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Normal frequencies of vibration of 1, 3-Butadiene

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THE NORMAL FREQUENCIES OF VIBRATION OF 1, 3- BUTADIENE

by

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A. INTRODUCTION

Within the past several decades, interest in the study of infra-red and Raman spectra has grown considerably. When Rawlins and Taylor published their book[1] on infra-red analysis in 1928, there wasn't a single book available concerned with infra-red study of molecular structure. Since then a number of books have appeared, and many articles have been published on the subject.

There are several reasons for the growth of interest. One of the important reasons is the application of infra-red study to chemical analysis. It is possible by an analysis of the infra-red spectrum of a substance not only to identify elements but atomic and molecular groups as well. For example, an ethyl or a methyl group in a compound will always exhibit certain characteristic frequencies.

Secondly, the study of molecular spectra has probably become the most important means for investigating molecular structure. Various energy levels may be obtained from a study of the spectra which, in turn, give detailed information on the electronic motion, vibration, and rotation of the atoms in the molecules. A theoretical understanding of valence has resulted from a study of electronic motion while the forces acting between atoms in a molecule may be obtained from the vibrational frequencies and accurate infor-

1. Rawlins, F. I. G., and Taylor, A.M., Infra-Red Analysis of Molecular Structure (Cambridge University Press, 1929)

mation concerning the geometrical arrangement of the atoms may be obtained from a study of the rotational spectra.

Furthermore, the Raman effect was discovered in 1928 which also has become important in the field of analysis and theoretical studies. It is sometimes possible to obtain information about a molecule from the Raman spectrum which cannot be obtained by other means.

The theoretical aspects of the study of molecular structure made considerable strides forward when group theory was introduced. The determination of the structure of polyatomic molecules and the forces acting between the atoms is an extremely complex problem but a great deal of simplification is introduced by the application of group theory to the symmetry of the molecule.

The advance of theoretical methods always requires an improvement of experimental techniques. The improved experimental methods then uncover further information for use in theoretical study. As a consequence of improved methods in both endeavors, much work is being done at the present time in molecular studies. It is with the theoretical aspects of the problem that this paper is concerned.

The infra-red spectrum is divided into three general regions called the photoelectric, near infra-red and far infra-red[2]. The photoelectric region extends from

2. Harrison, George R., Lord, Richard C., and Loofbourow, John R., Practical Spectroscopy (New York: Prentice-Hall, Inc., 1948)

about 0.75 microns to about 2 microns while the near infra-red extends from about 2 microns to about 25 microns and the far infra-red from about 25 microns to about 1 mm. It is divided into these regions because of the experimental techniques involved. In the photoelectric portion, ordinary prisms, gratings and photographic technique are utilized. However, in the near and far infra-red, the detection of the spectra is primarily accomplished by utilizing the heating effect of the radiant energy. In the near infra-red prisms are still used, but they are made of rock salt or potassium bromide, while in the far infra-red, gratings are used primarily.

These divisions in a general way agree with the division of the molecular energy levels into electronic, vibrational and rotational regions. Infra-red in general corresponds to oscillations of particles which are several hundred times slower than the motion of electrons. This motion is attained by the atoms in a molecule.

The Raman effect is a scattering process which differs from the Tyndall effect in that with the Raman effect there is a change of frequency associated with the scattering. The incident quanta collide with a vibrating atom and are scattered with either a higher or lower energy, depending on the nature of the collision, and hence will have a resultant higher or lower frequency. The change in frequency is characteristic of the frequency of vibration

of the atom with which the quantum of light collides. The Raman lines will then appear in a position displaced from the incident spectral line by an amount which is characteristic for the medium through which the light has been scattered. The lines which are displaced to the longer wave length side are called Stokes lines and those displaced to shorter wave lengths are called anti-Stokes after a similar phenomenon which appears in fluorescence and was discovered by Stokes. In fluorescence, however, there is an actual absorption of the light quanta which after a short time are reemitted with a change of wave length. Since a relatively small amount of the light quanta will collide with atoms, the intensity of the Raman lines will be rather low and hence the experimental difficulties in observing the lines are correspondingly greater.

The vibration of the atoms in a moleucle give rise to the major portion of the near infra-red and to Raman lines. A knowledge of the vibration of the atoms will yield information concerning the structure of the molecule and particularly the forces acting between the atoms in a molecule. These can then be used to calculate the energy of dissociation and other thermodynamic quantities for the molecule, such as, heat capacities, etc. It is with this facet of the problem, that is, a determination of the normal frequencies of vibration of 1, 3- butadiene, that we concern ourselves primarily in this paper.

B. THEORY OF MOLECULAR VIBRATIONAL SPECTRA

1. Molecular Structure

The atoms in a molecule are continually in motion vibrating about an equilibrium position and rotating about their center of mass as long as the molecule possesses any thermal energy. The equilibrium configuration is best determined from a study of the rotational spectra or electron diffraction patterns. The vibrations of the atoms are then considered in terms of the displacements from these equilibrium configurations.

A knowledge of the number and size of the atoms and their configuration permits a utilization of their symmetry properties in the determination of the frequencies of vibration. The particular configuration which the atoms will be in is determined by the forces which are acting between them. These forces also determine the normal frequencies of vibration.

2. Interatomic Forces

There are essentially two types of forces acting between the atoms in a molecule[3]. First, there are the forces of attraction which are often called the valence forces and which fall off rapidly as the distance between the atoms becomes larger. Secondly, there are forces of repulsion which are negligible at large distances but which

3. Slater, J. C., Introduction to Chemical Physics (New York: McGraw-Hill, 1939) p. 130

increase even more rapidly than the attraction at small distances. At the point where the attraction and repulsion forces just balance is the equilibrium position. This is the normal distance of separation for any two atoms, and any small displacement from this position will give rise to forces tending to restore the atoms to the equilibrium position. This point is then also a minimum potential energy position, and the amount of work required to pull the two atoms apart is the energy of dissociation.

When two atoms approach each other, there is first of all a small force between them which is the Van der Waal's attraction[4]. This force arises from the polarization of each atom by the fluctuating dipole of the other and the overall effect is rather small. As the atoms approach still closer, the electronic charge of one is attracted by the nuclear charge of the other. This is essentially a coulomb attraction even though each atom is electrically neutral. This results when the electronic charge distribution of one overlaps the electronic charge distribution of the other. As the overlapping increases and the nucleus of one begins to penetrate the electronic charge distribution of the other, strong repulsion sets up between the two nuclei.

A still more important factor must be considered, and that is the fact that when atoms begin to overlap, a

4. Ibid, p. 368

distortion of charge distribution takes place. When two atoms overlap, some of the charge shifts from the region between the atoms to the far sides of the nuclei. This results in an increase of energy and hence a repulsion between the atoms. However, this overlapping and distortion also results in a force of attraction which is greater than the previous forces of attraction. This is the exchange effect which refers to an exchange of electrons between the two atoms. This results in a piling up of electrons between the two atoms and a lowering of the potential energy, and hence a binding effect is produced. The electrons involved in this interaction are the outer or valence electrons and the type of attraction is called homopolar valence attraction. It is necessary, however, from the exclusion principle that the electrons entering into the exchange effect have opposite spins.

When more than two atoms are involved, the number of atoms which can enter into the attractive exchange type of interaction is determined by the number of valence electrons. Only two electrons can enter into an electron-pair bond and if there is only one valence electron on the atom involved, then there will be repulsion to any other atom that may approach. If an atom has a number of valence electrons, however, then it can form a bond with a number of other atoms depending on the number of valence electrons.

3. The Rotation of Molecules

To a fairly good approximation, the rotation and vibration of the atoms can be treated separately considering the vibrations as if the molecules were not rotating and the rotation as if there were no vibration[5]. This assumes that the amplitude of vibration is small as compared to the internuclear distances and that the forces between atoms that are induced by rotation are small as compared to the forces between atoms which give rise to the restoring forces resulting in vibrations.

The far infra-red bands correspond to a change of rotational quantum number alone and they will have an intensity only if the molecule possesses a permanent dipole moment since otherwise the average value of the dipole moment will be zero and no dipole radiation will occur. Any molecules which possess electrical symmetry will have no permanent dipole moment, and hence the only rotational spectra which can be observed in these cases are those that arise due to the formation of a dipole moment because of unsymmetrical vibration of the atoms. These are generally observed as fine structure on the vibrational band spectra. We are here concerned primarily with the vibrational spectra of molecules.

5. Dennison, David M., Rev. Mod. Phy. 3, 280 (1931)

4. Vibration of Molecules

When the atoms in a molecule are in their equilibrium position, there are forces acting on them, as previously discussed, which will tend to return them to this position if they are displaced. This point is a potential energy minimum and any displacement tends to increase the potential energy. If the force function tending to restore the atoms to the equilibrium position is linear in this neighborhood, then for small displacements the atoms will perform simple harmonic oscillations about this position. Dennison has shown that under these conditions the frequency of radiation absorbed or emitted is very nearly that of the classical frequency of mechanical vibrations. Since infra-red absorption bands are concerned with transitions from the lowest energy states to those immediately above it, it is possible to consider only vibrations of the lowest energy states where the force function is nearly linear and hence classical methods may be used for the determination of the vibrational frequencies. However, to determine intensities and selection rules quantum mechanics must be used.

In general, the normal modes of vibration of a molecule are determined as a function of the mutual displacements of the particles from their equilibrium positions. While normal vibrations may be determined by considering the forces acting on the particle, in practice usually the conservation of energy principle is utilized. This requires setting up the kinetic and potential energy in terms of the

displacement coordinates. The type of potential function that is used is determined to a certain extent by the type of molecule which is being considered.

5. Potential Functions

Usually the potential function is developed as a power series in the displacement coordinates in which case all linear terms are absent since they refer to the rest position: the quadratic terms give the normal vibrations, and higher order terms give an harmonic corrections. Several different choices of the coordinates are possible and the potential function will, to a certain extent, depend on the choice of these internal coordinates.

If the center of mass and angular momentum of the molecule are not considered fixed, there will be 3N coordinates where N is the number of atoms in the molecule. However, since there is no restoring force for simple translation or for rotation about any axis, these motions give non-genuine normal vibrations. Thus, if we fix the center of mass and set the angular momentum equal to zero, the number of coordinates will be reduced by five if it is a linear molecule or by six if it is non-linear. This will leave either 3N-5 or 3N-6 internal coordinates. One choice of coordinates will then be to use 3N-6 internuclear distances and deviations from these 3N-6 internuclear distances as internal coordinates. Such coordinates are sometimes called central force coordinates since they work particularly

well with a central force system[6]. In this type of force field, the assumption is made that the force acting on any one atom is the resultant of the attractions and repulsions of all the other atoms in the molecule and depends only on the distance between atoms and acts along the line connecting the atoms. This type of force field has been found to work fairly well for molecules composed of heavy atoms.

