboratory. Also to Dr. H. W. Thompson, F. R. S., Dr. J. W. Linnett, and Professor C. A. Coulson, for helpful discussions.

## APPENDIX I. ERRORS INTRODUCED THROUGH THE FACTORING OF THE C-H STRETCHING MODES

The following results were obtained with ethylene and ethylene-*d*<sub>4</sub>; the coordinates used are unnormalized and analogous to those used for the substituted ethylenes

(see Table XII). The un-primed  $d_{11}$ ,  $d_{22}$  are the constants obtained by solving explicitly,<sup>3</sup> assuming the interaction constants zero; the  $V_{11}$  are the energy-fractions, (given as percentages), going with this solution.  $d_{11}^c$ ,  $d_{22}^c$ , are the constants obtained by applying a correction for kinetic coupling in place of factoring and  $d_{22}''$  is the factored Wilson-Pitzer constant.  $\nu_i''$  and  $\nu_i^c$  are the frequencies predicted using  $d_{22}''$  and  $d_{22}^c$  respectively,  $d_{11}^c$  being used for both. The differences in the case of ethylene are seen to be very small; the constants  $d^c$  are the closer approximation. With ethylene- $d_4$ , the error introduced by factoring off the C—D stretching modes is considerably larger; this would be expected from the potential energy distributions. In general, the correction for kinetic coupling again gives the better approximation. Comparing the corresponding results for the hydrogen and deuterium compounds, it is seen that, with the exception of the constant for  $B_{1g}$  stretching, the C—D constants are higher than the C—H constants. This can be attributed to the different anharmonicity corrections required for motions involving hydrogen and deuterium atoms. The difference is of the order of 10 percent for  $B_{1g}$  rocking, 3 percent for  $B_{2u}$  rocking and 1 percent for  $B_{3u}$  deformation. If the C—D stretching vibrations are factored, the following values are obtained for the  $A_1$  and  $A_g$  C—D bending constants in *cis*- and *trans*-CDCl=CDCl respectively: *cis*-,  $d^0=0.1055$ ,  $d'=0.1039$ ; *trans*-,  $d^0=0.1312$ ,  $d'=0.1126$ ,  $\times 10^5$  dynes/cm. These values are higher than those obtained with the hydrogen compounds by 3 percent for the *cis*- isomer and 7–15 percent for the *trans*, which differences are significantly comparable with those found in  $C_2H_4$  and  $C_2D_4$ . Considerable difficulty has been experienced in finding the correct potential function for the ethylenes;<sup>11</sup> the data here suggest that it may be best to solve for the two molecules separately, choosing constants which give consistent anharmonicity increments.

If the partially-diagonalized matrix  $d'$  for  $CH_2=CBr_2$  is used to predict the fundamental frequencies of  $CD_2=CBr_2$ , the following results are obtained:

	$A_1$				$B_2$		
$\nu(\text{calc.})$	1548	1003	455	180	947	642	291
$\nu(\text{obs.})_{10}$	1544	1019	453	183	932	625	283

## APPENDIX II. THE DISPLACEMENTS ASSOCIATED WITH $d'$ AND THE ACCURACY OF THE REDUCTION $d^0 \rightarrow d'$

To illustrate the effect of partially diagonalizing the standard force constant matrix  $d^0$ , the results for  $A_1$  CH wagging in *cis*- $C_2H_2Cl_2$  are given below:

	With $d'$			
$\Delta_i[0.00255$	1	0.01693	—0.00556]	
$V_{ij}$	0.065	0.554	0.040	—0.005
		98.280	0	0
			0.485	—0.011
				0.012

	With $d^0$			
$\Delta_i[$	0	1	0.01155	—0.00173]
$V_{ij}$	0	0	0	0
		100.225	—0.227	0.001
			0.229	—0.002
				0.001

To illustrate the degree of accuracy of the reduction  $d^0 \rightarrow d'$ , the roots of the equation  $|d'A - \lambda I| = 0$  were found for the class  $A_1$  factor for *cis*- $C_2H_2Cl_2$ . The calculated fundamental frequencies are given below, together with the true values:

$\nu(\text{calc.})$	1588.1	1179.6	710.1	162.3
$\nu(\text{obs.})$	1587	1179	711	173

The error for the three higher frequencies is of the order of only 0.1 percent.

