[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

On the Assignment of Vibrational Frequencies to Particular Bonds with Reference to Methylacetylene and Ethane

BY FREDERICK T. WALL

When a polyatomic molecule undergoes a particular mode of vibration, in general all of the atoms are involved and all of the interatomic distances change in the course of the motion. If the molecule possesses symmetry, however, some of the atoms and some of the interatomic distances might not be involved in the motion depending upon the symmetry properties of the vibration. But since the vibratory motion cannot generally be associated with a particular bond type, it is not strictly proper to assign the various frequencies of polyatomic molecules to particular bonds. However, the practice of assigning frequencies to specific bonds persists in the literature principally because it is observed experimentally that many related molecules show frequencies of nearly the same value and which are accordingly attributed to those bonds which the molecules have in common.[1] For example, a hydrogen bonded to an acetylenic carbon atom gives rise to a frequency around 3300 cm.$^{-1}$ for a whole series of molecules. Likewise hydroxyl groups such as are present in the alcohols, show frequencies around 3600 cm.$^{-1}$.[2] In other cases, such as the frequency usually attributed to the carbon–carbon single bond, the variation in values for different molecules can be quite large. It is the purpose of the calculations reported in this paper to study quantitatively the contributions of the various bonds of ethane and methylacetylene to some of their normal modes of vibration, and to formulate rules from those results for treating similar vibrations by approximate methods.

Only the non-degenerate frequencies of ethane and methylacetylene will be considered. These vibrations are symmetric with respect to the threefold axes of the molecules and are therefore easily treated. Assuming valence forces, the potential energy of vibration of a molecule like methylacetylene ($CH_3C\equiv CH$) can be written

$$V = V_{\mathrm{C-H}} + V_\theta + V_{\mathrm{C-C}} + V_{\mathrm{C\equiv C}} + V_{\mathrm{H-C\equiv}} \quad (1)$$

where each term is the potential energy associated with the bond indicated as a subscript, except that θ refers to bending of angles in the methyl group and not to any bond. If the forces in the molecule are of a Hooke's law nature, the individual terms of equation (1) can be written as[3]

$$\begin{aligned} V_{\mathrm{C-H}} &= 3/2\, k_{\mathrm{C-H}}\, (\Delta r_{\mathrm{C-H}})^2 \\ V_\theta &= 6/2\, k_\theta\, r^2_{\mathrm{C-H}}\, (\Delta\theta)^2 \\ V_{\mathrm{C-C}} &= 1/2\, k_{\mathrm{C-C}}\, (\Delta r_{\mathrm{C-C}})^2 \\ V_{\mathrm{C\equiv C}} &= 1/2\, k_{\mathrm{C\equiv C}}\, (\Delta r_{\mathrm{C\equiv C}})^2 \\ V_{\mathrm{H-C\equiv}} &= 1/2\, k_{\mathrm{H-C\equiv}}\, (\Delta r_{\mathrm{H-C\equiv}})^2 \end{aligned} \qquad (2)$$

In these expressions, the Δ's represent displacements from equilibrium positions and the k's are Hooke's law force constants. Since for methylacetylene ($CH_3C\equiv CH$) there are three methyl carbon–hydrogen distances, and six valence angles in the methyl group (both types of which are assumed to have the same bending constant), the factors 3 and 6 appear in the terms for $V_{\mathrm{C-H}}$ and V_θ.

For a given non-degenerate mode of vibration of a molecule such as methylacetylene, the ratios of the displacements

$$\Delta r_{\mathrm{C-H}} : r_{\mathrm{C-H}}\Delta\theta : \Delta r_{\mathrm{C-C}} : \Delta r_{\mathrm{C\equiv C}} : \Delta r_{\mathrm{H-C\equiv}}$$

will have definite values. Likewise the ratios of the potential energy contributions

$$V_{\mathrm{C-H}} : V_\theta : V_{\mathrm{C-C}} : V_{\mathrm{C\equiv C}} : V_{\mathrm{H-C\equiv}}$$

will have definite values for each particular mode of vibration. In the subsequent discussion, the fraction of the total potential energy which can be assigned to a given bond type will be adopted as a measure of the extent to which the vibration is to be attributed to that kind of bond. If most of the potential energy can be associated with a certain bond type, then the vibration can reasonably be assigned to that bond, but if the energy is split more or less equally between two or more bond types, the vibration cannot be assigned to one kind of bond alone.