The type of internal coordinates that seem to work best in actual practice are symmetry coordinates[7,8,9]. These are based on the symmetry properties of the molecules. For a given value of one of these coordinates there correspond displacements of the nuclei in agreement with one of the symmetry types. These symmetry types will be discussed later in the discussion on symmetry and group theory.

In the establishment of the potential energy expression, there are usually more potential constants than normal frequencies. Hence only in a few cases is it possible to obtain the values of the potential constants on a purely theoretical basis. One way to solve this difficulty is to consider an isotope effect[10] where one or several atoms are

6. Shaffer, W. H. and Newton, R.R., J. Chem. Phy., 10, 405 (1942)
7. Howard, J. B. and Wilson, E. B. Jr., J. Chem. Phy. 2, 620 (1934)
8. Redlich, O. and Tompa, H., J. Chem. Phy. 5, 529 (1937)
9. Rosenthal, J. E. and Murphy, G. M., Rev. Mod. Phy. 8, 317 (1936)
10. Herzberg, Gerhardt, Molecular Spectra and Molecular Structure., II. Infra-red and Raman Spectra of Polyatomic Molecules (New York: D. Van Nostrand Co., Inc., 1945) p. 227 ff.

replaced by isotopic atoms for which the force constants are the same but the frequencies are different. This gives additional equations in the same constants and permits solving for them. Another solution is to make special assumptions about the forces acting in the molecules thus reducing the number of constants. One such assumption is the central force field assumption which has already been mentioned.

Another type of force field assumption is the valence force[11]. This assumes that there is a strong restoring force along the line of every valence bond and another opposing the change of the angle between two valence bonds. This type of force field appears to be a better approximation in most cases than the central force field.

Another type of more general force field could be mentioned and that is the Urey-Bradley field[12]. This type of field seems to apply fairly well to molecules containing heavy atoms in a tetrahedral form. A repulsive interaction is assumed between the corner atoms of the molecule thus adding terms of the order $1/r_j^n$ to the potential energy expression.

6. Mathematical Methods

(a) Classical - Since, as has been indicated, the vibrations of the atoms in the molecule for small displacements can be considered on the basis of classical

11. Wilson, E. B., Jr., J. Chem. Phy. 9, 76 (1941)
12. Urey, H. C. and Bradley, C. A., Phy. Rev. 38, 1969 (1931)

vibrations, it is possible to use classical methods to determine the normal frequencies of vibration. The mathematical methods outlined here follow in major part the development as given by Herzberg[13]. In practice, the energy principle is generally utilized in developing normal vibrations so that is the method that will be outlined here.

Consider a molecule which has N atoms. If a particle is displaced from rest, there will be a restoring force which will depend only on the components of the displacement from the rest position x_i, y_i, z_i. The particle oscillating in simple harmonic motion about its rest position will have a kinetic energy

$$T_i = 1/2\ m_i\ v_i^2 = 1/2\ m_i\ \dot{s}_i^2 \tag{1}$$

and potential energy

$$V_i = 2\pi^2 \nu_i^2\ m_i\ s_i^2 = 1/2\ k_i\ s_i^2 \tag{2}$$

where

$$k_i = 4\pi^2 \nu_i^2\ m_i. \tag{3}$$

If we let x_1, y_1, z_1, x_2, y_2, z_2, ... be represented by q_1, q_2, q_3, q_4, q_5, q_6..., we can write

$$V = 1/2 \sum_{ij} k_{ij}\ q_i\ q_j = 1/2\ k_{11}\ q_1^2 + 1/2 k_{22}\ q_2^2 + k_{12}\ q_1\ q_2 + \ldots \tag{4}$$

where the force constants $k_{ij} = k_{ji}$

The kinetic energy is then given by

$$T = \sum_i 1/2\ m_i\ (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \tag{5}$$

13. Herzberg, Op. Cit., p. 72 ff.

or $$T = 1/2 \sum_{ij} a_{ij} \dot{q}_i \dot{q}_j \tag{6}$$

where $a_{ij} = o$ for $i \neq j$, and $a_{11}=a_{22}=a_{33}=m_1$,

$$a_{44}=a_{55}=a_{66}=m_2 \ldots \tag{7}$$

We can now transform to new coordinates $\eta_1, \eta_2 \ldots \eta_{3N}$ by a linear transformation

$$\begin{aligned} q_1 &= c_{11}\,\eta_1 + c_{12}\,\eta_2 + c_{13}\,\eta_3 + \ldots \\ q_2 &= c_2\,\eta_1 + c_{22}\,\eta_2 + c_{23}\,\eta_3 + \ldots \\ q_3 &= c_{31}\,\eta_1 + c_{32}\,\eta_2 + c_{33}\,\eta_3 + \ldots \\ q_i &= c_{i1}\,\eta_1 + c_{i2}\,\eta_2 + c_{i3}\,\eta_3 + \ldots \end{aligned} \tag{8}$$

By appropriate choice of the coefficients c_{ik} both $\underline{V}$ and $\underline{T}$ can be brought to a simpler form in terms of the new coordinates.

$$V = 1/2\,(\lambda_1 \eta_1^2 + \lambda_2 \eta_2^2 + \ldots + \lambda_i \eta_i^2 + \ldots \lambda_{3n} \eta_{3n}^2) \tag{9}$$

$$T = 1/2\,(\dot{\eta}_1^2 + \dot{\eta}_2^2 + \ldots + \dot{\eta}_i^2 + \ldots + \dot{\eta}_{3n}^2) \tag{10}$$

The λ_i are roots of the secular equation [14]

$$\begin{vmatrix} k_{11} - a_{11}\lambda & k_{12} - a_{12}\lambda & k_{13} - a_{13}\lambda & \ldots \\ k_{21} - a_{21}\lambda & k_{22} - a_{22}\lambda & k_{23} - a_{23}\lambda & \ldots \end{vmatrix} = o \tag{11}$$

The total energy is now

$$H = T + V = 1/2(\dot{\eta}_1^2 + \lambda_1 \eta_1^2) + 1/2(\dot{\eta}_2^2 + \lambda_2 \eta_2^2) + \ldots \tag{12}$$

It is thus the sum of 3N mutually independent terms each of which has the form of a simple harmonic oscillator. The

14. Whittaker, E. T., Analytical Dynamics, 4th Ed. (New York, Dover Publications, 1944) p. 181

motion of the entire system is then equivalent to the superposition of 3N simple harmonic motions in the normal coordinates. Thus:

$$\eta_i = \eta_1^o \cos(2\pi\nu_i t + \phi_i) \tag{13}$$

where now

$$\lambda_i = 4\pi^2 \nu_i^{\,2} \tag{14}$$

We have that

$$k_{11} = k_{xx}^{11},\ k_{22} = k_{yy}^{11},\ \ldots\ k_{12} = k_{xy}^{11},\ \ldots \tag{15}$$

Substituting these values and those from Eq. (7) in Eq. (11) gives

$$\begin{vmatrix} k_{xx}^{11}-m_1\lambda & k_{xy}^{11} & k_{xz}^{11} & k_{xx}^{12} & \ldots & k_{xz}^{1N} \\ k_{yx}^{11} & k_{yy}^{11}-m_1\lambda & k_{yz}^{11} & k_{yx}^{12} & \ldots & k_{yz}^{1N} \\ k_{zx}^{11} & k_{zy}^{11} & k_{zz}^{11}-m_1\lambda & k_{zx}^{12} & \ldots & k_{zz}^{1N} \\ k_{xx}^{21} & k_{xy}^{21} & k_{xz}^{21} & k_{xx}^{22}-m_2\lambda & \ldots & k_{xz}^{2N} \end{vmatrix} = 0 \tag{16}$$

The form of any normal vibration is obtained by putting all other η's in Eq. (8) equal to zero. Then for η_j

$$\begin{aligned} x_1^{(j)} &= c_{1j}\eta_j, & y_1^{(j)} &= c_{2j}\eta_j, & z_1^{(j)} &= c_{3j}\eta_j \\ x_2^{(j)} &= c_{4j}\eta_j, & y_2^{(j)} &= c_{5j}\eta_j, & z_2^{(j)} &= c_{6j}\eta_j \end{aligned} \tag{17}$$

As previously discussed, either five or six of these roots are non-genuine and correspond to translation and rotation, hence there are actually only 3N-5 or 3N-6 normal vibrations. This still gives a large secular equation to solve even if N

is only moderately large. A considerable amount of simplification can be realized if the molecule possesses any symmetry. The application of group theory to polyatomic molecules is discussed in detail by Rosenthal and Murphy[15] and others[16,17].

It is shown in the references cited that if a symmetry operation is carried out which transforms the molecule into a form indistinguishable from its original form, then the force field and potential energy will also be the same as before and, of course, the normal vibrations will be the same. However, this need not necessarily be the case for the displacements in a vibrating molecule. The N normal frequencies may then be divided into a number of symmetry classes each of which will contain a given number of frequencies. These classes or irreducible representations, as they are called in group theory, will all be along the principal diagonal of the secular equation and can be treated as separate equations. These symmetry operations aid in assigning the normal modes of vibration to certain displacements of the atoms.

The actual determination of the frequencies of vibration now requires the complete solution of the secular equation which can usually only be done for very simple cases if the force constants are not known. In order to reduce the

15. Rosenthal, J.E. and Murphy, Rev. Mod. Phy., 8, 317 (1936)
16. Meister, A.G., Cleveland, F.F. and Murray, M.J., Am. J. Phy. 11, 239 (1943)
17. Herzberg, Op. Cit., P. 1 ff. and p. 82 ff.

number of force constants, it is necessary to introduce a force field assumption. The various types of assumptions that have been made and the manner in which the calculations are then carried out are given in detail in Herzberg[18].

When the molecule is rather large, the calculations become complex and it is almost impossible to carry out algebraic calculations and obtain expressions relating the force constants to the frequencies. The computations are then best carried out numerically. An important factor that is of great aid in these cases is the fact that both bond stretching and bending force constants are invariant from one molecule to another if the bonds are in similar surroundings[19,20]. Also for a general check on results characteristic groups of atoms have vibrational frequencies that are essentially the same in different molecules if their frequencies differ sufficiently from the vibrational frequencies of the rest of the molecule[21]. The calculated values of the frequencies can then be used as an aid in assigning the observed bands to various atomic vibrations.