## APPENDIX III. THE RELATIVE EFFECTS OF A GIVEN INCREMENT TO A PRINCIPAL CONSTANT AND TO AN INTERACTION CONSTANT, FOR CH BENDING MODES IN SUBSTITUTED ETHYLENES

The derivatives  $(\partial \lambda_k / \partial d_{ij})$  are readily obtained for the standard solution, as described in a previous paper.<sup>2</sup> These quantities are given here for vinyl chloride:

$i \backslash k$	2				
2	101.1	—3.917	—0.091	0.890	1.084
3		0.152	0.0035	—0.034	—0.042
4			0.0001	—0.0008	—0.0010
5				0.0078	0.0095
6					0.0116

$i \backslash k$	3				4		
3	52.85	4.070	—1.766	1.783			
4		0.313	—0.136	0.137	31.78	—1.167	4.227
5			0.059	—0.060		0.043	—0.155
6				0.060			0.562

The elements for the other vinyl compounds only differ slightly from the above. Inspection shows that a given increment in the interaction constant possessing the largest derivative has only 4 percent, 8 percent and 15 percent on the frequencies  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  respectively as the same increment in the main constant. These constants, ( $d_{23}$ ,  $d_{34}$  and  $d_{46}$ ), have values 0.00775, —0.0142 and —0.0597 in the standard solution for vinyl chloride. The effect of reducing them separately to zero is to produce the following increments in the three vibration frequencies:

$$\Delta \nu_2 = +3.14, \quad \Delta \nu_3 = +6.37, \quad \Delta \nu_4 = +34.11 \text{ cm}^{-1}.$$

The same effect would be produced by the following increments to the principal constants:

$$\Delta d_{22} = +0.00060, \quad \Delta d_{33} = +0.00219, \\ \Delta d_{44} = +0.01589 \times 10^5 \text{ dynes/cm.}$$

The increment in the diagonal element  $A_{33}$  in passing from chloride to iodide is equivalent to a shift  $\Delta \nu_3 = -4.53 \text{ cm}^{-1}$ ; for the other two modes, the diagonal

elements remain constant and no frequency-shift can arise from this source.

It is seen from the above results that, with the possible exception of the  $\text{CH}_2$  bending mode, it is most unlikely that the observed frequency-shifts encountered on passing from chloride to iodide could be accounted for

by variations in small interaction constants normally assumed zero. Since we are dealing here with closely-related structures, there seems no justification for postulating the existence of small interaction constants which undergo relatively large variations in passing along the series.

## Physical Properties of Polonium. I. Melting Point, Electrical Resistance, Density, and Allotropy\*

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Measurements on the electrical resistance, thermal coefficient of electrical resistance, melting point and density of polonium are reported. An abrupt change in the electrical resistance near  $100^\circ\text{C}$  indicates that polonium exists in two allotropic forms. Observations which indicate that the temperature for crystal transformation is a function of the size and history of the specimen are reported.

SINCE its discovery in 1898, many investigations have been made into the chemical properties of polonium but the small quantities of the element available in the past made the determination of its ordinary physical properties impractical if not impossible. The larger, though still minute, amounts of polonium available today in the Manhattan Project have made possible the development of techniques by which rough measurements on some of the physical properties of polonium have been made.

The selection of a method and the accuracy of the method were influenced not only by the small amount of

material available but by the radioactivity of the element: (1) The high specific activity of polonium makes it extremely toxic if absorbed into the body, hence any method employed must keep mechanical scattering and general contamination of the laboratory at a minimum; (2) Since polonium has a half-life of 138 days,<sup>1</sup> the lead content of a freshly prepared sample increases at the rate of one-half percent per day. Methods requiring a long time to attain equilibrium or requiring successive measurements over an appreciable period are impractical; (3) The heat produced by the radioactivity (0.12 calorie per microgram per hour)<sup>1</sup> maintains polonium and its immediate surroundings at a temperature higher than the ambient temperature. The magnitude of this temperature differential varies with the size of the sample and the heat transfer characteristics of its immediate environment. This phenomenon makes the determination or reproducibility of temperature difficult.

### PREPARATION AND PURITY OF POLONIUM

Metallic polonium was prepared by electro-deposition on platinum foils from dilute nitric acid solution of polonium nitrate. Earlier work by other members of the laboratory had shown that metal prepared in this manner was very pure, except, of course, for lead which is formed in the metal after deposition. A further check of the purity was made by the spectrochemical analysis of a sample used for a melting point determination. The analysis showed only the expected amount of lead and small amounts of aluminum and calcium. It is believed that these latter impurities were introduced with the acid used to dissolve the sample in preparing it for spectrochemical analysis. In the chemical process used in the recovery of the material for subsequent experiments it is possible but unlikely that other impurities

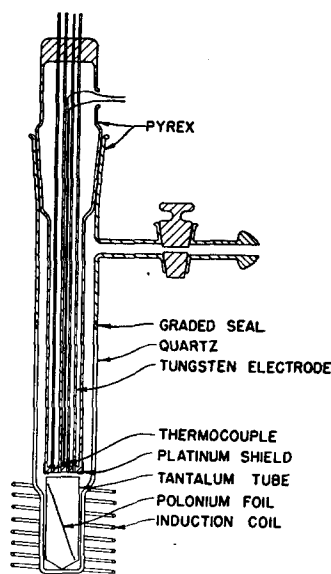


FIG. 1. Apparatus for measuring electrical resistance.

\* This paper is based on a portion of thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State College, Ames, Iowa.

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<sup>1</sup> W. H. Beamer and W. E. Easton, *J. Chem. Phys.* **17**, 1298 (1949).