In treating the non-degenerate vibrations of methylacetylene and ethane by the normal coordinate method, there are obtained a number of homogeneous linear equations. For methylacetylene these equations are[3]

$$\begin{aligned} (\lambda + A)\Delta r_{\mathrm{C-H}} + B\Delta\theta + C\Delta r_{\mathrm{C-C}} &= 0 \\ D\Delta r_{\mathrm{C-H}} + (\lambda + E)\Delta\theta + F\Delta r_{\mathrm{C-C}} &= 0 \\ G\Delta r_{\mathrm{C-H}} - 3B\Delta\theta + (\lambda - 6C)\Delta r_{\mathrm{C-C}} + H\Delta r_{\mathrm{C\equiv C}} &= 0 \end{aligned} \qquad (3)$$

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[1] K. W. F. Kohlrausch, "Der Smekal-Raman Effekt," Verlag von Julius Springer, Berlin, 1931.

[2] Hibben, *Chem. Rev.*, **18**, 1 (1936); Stuart, "Molekülstruktur," Verlag von Julius Springer, Berlin, 1934.

[3] Glockler and Wall, *J. Chem. Phys.*, **5**, 813 (1937).

$$3C\Delta r_{\mathrm{C-C}} + (\lambda - 2H)\Delta r_{\mathrm{C\equiv C}} + I\Delta r_{\mathrm{H-C\equiv}} = 0$$
$$H\Delta r_{\mathrm{C\equiv C}} + (\lambda + J)\Delta r_{\mathrm{H-C\equiv}} = 0$$

where $\lambda = 4\pi^2\nu^2$, ν = vibrational frequency and

$$A = -k_{\mathrm{C-H}}\left(\frac{1}{3m_2} + \frac{1}{m_1}\right) \qquad F = -\sqrt{8}\,k_{\mathrm{C-C}}/3m_2r_{\mathrm{C-H}}$$
$$B = 2\sqrt{8}\,k_\theta r_{\mathrm{C-H}}/3m_2 \qquad G = k_{\mathrm{C-H}}/m_2$$
$$C = k_{\mathrm{C-C}}/3m_2 \qquad H = k_{\mathrm{C\equiv C}}/m_2$$
$$D = \sqrt{8}\,k_{\mathrm{C-H}}/3m_2r_{\mathrm{C-H}} \qquad I = k_{\mathrm{H-C}}/m_2$$
$$E = -2k_\theta\left(\frac{8}{3m_2} + \frac{1}{m_1}\right) \qquad J = -k_{\mathrm{H-C\equiv}}\left(\frac{1}{m_2} + \frac{1}{m_1}\right)$$

m_1 = mass of hydrogen atom m_2 = mass of carbon atom

From the equations (3) there is obtained by the usual methods a secular equation which is the determinant of the constant coefficients set equal to zero. This equation will have five roots for λ corresponding to five vibrational frequencies. Introducing the roots of the secular equation back into the equations of motion (3), the ratios of the displacements can be calculated for each frequency. From the ratios of the displacements, the ratios of the potential energies can be determined by use of equations (2).