(b) Quantum Mechanical - While the calculation of the normal frequencies can generally be carried out entirely by classical methods, the frequencies can be determined by

18. Herzberg, Op. Cit., pp. 159-191.
19. Crawford, B.L., Jr., J. Chem. Phy. 7, 555 (1939)
20. Crawford, B.L., Jr., and Brinkley, S.R., Jr., J. Chem. Phy. 9, 69 (1941)
21. Wilson, E.B.Jr., and Wells, A.J., J. Chem. Phy. 9, 314 (1941)

quantum mechanical methods and the selection rules are determined by quantum treatment. In a wave mechanical treatment, the vibrational motion of the molecule as in the classical method may be considered as a superposition of 3N simple harmonic motions to a good approximation. The Schrodinger equation in normal coordinates is[22]

$$\frac{1}{\psi_i}\frac{d^2\psi_i}{d\xi_i^2} + \frac{8\pi^2}{h^2}\left(E_i - \frac{1}{2}\lambda_i \xi_i^2\right) = 0 \qquad (1)$$

where

$$E = E_1 + E_2 + \ldots + E_{3n}. \qquad (2)$$

The eigenfunctions of Eq. (1) are the eigenfunctions of the ordinary simple harmonic oscillator

$$\psi_i(\xi_i) = N_{v_i}\, e^{-\left(\frac{\alpha_i}{2}\right)\xi_i^2} H_{v_i}(\sqrt{\alpha_i}\,\xi_i) \qquad (3)$$

where N_{vi} is a normalization constant, $\alpha_i = \frac{2\pi\nu_i}{h}$ and H_{vi} $(\sqrt{\alpha_i}\,\xi_i)$ is a Hermite polynomial of the v_ith degree. The total vibrational eigenfunction is then the product of the 3N-5 or 3N-6 harmonic oscillator eigenfunctions.

The eigenvalues of the ith harmonic oscillator are given by

$$E_i = h\nu_i\,(v_i + 1/2),\quad v_i = 0, 1, 2, \ldots \qquad (4)$$

where

$$\nu_i = 1/2\pi\sqrt{\lambda_i} \qquad (5)$$

is the classical frequency of vibration of the ith normal

22. See Herzberg, Op. Cit.; Pauling, L., and Wilson, E.B. Jr., Introduction to Quantum Mechanics (New York: McGraw-Hill, 1935) or Eyring, Henry, Walter, John, and Kimball, George E., Quantum Chemistry (New York: John Wiley and Sons, 1944)

vibration. The total vibrational energy of the system can then have the values

$$E(v_1, v_2, v_3 \ldots) = h\nu_1(v_1+1/2)+h\nu_2(v_2+1/2)+\ldots \qquad (6)$$

The eigenfunctions are either even or odd functions of the normal coordinates depending on whether the energy quantum number is even or odd. Thus if a normal vibration is antisymmetric with respect to a symmetry element, $\Psi_i(\xi_i)$ changes sign for odd v_i but remains unchanged for even v_i if the particular symmetry operation is carried out. Since the total vibrational eigenfunction is a product of the harmonic oscillator eigenfunctions, for only nondegenerate vibrations the total eigenfunction will be symmetric with respect to a given symmetry operation if the total number of components of the $\Psi_i(\xi_i)$ that are antisymmetric is even; and of course, it will be odd if the total number of antisymmetric components is odd. When there are degenerate vibrations, each of the degenerate eigenfunctions goes into a linear combination of the eigenfunctions belonging to the same energy level.

There are only certain combinations of symmetry properties of the normal vibrations and vibrational eigenfunctions possible because only certain combinations of symmetry elements occur in each point group and some of these are necessary consequences of others. These combinations are the symmetry types or species and are the irreducible representations of group theory. For example, if a point

group has two necessary elements of symmetry there are four possible symmetry types ++, --, +-, -+. These species along with the character tables have been worked out for all of the different point groups[23].

Now, since the vibrations of the atoms have been considered as a superposition of simple harmonic oscillators, the selection rule to a good approximation is given by

$$\Delta v_i = \pm 1 \tag{7}$$

for each normal vibration v_i. However, the presence of a fundamental in either the infra-red or Raman spectra depends on the change of the dipole moment or polarizability.

The dipole moment of a molecule is represented by the matrix[24]

$$\int \psi_n \psi_m^* M d\tau \tag{8}$$

where M is a vector with components

$$M_x = \sum e_i x_i, \; M_y = \sum e_i y_i, \; M_z = \sum e_i z_i \tag{9}$$

where e_i is the charge on the ith particle with coordinates x_i, y_i, z_i, and ψ_n and ψ_m are the time dependent eigenfunctions in the states m and n, then

$$\Psi_n = \psi_n e^{2\pi i(\frac{E_n}{h})t}, \quad \Psi_m = \psi_m e^{2\pi i(\frac{E_m}{h})t}. \tag{10}$$

The diagonal elements represent the permanent dipole moments in the states n; the off-diagonal elements correspond to a transition from the state n to m. The transition probability is proportional to the square of the time dependent component of Eq. (8). The vibrational selection rule is

23. See Herzberg, Op. Cit., Rosenthal + Murphy, Op. Cit., Kohlrausch, K. W. F., Der Smekal-Raman-Effekt (Berlin: J. Springer, 1931), etc.
24. Herzberg, Op. Cit., p. 251

then given by the condition that at least one of the quantities

$$\psi_{v'}\,\psi_{v''}^{*}\,M_x,\quad \psi_{v'}\,\psi_{v''}^{*}\,M_y,\quad \psi_{v'}\,\psi_{v''}^{*}\,M_z \tag{11}$$

is totally symmetrical. The rule may also be stated as: a vibrational transition $v' \leftrightarrow v''$ is allowed only when there is at least one component of the dipole moment $\underline{M}$ that has the same species as the product $\psi_{v'}\,\psi_{v''}$.

For the Raman effect the intensity depends on the induced dipole $\vec{P}$ which is represented by

$$\int \psi_n\, P^{*}\, \psi_m\, d\tau \tag{12}$$

where

$$P_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \tag{13}$$

$$P_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \tag{14}$$

$$P_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \tag{15}$$

where the α's are the components of the polarizability and $\vec{E}$ is the electric vector. The time independent part of Eq. (12) is

$$[P^{o}]^{nm} = \int \psi_n\, P^{o*}\, \psi_m\, d\tau \tag{16}$$

where P^{o} is the amplitude of $\vec{P}$. The intensity of a Raman transition is proportional to the square of $[P^{o}]^{nm}$.

If the values for $\vec{P}$ are substituted in this equation, we get the components

$$[P_x^{o}]^{nm}\; E_x^{o} \int \alpha_{xx}\, \psi_n\, \psi_m^{*}\, d\tau + E_y^{o} \int \alpha_{xy}\, \psi_n\, \psi_m^{*}\, d\tau + E_z^{o} \int \alpha_{xz}\, \psi_n\, \psi_m^{*}\, d\tau \tag{17}$$

$$[P_y^{o}]^{nm}\; E_x^{o} \int \alpha_{xy}\, \psi_n\, \psi_m^{*}\, d\tau + E_y^{o} \int \alpha_{yy}\, \psi_n\, \psi_m^{*}\, d\tau + E_z^{o} \int \alpha_{yz}\, \psi_n\, \psi_m^{*}\, d\tau \tag{18}$$

$$[P_z^{o}]^{nm}\; E_x^{o} \int \alpha_{xz}\, \psi_n\, \psi_m^{*}\, d\tau + E_y^{o} \int \alpha_{yz}\, \psi_n\, \psi_m^{*}\, d\tau + E_z^{o} \int \alpha_{zz}\, \psi_n\, \psi_m^{*}\, d\tau \tag{19}$$

Here E^o_x, E^o_y, E^o_z are the components of the amplitude of the light wave and the integrals are the matrix elements of the six components of the polarizability tensor. The diagonal elements correspond to Rayleigh scattering while the off diagonal elements correspond to Raman scattering. The Raman selection rule is then given by the fact that at least one of the six integrals of polarizability must be different for a Raman transition to occur or again a Raman transition is allowed if at least one of the six products

$$\alpha_{xx}\, \psi_{v'}\, \psi^*_{v''},\ \alpha_{xy}\, \psi_{v'}\, \psi^*_{v''}, \ldots$$

is totally symmetrical.

C. THE NORMAL VIBRATIONS OF 1, 3-Butadiene

1. <u>The Configuration of 1, 3, Butadiene</u>

The normal configuration for butadiene could conceivably be either in the trans- or cis- form and no final conclusion has yet been reached as to which form is the lowest energy state. Mulliken has shown[25] that it is possible to have isomerism about a single bond as might be the case with butadiene and his calculations with molecular orbitals seem to indicate that the trans-form is the lowest energy form. The work of Carr, Pickett and Stucklen[26] in the ultraviolet absorption spectrum of butadiene seems to indicate that the trans-form predominates at room temperature at least.

Rasmussen, Tunnicliff and Brattain[27] have obtained

25. Mulliken, R.S., <u>Rev. Mod. Phy.</u> 14, 269 (1942)
26. Carr, E.P., Pickett, L.W., and Stucklen, H., <u>Rev. Mod. Phy.</u> 14, 260 (1942)
27. Rasmussen, R.S., Tunnicliff, D.D., and Brattain, R.R., <u>J. Chem. Phy.</u> 11, 432 (1943)

the infra-red spectrum of butadiene and compared it with the Raman spectrum taken with the butadiene in the liquid state at the temperature of dry ice by Bradacs and Kahovec[28]. They found a coincidence between six frequencies in the Raman and infra-red. This seems to indicate that, since no coincidences should occur if the butadiene was in the trans-form due to its center of symmetry, the cis-form is predominant at the temperature of dry ice. Thus it would appear that the cis-form is the lower energy form but at room temperature the trans-form predominates.

The cis-form (Fig. 1) has been selected as the configuration for the present work. The work of Mulliken[29] and Bradac and Kahovec[28] indicates that all the atoms are in a plane and that all bond angles both H-C-H and C-C-H are very nearly 120°. The carbon-hydrogen bond distances are fairly well known from electron diffraction studies[30] and were taken to be 1.09 angstroms. The carbon-carbon single bond and carbon-carbon double bond distances were taken from the work of Mulliken who based his conclusions on the calculations of Lennard-Jones[31] and Penney[32]. The C-C distance was chosen as 1.44A. and the C=C distance as 1.35A.

28. Bradacs, K., and Kahovec, L., Zeits. fr. Physik, Chemie B48, 63 (1941)
29. Mulliken, R. S., J. Chem. Phy., 7, 121 (1939)
30. Pauling, L., Nature of the Chemical Bond (Cornell University Press, 1939)
31. Lennard-Jones, J. E., Proc. Roy. Soc. 158A, 293 (1937)
32. Penney, W. G., Proc. Roy. Soc. 158A, 318 (1937)

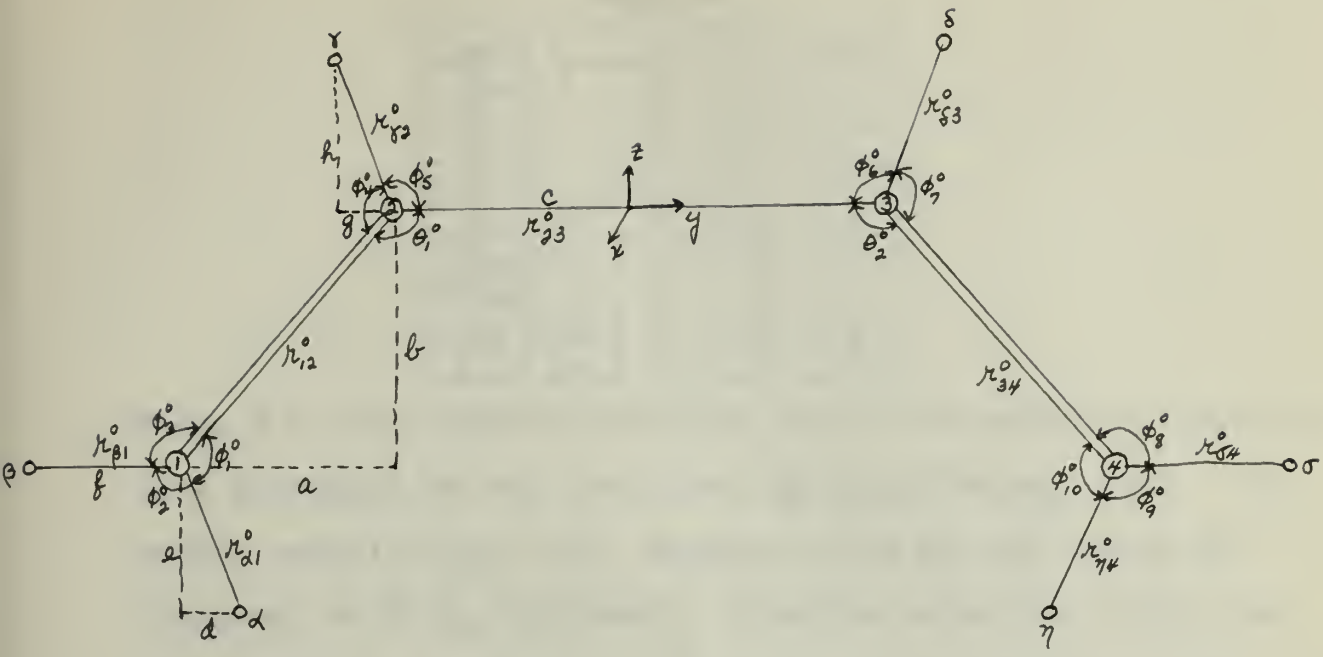

Fig. 1

The following notation has been adopted in the work that follows. The carbon atoms have been labelled with numbers from 1 to 4 while the hydrogen atoms have been lettered with Greek letters as shown in Fig. 1. The masses of the carbon atoms have been denoted by M and the hydrogen atoms by m. The C-C-C angles have been denoted by θ and the C-C-H and H-C-H angles by ϕ. The principle axis of symmetry is chosen as the z axis.

With the configuration that was decided upon the point group for the molecule is C_{2_v} with the character table as given in Table 1[33].

33. See Rosenthal and Murphy, Rev. Mod. Phys., 8, 317 (1936)

Table 1

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
B_2	1	-1	-1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
ϕ_R	0	π	0	0
π_R	10	0	10	0
$\pm 1+\cos\phi_R$	3	-1	1	1
χ_R	30	0	10	0
Ξ	24	2	10	0

where $\emptyset$ is the angle of rotation. U_R is the number of particles left unchanged by any operation, $\chi_R = U_R(\pm 1+2\cos\emptyset_R)$ with + for proper rotation and - for improper rotation and $\Xi = (U_C-2)\times(1+2\cos\emptyset)$ or $\Xi = U_S(-1+2\cos\theta)$. From the selection rules the frequencies in species A_1, B_1 and B_2 are infra-red active; A_1, A_2, B_1 and B_2 are Raman active. The Raman lines in A_1 are polarized; those in A_2, B_1 and B_2 are depolarized.

From the relation

$$a^{(k)} = \frac{1}{h}\left\{\sum_c (U_c-2)(1+2\cos\emptyset)\chi^{(k)} + \sum_s U_s(-1+2\cos\emptyset)\chi^{(k)}\right\} \quad (1)$$

the number of frequencies in each species may be calculated[34]. Applying this gives the following results

$$a^{(1)} = \frac{1}{4}(24+2+10) = 9 \quad (2)$$

$$a^{(2)} = \frac{1}{4}(24-2-10) = 3 \quad (3)$$

$$a^{(3)} = \frac{1}{4}(24+2-10) = 4 \quad (4)$$

$$a^{(4)} = \frac{1}{4}(24-2+10) = 8 \quad (5)$$

When the symmetry operations are applied to the molecule together with the character sign (either symmetric

34. Rosenthal and Murphy, Loc. Cit.

or antisymmetric) from the character table and the conditions that the center of mass shall be fixed and the angular momentum shall be zero, the following cartesian coordinates are the only ones that remain for each species:

A_1: $z_1, z_2, z_\alpha, z_\beta, y_1, y_2, y_\alpha, y_\beta, y_\gamma$

A_2: $x_1, x_2, x_\alpha, x_\beta$

B_1: $z_1, z_2, z_\alpha, z_\beta, y_1, y_2, y_\alpha, y_\beta$

B_2: x_1, x_2, x_α.

The only vibrations which will be considered are in-plane vibrations; hence, species A_2 and B_2 will give no frequencies since these vibrations are out of the plane.

2. The Potential Function

The force field which was chosen for this determination was the valence type force field. Thus the changes in bond length and changes in the bond angles were chosen as the coordinates for the potential function. The kinetic energy expression can be written directly in cartesian coordinates as

$$2T = M(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) + m(\dot{x}_j^2 + \dot{y}_j^2 + \dot{z}_j^2), \quad i = 1 \text{ to } 4, \; j = \alpha, \beta, \gamma, \delta, \sigma, \eta \qquad (1)$$

The potential energy in symmetry coordinates is

$$\begin{aligned} 2V = {} & K_{12}|\Delta r_{12}|^2 + K_{23}|\Delta r_{23}|^2 + K_{34}|\Delta r_{34}|^2 + K_{\alpha 1}|\Delta r_{\alpha 1}|^2 \\ & + K_{\beta 1}|\Delta r_{\beta 1}|^2 + K_{\gamma 2}|\Delta r_{\gamma 2}|^2 + K_{\delta 3}|\Delta r_{\delta 3}|^2 + K_{\sigma 4}|\Delta r_{\sigma 4}|^2 \\ & + K_{\eta 4}|\Delta r_{\eta 4}|^2 + K_{\theta_1}|\Delta\theta_1|^2 + K_{\theta_2}|\Delta\theta_2|^2 + K_{\phi_1}|\Delta\phi_1|^2 \\ & + K_{\phi_2}|\Delta\phi_2|^2 + K_{\phi_3}|\Delta\phi_3|^2 + K_{\phi_4}|\Delta\phi_4|^2 + K_{\phi_5}|\Delta\phi_5|^2 \end{aligned}$$

(2)

$$+K\phi_6|\Delta\phi_6|^2+K\phi_7|\Delta\phi_7|^2+K\phi_8|\Delta\phi_8|^2+K\phi_9|\Delta\phi_9|^2+K\phi_{10}|\Delta\phi_{10}|^2.$$

The values of $|\Delta r_{12}|^2$, $|\Delta r_{23}|^2$,... are determined by taking the vector difference of the distances between two atoms in the rest position and when they have been given a small arbitrary displacement. These are

$$|\Delta r_{\alpha 1}|^2 = \left\{\sqrt{(x_1-x_\alpha)^2+(y_1-y_\alpha-d)^2+(z_1-z_\alpha+e)^2}-|r^\circ_{\alpha 1}|\right\}^2$$

$$|\Delta r_{\beta 1}|^2 = \left\{\sqrt{(x_1-x_\beta)^2+(y_1-y_\beta+f)^2+(z_1-z_\beta)^2}-|r^\circ_{\beta 1}|\right\}^2$$

$$|\Delta r_{12}|^2 = \left\{\sqrt{(x_2-x_1)^2+(y_2-y_1+a)^2+(z_2-z_1+b)^2}-|r^\circ_{12}|\right\}^2$$

$$|\Delta r_{\gamma 2}|^2 = \left\{\sqrt{(x_2-x_\gamma)^2+(y_2-y_\gamma+g)^2+(z_2-z_\gamma-h)^2}-|r^\circ_{\gamma 2}|\right\}^2$$

$$|\Delta r_{23}|^2 = \left\{\sqrt{(x_3-x_2)^2+(y_3-y_2+c)^2+(z_3-z_2)^2}-|r^\circ_{23}|\right\}^2$$

$$|\Delta r_{\delta 3}|^2 = \left\{\sqrt{(x_3-x_\delta)^2+(y_3-y_\delta-g)^2+(z_3-z_\delta-h)^2}-|r^\circ_{\delta 3}|\right\}^2$$

$$|\Delta r_{34}|^2 = \left\{\sqrt{(x_4-x_3)^2+(y_4-y_3+a)^2+(z_4-z_3-b)^2}-|r^\circ_{34}|\right\}^2$$

$$|\Delta r_{\sigma 4}|^2 = \left\{\sqrt{(x_4-x_\sigma)^2+(y_4-y_\sigma-f)^2+(z_4-z_\sigma)^2}-|r^\circ_{\sigma 4}|\right\}^2$$