This procedure has been carried out for the non-degenerate frequencies of liquid methylacetylene and liquid ethane using the same force constants for both molecules. The values of the force constants taken from the work of Glockler and Wall[3] are

$k_{\mathrm{C-H}}$ = 4.76 × 10^5 dynes/cm.
k_θ = 0.400
$k_{\mathrm{C-C}}$ = 6.37
$k_{\mathrm{C\equiv C}}$ = 15.34
$k_{\mathrm{H-C\equiv}}$ = 5.74

The results of the calculations are shown in Table I. The figures in the columns headed $V_{\mathrm{C-H}}$, etc., are the percentages of the total potential energy due to the bonds indicated. The frequencies are given in the first column and except for two cases where experimental values were not available (*liquid* antisymmetrical frequencies of ethane) the observed frequencies were used.[2,3] The frequency 2896.6 cm.$^{-1}$ for methylacetylene is the mean of two frequencies arising because of resonance and accidental degeneracy.[4] For ethane, (s) and (a) refer, respectively, to *symmetric* and *antisymmetric* vibrations.

TABLE I

$CH_3C{\equiv}CH$

ν cm.$^{-1}$	$V_{\mathrm{C-C}}$	V_θ	$V_{\mathrm{C\equiv C}}$	$V_{\mathrm{C-H}}$	$V_{\mathrm{H-C\equiv}}$
929.5	62.8	25.7	11.3	0.1	0.2
1382.5	18.5	73.7	7.2	.4	.2
2123.5	8.4	0.3	87.1	.1	4.1
2896.6	0.7	.2	0.1	99.1	0.0+
3305	1.2	.0+	4.9	0.0+	93.9

CH_3CH_3

ν cm.$^{-1}$	$V_{\mathrm{C-C}}$	V_θ	$V_{\mathrm{C-H}}$
990 (s)	47.1	52.8	0.1
1460 (s)	30.3	68.8	.8
2920 (s)	6.4	0.4	93.2
1288 (a) (calcd.)	0	99.8	0.2
2890 (a) (calcd.)	0	0.2	99.8

Discussion of Results

It will be seen from Table I that the frequencies around 2900 cm.$^{-1}$ can be assigned to methyl carbon–hydrogen vibrations almost entirely. Similarly the frequency 3305 cm.$^{-1}$ for methylacetylene can be considered mainly due to vibration of the acetylenic hydrogen against the rest of the molecule. The frequency 2123.5 cm.$^{-1}$, although mostly due to the carbon–carbon triple bond, shows appreciable interaction with the adjacent bonds. Except for the low antisymmetric ethane frequency, the low frequencies exhibit a considerable interaction between angle bending and carbon–carbon single bond displacements. The antisymmetric frequencies of ethane necessarily involve no carbon–carbon single bond potential energy because of the nature of the vibrations.

It will be seen, from the standpoint of the potential energies, that the 990 cm.$^{-1}$ frequency of ethane involves angle bending to a greater extent than displacement of the carbon–carbon bond, even though this frequency is usually assigned to vibrations along the carbon–carbon bond. Although the bending force constant is much smaller than the valence bond constants, the fact that there are twelve angles to but one carbon–carbon bond brings up the angular contribution. For the 990 cm.$^{-1}$ frequency the bending motion moves the hydrogens by about the same amount as does the motion of the carbons. The 929.5 cm.$^{-1}$ frequency for methylacetylene is more nearly a carbon–carbon frequency because there is only one methyl group to interfere.

The carbon–carbon single bond motion interacts but little with the adjacent carbon–hydrogen bonds because the tetrahedral angle (109°28′) is much nearer 90° than it is to 180° for which a larger interaction would be expected. However, the closer the angles are to 90°, the greater will be the interaction to be expected between carbon–carbon motion and angle bending. This accounts for the fact that approximate calculations by

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[4] Adel and Barker, *J. Chem. Phys.*, **2**, 627 (1934).