$$|\Delta r_{\eta 4}|^2 = \left\{\sqrt{(x_4-x_\eta)^2+(y_4-y_\eta+d)^2+(z_4-z_\eta+e)^2}-|r^\circ_{\eta 4}|\right\}$$

$$|\Delta\theta_1|^2 = \frac{1}{\sin^2\theta_1^\circ}\left\{-\left[\frac{(x_2-x_1)(x_3-x_2)+(y_2-y_1+a)(y_3-y_2+c)+(z_2-z_1+b)(z_3-z_2)}{\sqrt{[(x_2-x_1)^2+(y_2-y_1+a)^2+(z_2-z_1+b)^2][(x_3-x_2)^2+(y_3-y_2+c)^2+(z_3-z_2)^2]}}\right]-\cos\theta_1^\circ\right\}^2$$

$$|\Delta\theta_2^\circ| = \frac{1}{\sin^2\theta_2^\circ}\left\{-\left[\frac{(x_3-x_2)(x_4-x_3)+(y_3-y_2+c)(y_4-y_3+a)+(z_3-z_2)(z_4-z_3-b)}{\sqrt{[(x_3-x_2)^2+(y_3-y_2+c)^2+(z_3-z_2)^2][(x_4-x_3)^2+(y_4-y_3+a)^2+(z_4-z_3-b)^2}}\right]-\cos\theta_2^\circ\right\}$$

$$|\Delta\phi_1|^2 = \frac{1}{\sin^2\phi_1^\circ}\left\{-\left[\frac{(x_1-x_\alpha)(x_2-x_1)+(y_1-y_\alpha-d)(y_2-y_1+a)+(z_1-z_\alpha+e)(z_2-z_1+b)}{[(x_1-x_\alpha)^2+(y_1-y_\alpha-d)^2+(z_1-z_\alpha+e)^2][(x_2-x_1)^2+(y_2-y_1+a)^2+(z_2-z_1+b)^2]}\right]-\cos\phi_1^\circ\right\}^2$$

$$|\Delta\phi_2|^2 = \frac{1}{\sin^2\phi_2^\circ}\left\{\left[\frac{(x_1-x_\alpha)(x_1-x_\beta)+(y_1-y_\alpha-d)(y_1-y_\beta+f)+(z_1-z_\alpha+e)(z_1-z_\beta)}{\sqrt{[(x_1-x_\alpha)^2+(y_1-y_\alpha-d)^2+(z_1-z_\alpha+e)^2][(x_1-x_\beta)^2+(y_1-y_\beta+f)^2+(z_1-z_\beta)^2]}}\right] - \cos\phi_2^\circ\right\}^2$$

$$|\Delta\phi_3|^2 = \frac{1}{\sin^2\phi_3^\circ}\left\{\left[\frac{(x_1-x_\beta)(x_2-x_1)+(y_1-y_\beta+f)(y_2-y_1+a)+(z_1-z_\beta)(z_2-z_1+b)}{\sqrt{[(x_1-x_\beta)^2+(y_1-y_\beta+f)^2+(z_1-z_\beta)^2][(x_2-x_1)^2+(y_2-y_1+a)^2+(z_2-z_1+b)^2]}}\right] - \cos\phi_3^\circ\right\}^2$$

$$|\Delta\phi_4|^2 = \frac{1}{\sin^2\phi_4^\circ}\left\{\left[\frac{(x_2-x_\gamma)(x_2-x_1)+(y_2-y_\gamma+g)(y_2-y_1+a)+(z_2-z_\gamma-h)(z_2-z_1+b)}{\sqrt{[(x_2-x_\gamma)^2+(y_2-y_\gamma+g)^2+(z_2-z_\gamma-h)^2][(x_2-x_1)^2+(y_2-y_1+a)^2+(z_2-z_1+b)^2]}}\right] - \cos\phi_4^\circ\right\}$$

$$|\Delta\phi_5|^2 = \frac{1}{\sin^2\phi_5^\circ}\left\{-\left[\frac{(x_2-x_\gamma)(x_3-x_2)+(y_2-y_\gamma+g)(y_3-y_2+c)+(z_2-z_\gamma-h)(z_3-z_2)}{\sqrt{[(x_2-x_\gamma)^2+(y_2-y_\gamma+g)^2+(z_2-z_\gamma-h)^2][(x_3-x_2)^2+(y_3-y_2+c)^2+(z_3-z_2)^2]}}\right] - \cos\phi_5^\circ\right\}$$

$$|\Delta\phi_6|^2 = \frac{1}{\sin^2\phi_6^\circ}\left\{\left[\frac{(x_3-x_\delta)(x_3-x_2)+(y_3-y_\delta-g)(y_3-y_2+c)+(z_3-z_\delta-h)(z_3-z_2)}{\sqrt{[(x_3-x_\delta)^2+(y_3-y_\delta-g)^2+(z_3-z_\delta-h)^2][(x_3-x_2)^2+(y_3-y_2+c)^2+(z_3-z_2)^2]}}\right] - \cos\phi_6^\circ\right\}$$

$$|\Delta\phi_7|^2 = \frac{1}{\sin^2\phi_7^\circ}\left\{-\left[\frac{(x_3-x_\delta)(x_4-x_3)+(y_3-y_\delta-g)(y_4-y_3+a)+(z_3-z_\delta-h)(z_4-z_3-b)}{\sqrt{[(x_3-x_\delta)^2+(y_3-y_\delta-g)^2+(z_3-z_\delta-h)^2][(x_4-x_3)^2+(y_4-y_3+a)^2+(z_4-z_3-b)^2]}}\right] - \cos\phi_7^\circ\right\}$$

$$|\Delta\phi_8|^2 = \frac{1}{\sin^2\phi_8^\circ}\left\{\left[\frac{(x_4-x_3)(x_4-x_\sigma)+(y_4-y_3+a)(y_4-y_\sigma-f)+(z_4-z_3-b)(z_4-z_\sigma)}{\sqrt{[(x_4-x_3)^2+(y_4-y_3+a)^2+(z_4-z_3-b)^2][(x_4-x_\sigma)^2+(y_4-y_\sigma-f)^2+(z_4-z_\sigma)^2]}}\right] - \cos\phi_8^\circ\right\}$$

$$|\Delta\phi_9|^2 = \frac{1}{\sin^2\phi_9^\circ}\left\{\left[\frac{(x_4-x_\sigma)(x_4-x_n)+(y_4-y_\sigma-f)(y_4-y_n+d)+(z_4-z_\sigma)(z_4-z_n+e)}{\sqrt{[(x_4-x_\sigma)^2+(y_4-y_\sigma-f)^2+(z_4-z_\sigma)^2][(x_4-x_n)^2+(y_4-y_n+d)^2+(z_4-z_n+e)^2]}}\right] - \cos\phi_9^\circ\right\}^2$$

$$|\Delta\phi_{10}|^2 = \frac{1}{\sin^2\phi_{10}^\circ}\left\{\left[\frac{(x_4-x_n)(x_4-x_3)+(y_4-y_n+d)(y_4-y_3+a)+(z_4-z_n+e)(z_4-z_3-b)}{\sqrt{[(x_4-x_n)^2+(y_4-y_n+d)^2+(z_4-z_n+e)^2][(x_4-x_3)^2+(y_4-y_3+a)^2+(z_4-z_3-b)^2]}}\right] - \cos\phi_{10}^\circ\right\}$$

3. Calculation of the Vibrational Frequencies

Now from the application of group theory we have that for species A_1 all X's are zero and

$$z_4 = z_1,\ z_3 = z_2,\ z_\eta = z_\alpha,\ z_\sigma = z_\beta,$$
$$y_4 = y_1,\ y_3 = -y_2,\ y_\eta = -y_\alpha,\ y_\sigma = -y_\beta,\ y_\delta = -y_\gamma,$$

and
$$z_\delta = z_\gamma = -\frac{M}{m} z_1 - \frac{M}{m} z_2 - z_\alpha - z_\beta . \tag{3}$$

For species B_1 all X's are zero and

$$z_4 = -z_1,\ z_3 = -z_2,\ z_\eta = -z_\alpha,\ z_\sigma = -z_\beta,$$
$$y_4 = y_1,\ y_3 = y_2,\ y_\eta = y_\alpha,\ y_\sigma = y_\beta$$
$$y_\delta = y_\gamma = -\frac{M}{m} y_1 - \frac{M}{m} y_2 - y_\alpha - y_\beta,$$

and
$$-z_\delta = z_\gamma = \Omega y_1 + K y_2 + \rho y_2 + \lambda y_\beta - \nu z_1 - \chi z_2 - \zeta z_\alpha - \xi z_\beta \tag{4}$$

where the constants have the following values:

$$K = \frac{2Mh}{m(2g+c)},\quad \lambda = \frac{2(b+h)}{2g+c},\quad \rho = \frac{2(b+e+h)}{2g+c},$$

$$\xi = \frac{2a+2f+c}{2g+c},\quad \zeta = \frac{2a-2d+c}{2g+c},\quad \chi = \frac{Mc}{m(2g+c)},$$

$$\Omega = \frac{2M(b+h)}{m(2g+c)},\quad \nu = \frac{M(2a+c)}{m(2g+c)}$$

These substitutions are made in the expressions given for the symmetry coordinates and these are then expanded in a Taylor's series leaving only second order terms. The final expressions are then substituted into the potential energy expression given previously and the coefficients of the cartesian coordinates are grouped together giving the constants b_{ij} in the secular equation

$$\left| b_{ij} - \lambda a_{ij} \right| = 0. \tag{5}$$

The constants A_{ij} are similarly obtained by applying the symmetry conditions above to the kinetic energy expression and grouping the coefficients of the cartesian coordinates.

The constants can now be evaluated numerically and substituted into the secular equation. The values for the constants that were used throughout this work are given in Table II. The masses of the atoms were taken from Birge's[35] table of values of physical constants. The values for the force constants were transferred from the work by Wilson and Wells[36] on propylene and the paper by Crawford and Brinkley[37] on force constants in organic molecules.

Table II

$M = 19.93 \times 10^{-24}$ gm
$m = 1.673 \times 10^{-24}$ gm
$\theta_1^\circ = \theta_2^\circ = \phi_1^\circ \longrightarrow \phi_{10}^\circ = 120^\circ$
$r_{12}^\circ = r_{34}^\circ = 1.35 \times 10^{-8}$ cm
$r_{23}^\circ = 1.44 \times 10^{-8}$ cm
$r_{21}^\circ \rightarrow r_{74}^\circ = 1.09 \times 10^{-8}$ cm

$k_{12} = k_{34} = 9.72 \times 10^5$ dynes/cm
$k_{23} = 4.50 \times 10^5$ dynes/cm
$k_{21} \rightarrow k_{74} = 4.79 \times 10^5$ dynes/cm
$k_{\theta_1} = k_{\theta_2} = 1.20 \times 10^{-11}$ dyne cm/rad^2
$k_{\phi_1} = k_{\phi_3} = k_{\phi_4} = k_{\phi_7} = k_{\phi_8} = k_{\phi_{10}}$
$= 0.939 \times 10^{-11}$ dyne cm/rad^2
$k_{\phi_2} = k_{\phi_9} = 0.535 \times 10^{-11}$ dyne cm/rad^2
$k_{\phi_5} = k_{\phi_6} = 0.654 \times 10^{-11}$ dyne cm/rad^2

This gives two secular equations, one of eigth order and one of ninth order. The expansion of secular equations of this size is a laborious task, and usually approximations of various kinds or iteration schemes are used for solving them. A very powerful method for an exact expansion of determinants of this type which was used in this work will now be described.

35. Birge, R.T., Rev. Mod. Phys. 13, 233 (1941)
36. Wilson, E.B., Jr. and Wells, A.J., J. Chem. Phy. 9, 314 (1941)
37. Crawford, B.L., Jr. and Brinkley, S.R., Jr., J. Chem. Phys. 9, 69, (1941)

(a) <u>An Exact Method for Expanding the Secular Equation</u> - The method here described is due to J. G. Bryan[38] who devised the method to permit an exact expansion of the characteristic equation and latent vectors of a matrix. The characteristic equation is defined by

$$|A - \lambda I| = 0 \tag{6}$$

where I is the unit matrix. The process of expanding this equation consists of building an auxiliary matrix and row vector from the original matrix A.

A vector f_1 is built as follows

$$f_1 = -1 \quad a_{11} \, . \tag{7}$$

This vector is then used as the basis for building the auxiliary matrix B_2. A matrix A_2 is written down first which is composed of the first two elements of the first two rows of A. This is divided into two parts with the last row being indicated by a_2 and the first row by α . Thus

$$A_2 = \begin{array}{cc|c} a_{11} & a_{12} & \alpha \\ \hline a_{21} & a_{22} & a_2 \end{array} \tag{8}$$

The auxiliary matrix B_2 is then built by first writing down the vector f_1. The first row is built by multiplying α in A_2 times a null column for the first term, and then multiplying α times this first column so built for the second term. Thus

$$\begin{array}{ll} B_2 = & 0 \quad -a_{12} \\ \hline f_1 = & -1 \quad a_{11} \end{array} \tag{9}$$

38. Bryan, J. G., <u>A Method for the Exact Determination of the Characteristic Equation and Latent Vectors of a Matrix with Applications to the Discriminant Function for More than Two Groups</u>. Harvard Graduate School of Education Dissertation (1950)

The process is then repeated by writing down the first three terms from the first three rows of the original matrix for A_3. That is

$$A_3 = \begin{array}{ccc} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ \hline a_{31} & a_{32} & a_{33} \end{array} \quad \begin{array}{c} \alpha \\ \\ a_3 \end{array} \tag{10}$$

where the last row is now designated by a_3 and the remaining rows are designated by α. The vector f_2 is now built by multiplying a_2 by the null column in B_2 and f_1 and subtracting the next number in f_1, that is, -1 for the first term of f_2. The second term is then obtained by multiplying a_2 by the first column of B_2 and f_1 and subtracting the next term in f_1. The last term is obtained by multiplying a_2 times the last column in B_2 and f_1. Thus

$$f_2 = 1 - (a_{22} \quad a_{11}) \quad a_{11} \; a_{22} \tag{11}$$

The matrix B_3 is then built in the same manner as B_2 was. First f_2 is written down and then the first term of the first column of B_3 is obtained by multiplying the first row of α in A_3 by the null column in B_3 and f_2. The second term in the column is similarly obtained by multiplying the second row in α by the null column. Thus there will always be a column of zeros as the first column in the auxiliary matrix. The first and second terms of the second column in B_3 are then obtained similarly by multiplying this first column of B_3 and f_2 by the first row of α in A_3 for the first term and by the second

row of α for the second term. The last column in B_3 is similarly obtained. The vector f_3 is obtained in the same manner as f_2 and the entire process is continued until the entire matrix has been written down as A_n. The coefficients of the expanded characteristic equation will then be given by the terms in f_n which is obtained in the manner described above by multiplying a_n by the columns of B_n and f_{n-1} and subtracting the next term in f_{n-1}.

There are several advantages to this method besides the obvious advantage of permitting an exact expansion of the characteristic equation with even less labor than is involved in previous approximation methods. One of these is the fact that the method is readily adaptable to use by I.B.M. computing machines or hand computing machines. The other is the fact that there is a continuous check on the work that has been performed. The check is obtained by summing the columns of α and multiplying this row of sums times the columns of B_i and f_{i-1} that is being built by this particular α. The product of this row of sums of α in some A_i times a given column in B_i and f_{i-1} must equal the sum of the terms in the next column of B_i. Furthermore, once B_i has been completed the product of any row in α times the last column in B_i and f_{i-1} must equal zero. An example will probably serve best to clarify the operations involved. Consider the matrix

$$\begin{vmatrix} 2-\lambda & -1 & -4 \\ 4 & 3-\lambda & 2 \\ -2 & 3 & 1-\lambda \end{vmatrix} = 0.$$

This can be written as

$$\begin{vmatrix} 2 & -1 & -4 \\ 4 & 3 & 2 \\ -2 & 3 & 1 \end{vmatrix} - \lambda \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = 0$$

where the first matrix is the matrix A in our previous discussion. Then

$$f_1 = -1 \quad 2$$

and

	A_2	2	-1		α
		4	3		a_2
Sum	(α)	2	-1		
	B_2	0	1	0	
	f_1	-1	2		
Sum	(B_2)	0	1		
Check		0	1		

		2	-1	-4		α
		4	3	2		
	A_3	-2	3	1		a_3
Sum	(α)	6	2	-2		
	B_3	0	-4	10	0	
		0	2	-20	0	
	f_2	1	-5	10		
Sum	(B_3)	0	-2	-10		
Check		0	-2	-10		

$$f_3 = -1 \quad 6 \quad -1 \quad -70$$

Thus the expanded characteristic equation in

$$\lambda^3 - 6\lambda^2 + \lambda + 70 = 0.$$

Now the secular equation considered in this work is in general not in the form of the characteristic equation but by proper addition and subtraction of rows and columns and then division of each column by the coefficient of λ in that column after there are λ's only on the principal diagonal it can be put into the proper form. Then the pro-

cess described can be used to obtain the expanded secular equation. As a further example, the entire solution of the eighth order secular equation is presented. The original secular equation is as follows:

1.	2.
2585.223001 - λ919.445462	1566.097331 - λ533.133809
1566.097331 - λ533.133809	1031.210323 - λ389.394129
285.972608 - λ100.388702	172.922857 - λ 55.872969
211.339583 - λ 75.544711	132.222504 - λ 44.774624
-1261.519224 + λ437.160272	-708.579705 + λ195.288892
-749.750371 + λ225.631124	-413.541948 + λ100.794274
-63.368231 + λ 22.370756	-35.941267 + λ 9.993498
-188.782090 + λ 65.401606	-106.436015 + λ 29.216303

3.	4.
285.972608 - λ100.388702	211.339583 - λ 75.544711
172.922857 - λ 55.872969	132.222504 - λ 44.774624
34.489040 - λ 13.123452	24.163362 - λ 8.431028
24.163362 - λ 8.431028	22.942814 - λ 8.018383
-141.764534 + λ 53.115492	-105.753050 + λ 36.714398
-85.888794 + λ 27.414450	-62.626083 + λ 18.949368
-9.308504 + λ 2.718074	-5.412186 + λ 1.878782
-21.970341 + λ 7.946372	-15.822713 + λ 5.492679

5.	6.
-1261.519244 + λ437.160272	-749.750371 + λ225.631124
-708.579705 + λ195.288892	-413.541948 + λ100.794274
-141.764534 + λ 53.115492	-85.888794 + λ 27.414450
-105.753050 + λ 36.714398	-62.626083 + λ 18.949368
695.144505 - λ308.527845	397.096281 - λ148.953422
397.096281 - λ148.953422	254.216094 - λ 96.809801
30.793178 - λ 14.768355	20.538526 - λ 7.622377
99.841587 - λ 43.175750	60.830535 - λ 22.284260

7.	8.
-63.358231 + λ 22.370756	-188.782090 + λ 65.401606
-35.941267 + λ 9.993498	-106.436015 + λ 29.216303
-9.308504 + λ 2.718073	-21.970341 + λ 7.946372
-5.412186 + λ 1.878782	-15.822713 + λ 5.492679
30.793178 - λ 14.768355	99.841587 - λ 43.175750 = 0
20.538526 - λ 7.622377	60.830535 - λ 22.284260
5.676052 - λ 2.429588	5.409625 - λ 2.209429
5.409625 - λ 2.209429	16.397630 - λ 8.133182

After adding and subtracting rows and columns until the terms in λ remained only on the diagonal and then dividing each column by the coefficient of λ in the column, the following matrix resulted:

$$
\begin{array}{cccc}
1. & 2. & 3. & 4. \\
\left|\begin{array}{c} 2.067366-\lambda \\ .260648 \\ 1.056297 \\ .893082 \\ -.212079 \\ -.170916 \\ .475468 \\ -.165267 \end{array}\right. &
\begin{array}{c} .297095 \\ 1.510432-\lambda \\ .259149 \\ .850230 \\ .174022 \\ -.274173 \\ -.932967 \\ .206441 \end{array} &
\begin{array}{c} .631730 \\ .135973 \\ 2.419432-\lambda \\ -.739404 \\ .121093 \\ .113293 \\ -.026247 \\ .033435 \end{array} &
\begin{array}{c} .283279 \\ .236602 \\ -.392156 \\ 2.311303-\lambda \\ -.112740 \\ -1.208686 \\ -.595243 \\ .017732 \end{array} \\
5. & 6. & 7. & 8. \\
\begin{array}{c} -.337603 \\ .243037 \\ .322316 \\ -.565803 \\ .829401-\lambda \\ -.946340 \\ -1.309634 \\ .203969 \end{array} &
\begin{array}{c} -.044726 \\ -.062945 \\ .049572 \\ -.997172 \\ -.155567 \\ 1.900935-\lambda \\ 1.056800 \\ -.007546 \end{array} &
\begin{array}{c} .641858 \\ -1.104950 \\ -.059245 \\ -2.533311 \\ -1.110603 \\ 5.451680 \\ 6.498104-\lambda \\ -.375795 \end{array} &
\begin{array}{c} -2.341203 \\ 2.565703 \\ .791970 \\ .791960 \\ 1.815131 \\ -.408514 \\ -3.943537 \\ 2.082605-\lambda \end{array}\left.\right| = 0
\end{array}
$$