Bonner[5] gave consistently lower values for the C–C Hooke's law constant than other calculations presumably more accurate since they took into account interactions.[3,6] Bonner assumed that hydrocarbons and alkyl groups could be regarded as simpler molecules by grouping together certain atoms. Thus he took ethane to be R–R and propane to be R–R′–R (non-linear) in which $R = CH_3$ and $R' = CH_2$. On this basis the force constants average around 3.8×10^5 dynes/cm., whereas calculations which take into account interactions show values averaging about 6.0×10^5 dynes/cm. In spite of this large difference, Bonner's results are quite useful as long as they are used in the same way as they were obtained.

For the frequencies 2123.5 cm.$^{-1}$ and 3305 cm.$^{-1}$ of methylacetylene it appears from the table that the molecule can be regarded as $R-C\equiv C-H$ where $R(= CH_3)$ behaves like a single atom of atomic weight 15. It is probably true that for any molecule which is linear or partially linear, bonds farther away than the bond adjacent to the one of most importance in the vibration have little effect on the frequency.

As to the accuracy of the results in Table I, the following remarks can be made. The values of the percentages for frequencies around 1400 cm.$^{-1}$ are probably the least accurate of those given since those results are quite sensitive to changes in the force constants and to changes in the frequencies. The results are nevertheless correct to the right order of magnitude. The other values are more accurate, particularly the high percentage figures. The percentage error of the low percentages may be large, but such errors would not alter the interpretation nor change the picture of the motion greatly. In conclusion the author wishes to express his appreciation to Professor W. H. Rodebush for his kind interest in the calculations.

Summary

The fractions of the total potential energy contributed by the various bonds of methylacetylene and ethane were calculated for each of the nondegenerate frequencies of the molecules. These fractions are taken as a measure of the extent to which a given mode of vibration can be assigned to a particular bond type. It is found that the so-called "carbon–carbon" single bond frequencies in particular are not pure carbon–carbon vibrations. Some generalizations are indicated which show when molecules can be treated successfully by approximate methods.

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(5) L. G. Bonner, *J. Chem. Phys.*, **5**, 293 (1937).

(6) J. B. Howard, *ibid.*, **5**, 442 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND AND THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Two Alkoxyacetaldehydes, their Preparation and Properties[1]

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Inasmuch as several β-alkoxyethanols are now readily available and cheap substances, it seemed to us that the dehydrogenation of such substances should offer the most convenient approach to the corresponding aldehydes.

Alkoxyacetaldehydes have been prepared by various methods, and a review of earlier work is to be found in an article by Rotbart,[2] who synthesized a number of these substances by way of their acetals. Sabetay[3] has also described the preparation of alkoxyacetaldehydes by the action of lead tetraacetate on α-monoethers of glycerol. The failure of attempts[4] to dehydrogenate β-ethoxyethanol over copper, silver, and copper chromite in the presence of air at temperatures of 300–400° is understandable in view of the conditions of the experiments, and no attempt seems to have been made to prepare methoxyacetaldehyde by a similar method.

Ethoxyacetaldehyde was first prepared by Klüger,[5] who reported a boiling point of 71–73°. Later workers[4,6] were unable to check this boiling point, and were usually satisfied with a concentrated aqueous solution of the aldehyde, boiling

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(1) An investigation of methoxyacetaldehyde was carried out in the laboratories of the University of Maryland during the summer of 1933. When it was later learned that similar work was being conducted in the Harvard Laboratories, it was decided to present the results in a joint publication. Part I describes the work at the University of Maryland and Part II describes the work at Harvard University, which was carried out during the summers of 1936 and 1937.

(2) Rotbart, *Ann. chim.*, [11] **1**, 439 (1934).

(3) Sabetay, *Bull. soc. chim.*, [5] **2**, 1744 (1935).

(4) Dunn, Redemann and Smith, *J. Biol. Chem.*, **104**, 511 (1934).

(5) Klüger, *Monatsh.*, **26**, 879 (1905).

(6) Eissler and Pollak, *ibid.*, **27**, 1129 (1906); Fried, *ibid.*, **27**, 1251 (1906); Leuchs and Geiger, *Ber.*, **39**, 2644 (1906).