This can now be expanded by the method outlined above. Then

$f_1 = -1 \quad 2.067366$

A_2	2.067366	.297095	α
	.260648	1.510432	a_2
B_2	0	-.297095	
f_1^2	-1	2.067366	

	2.067366	.297095	.631740	α
A_3	.260648	1.510432	.135973	
	1.056297	.259149	2.419432	a_3
Sum (α)	2.328014	1.807527	.767703	

	0	.631730	-.913788
B_3	0	.135973	-.116447
f_2	1	-3.577798	3.045179
Sum (B_3)	0	.767703	-1.030235
Check	0	.767703	-1.030235

	2.067366	.297095	.631740	.283279	
	.260648	1.510432	.135973	.236602	α
A_4	1.056297	.259149	2.419432	-.392156	
	.893082	.850230	-.739404	2.311303	a_4
Sum (α)	3.384311	2.066676	3.187135	.127725	

	0	-.283279	1.290691	-1.252243
B_4	0	-.236602	1.041072	-.933276
	0	.392156	-1.763597	1.679522
f_3	-1	5.997230	-10.998886	6.372195
Sum(B_4)	0	-.127725	.568166	-.505997
Check	0	-.127725	.568166	-.505996

	2.067366	.297095	.631730	.283279	-.337603	
	.260648	1.510432	.135973	.236602	.243037	
A_5	1.056297	.259149	2.419432	-.392156	.322316	α
	.893082	.850230	-.739404	2.311303	-.565803	
	-.212079	.174022	.121093	-.112740	.829401	a_5
Sum (α)	4.277393	2.916906	2.447731	2.439028	-.338053	

	0	-.337603	2.222578	-4.468156	2.593151
B_5	0	.243037	-1.830229	4.132162	-2.446678
	0	.322316	-1.969895	3.680384	-2.076983
	0	-.565803	3.060059	-4.686908	2.066986
f_4	1	-8.308533	24.116182	-28.452099	11.574373
Sum(B_5)	0	-.338053	1.482514	-1.342518	.136476
Check	0	-.338053	1.482513	-1.342518	.136477

	2.067366	.297095	.631730	.283279	-.337603	-.044726	
	.260648	1.510432	.135973	.236602	.243037	-.062945	
A_6	1.056297	.259149	2.419432	-.392156	.322316	.049572	α
	.893082	.850230	-.739404	2.311303	-.565803	-.997172	
	-.212079	.174022	.121093	-.112740	.829401	-.155567	
	-.170916	-.274173	.113293	-1.208686	-.946340	1.900935	a_6
Sum(α)	4.065314	3.090928	2.568824	2.326288	.491348	-1.210838	

	0	.044726	-.098896	-.292578	.534401	-.087166	
	0	.062945	-.201454	-.327598	1.299894	-.738005	
B_6	0	-.049572	.055700	.650466	-1.179141	.381805	
	0	.997172	-6.765230	15.563708	-14.472034	4.480598	
	0	.155567	-1.409489	4.376339	-5.365307	2.212552	
f_5	-1	9.137934	-30.790576	47.080691	-32.531812	8.139528	
Sum(β)	0	1.210838	-8.419369	19.970337	-19.182187	6.249784	
Check	0	1.210838	-8.419369	19.970337	-19.182188	6.249783	
		2.067366	.297095	.631730	.283279	.337603	
		.260648	1.510432	.135973	.236602	.243037	
A_7		1.056297	.259149	2.419432	-.392156	.322316	
		.893082	.850230	-.739404	2.311303	-.565803	
		-.212079	.174022	.121093	-.112740	.829401	
		-.170916	-.274173	.113293	-1.208686	-.946340	
		.475468	-.932967	-.026247	-.595243	-1.309634	
					.044726	.641858	
					-.062945	-1.104950	
					.049572	-.059245	α
					-.997172	-2.533311	
					-.155567	-1.110603	
					1.900935	5.451680	
					1.056800	6.498104	a_7
Sum(α)		3.894398	2.816755	2.682117	1.117602	-.454992	
					.690097	1.285429	
	0	.641858	-6.710656	23.429747	-32.789724		
	0	-1.104950	9.475230	-29.459247	40.224360		
	0	-.059245	1.808043	-8.579664	12.915582		
B_7	0	-2.533311	16.979335	-39.051691	38.467198		
	0	-1.110603	10.440585	-34.834754	49.730319		
	0	5.451680	-45.517575	136.844683	-180.082491		
f_6	1	-11.038869	46.778189	-96.022233	99.289523		
					18.213245	-3.312372	
					-23.221188	4.395140	
					-6.828934	1.160792	
					-15.820024	2.298122	
					-29.828843	5.830528	
					101.452143	-18.954283	
					-47.992160	8.223746	
Sum(B_7)		1.285429	-13.525038	48.349074	-71.534756		
					43.966399	-8.582073	
Check		1.285429	-13.525037	48.349074	-71.534755		
					43.966399	-8.582073	

	2.067366	.297095	.631730	.283279	-.337603	
	.260648	1.510432	.135973	.236602	.243037	
	1.056297	.259149	2.419432	-.392156	.322316	
A_8	.893082	.850230	.739404	2.311303	-.565703	
	-.212079	.174022	.121093	-.112740	.829401	
	-.170916	-.274173	.113293	-1.208686	.946340	
	.475468	-.932967	-.026247	-.595243	-1.309634	
	-.165267	.206441	.033435	.017732	.203969	
			-.044726	.641858	-2.341203	
			-.062945	-1.104950	2.565703	
			.049572	-.059245	.791970	
			-.997172	-2.533311	.791960	α
			-.155567	-1.110603	1.815131	
			1.900935	5.451680	-.408514	
			1.056800	6.498104	3.943537	
			-.007546	-.375795	2.082605	a_8
Sum(α)	4.369866	1.883788	2.655870	.522359	-1.764626	
			1.746897	7.783533	-.728490	

	0	2.341203	-34.578691	169.794569	-368.924785
	0	2.565703	36.610239	-183.896618	405.450890
	0	-.791970	13.292887	-70.908184	166.565841
B_8	0	-.791960	3.182598	-27.136810	145.839614
	0	-1.815131	24.933551	-123.227256	285.384102
	0	.408514	17.999896	-151.753276	413.366798
	0	3.943537	-36.724235	122.560845	-178.539182
f_7	1.	17.536973	-108.448533	316.030387	-470.918704
			377.377522	-170.460830	26.887299
			-394.220247	163.557080	-22.645782
			-188.719756	93.029443	-15.931958
			-265.155967	180.066682	-40.977042
			-331.574786	184.716806	-38.351770
			-470.760675	241.720995	-47.787798
			115.150376	-30.148225	2.334004
			361.391323	-133.881886	18.698157
Sum (B_8)	0	.728490	24.716245	-264.566730	869.143278
			-1157.903533	662.481951	-136.473047
Check	0	.728490	24.716246	-264.566730	869.143278
			-1157.903534	662.481952	-136.473049
f_8	1	-19.619578	142.158734	-509.361764	990.160760
			-1067.116658	624.402846	-182.009395
					+ 20.223912

These are the coefficients of the expanded secular equation.

(b) <u>The Determination of the Normal Frequencies</u> - The solution of the expanded equation, which was accomplished by Horner's method, yields the following eight roots:

$.283785 \times 10^{29}$, $.535005 \times 10^{29}$, $.691997 \times 10^{29}$, 1.062514×10^{29}
2.091375×10^{29}, 3.101651×10^{29}, 3.244094×10^{29}, 8.609156×10^{29}

But these are equal to $4\pi^2 \nu_i^{\,2}$ where the ν_i are the frequencies of vibration. Then solving for the wave numbers gives

$$\frac{1}{\lambda_1} = 894 \text{ cm}^{-1}, \qquad \frac{1}{\lambda_2} = 1228 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_3} = 1397 \text{ cm}^{-1}, \qquad \frac{1}{\lambda_4} = 1731 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_5} = 2428 \text{ cm}^{-1}, \qquad \frac{1}{\lambda_6} = 2957 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_7} = 3024 \text{ cm}^{-1}, \qquad \frac{1}{\lambda_8} = 4926 \text{ cm}^{-1},$$

The expansion of the ninth order secular equation and the solution for the wave numbers by the same method as described above gives the following nine values:

$$\frac{1}{\lambda_1} = 434 \text{ cm}^{-1}, \quad \frac{1}{\lambda_2} = 1182 \text{ cm}^{-1}, \quad \frac{1}{\lambda_3} = 1324 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_4} = 1642 \text{ cm}^{-1}, \quad \frac{1}{\lambda_5} = 1642 \text{ cm}^{-1}, \quad \frac{1}{\lambda_6} = 2062 \text{ cm}^{-1},$$

$$\frac{1}{\lambda_7} = 2846 \text{ cm}^{-1}, \quad \frac{1}{\lambda_8} = 2992 \text{ cm}^{-1} \quad \frac{1}{\lambda_9} = 2994 \text{ cm}^{-1},$$

The values for ν_4, ν_5, ν_8 and ν_9 indicate degeneracy; however, these are not first order degeneracies. The pair of roots for ν_4 and ν_5 in the solution of the equation turned out to be just barely imaginary; that is, the curve just barely missed crossing the axis. A recheck of all of the

work showed that there did not seem to be an error which indicates that one or possibly more of the potential constants should probably be adjusted slightly. However, it may also be the case that these two pair of roots may be accidental degeneracies. The general grouping of the lines seems to check fairly well with observed spectra, as will be demonstrated later, so that these may very well be accidental degeneracies produced by interactions between vibrations.

4. Comparison of Results with Observed Spectra

The observed frequencies for butadiene that are listed in Table III were obtained from results published by Rasmussen, Tunnicliff and Brattain[39], Creitz and Smith[40], Richards and Nielson[41], and The American Petroleum Institute[42]. The calculated frequencies are listed in the adjacent column with matching between observed and calculated frequencies indicated. A comparison of observed and calculated spectra is also made in Fig. 2. As is apparent from the table and figure, there seems to be fairly good matching of the general distribution of the calculated lines with the observed.

So long as interaction between the end groups of atoms in the chain is not taken into consideration, as was

39. Rasmussen, Tunnicliff, and Brattain, Loc. Cit.
40. Creitz, E. C. and Smith, F. A., J. Res. Nat. Bu. Stand. 43, 365 (1949)
41. Richards, Charles M., and Nielsen, J. Rud, J. Op. Soc. Am. 40, 438 (1950)
42. Am. Petroleum Inst. Res. Proj. 44 at N.B.S. Cat. of Infrared Spectrograms.

the case in the present work, the calculated frequencies will be the same for either the cis-or trans-form of the molecule. The only difference will be in the selection rules applying. Thus the C_{2h} point group was assumed as applying to the molecule since the selection rules with this assumption permitted better agreement between the more intense observed lines and calculated lines. The matching required between the calculated accidental degeneracies and observed lines indicates that the resonance has caused a rather large shift in the position of these observed lines.

TABLE III

Comparison of Calculated and Observed Frequencies, in Wave Numbers

Observed I.R.	Ra.	Calculated
	320 v.w.(?)	
	513 S. (P)	434 Ra
520		
	686 v.w.(?)	
909 v.v.S.		894 I.R.
	910 m(D)	
1014 v.s.		
	1205 vS(P)	1180 Ra
1282 m.	1279 vS(P)	1230 I.R.
	1302 S.(P)	1320 Ra
1374 S.		
1391 S.		1400 Ra
	1442 v.S.(P)	1640 Ra
1479 w.		
1497 w.		
1597 v.v.S.		
1608 v.v.S.		
	1643 v.v.S.(P)	1640 Ra
1759 w.		1730 I.R.
	1780 w(P)	
1812 m.		
1821 m.		
1969 w.		
	2092 v.w.(?)	2062 Ra
2495 w.		2430 I.R.
	2842 v.w.(?)	2846 Ra

TABLE III (Continued)

Observed		Calculated
	2879 vn.w(?)	
2981 w.		2960 I.R.
	3014 v.S.(P)	2990 Ra
3015 v.S.		3020 I.R.
3095 v.S.		
	3101 m(P)	2990 Ra
4938 w		4930 I.R.

The form of the normal vibrations can be determined[43] by substituting the corresponding value of λ in the secular equation and solving for the ratios of the coordinates which are equal to the ratios of the minors of any one row of the determinant. These ratios always remain equal during the oscillation of the particles for any one normal vibration. For λ_1, in species B_1, the ratios of the coordinates

$$y_1 : y_2 : y_\alpha : y_\beta : z_1 : z_2 : z_\alpha : z_\beta$$

were calculated to be in the ratios

.171063: -.020901: -.155850: .950302: -.812493

: 1.039836: -.031805: -.108816

43. Herzberg, Op. Cit., p. 69

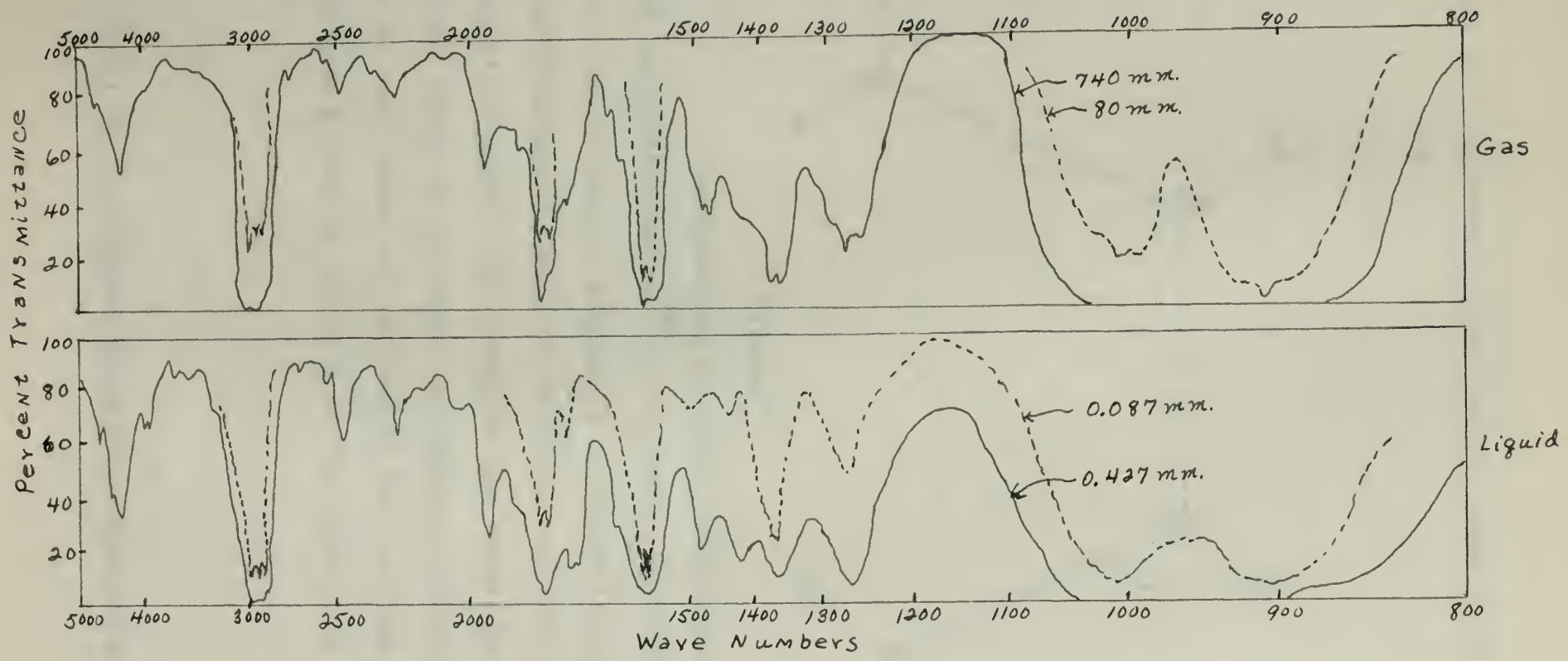
5000
4000
3000
2500
2000
1500
1400
1300
1200
1100
1000
900
800
100
80
60
40
20
Percent Transmittance
740 mm.
80 mm.
Gas
0.087 mm.
0.427 mm.
Liquid
Wave Numbers

Figure 2.

The form of this normal vibration is shown in Fig. 3.

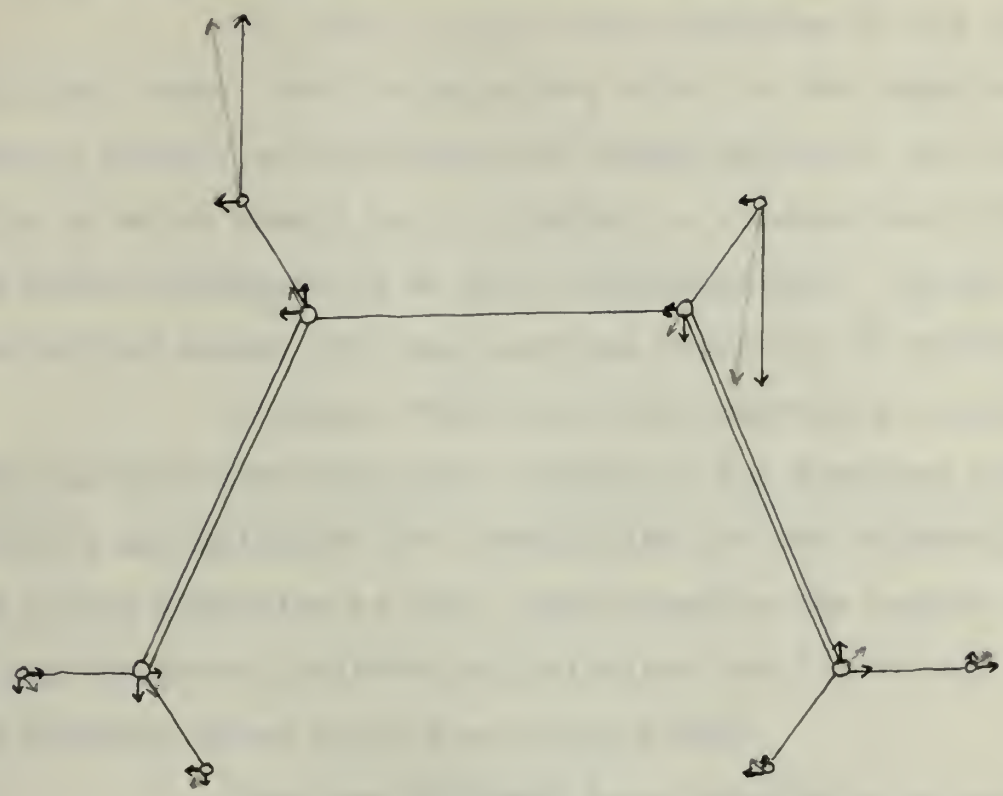

Figure 3.

The solution of these determinants was accomplished by Crout's method[44] for solving determinants. This method is also readily adaptable to computing machines and has the advantage as well of having a continual check on the numerical work. The forms of the remaining normal coordinates could be obtained, if desired, by determining the ratios of the minors of any row of both of the determinants for species A_1 and B_1 for all of the remaining values of λ.

44. Crout, P. D., Transactions Am. Inst. Elec. Eng. LX (1941)

5. An Approximate Calculation

In order to avoid the expansion of the eighth and ninth order secular equations prior to the adoption of Bryan's method, an approximation scheme was used, the results of which should be of interest in a comparison with the results obtained by an exact determination. The approximation scheme that was used was suggested by Herzberg[45].

Consider first the force constants associated with the bond stretching and bending of the hydrogen atoms infinite and calculate the frequencies for the carbon-hydrogen groups vibrating as one. Then consider the masses of the carbon atoms infinite and calculate the vibrations of the hydrogen atoms about the carbon atoms.

When the hydrogen force constants are considered infinite, the only symmetry coordinates that remain in the potential energy expression are Δr_{12}, Δr_{23}, Δr_{34}, $\Delta\theta_1$, and $\Delta\theta_2$. The only cartesian coordinates that need be considered then are z_1, z_2, z_3, z_4, y_1, y_2, y_3 and y_4. For species A_1 these are related by the symmetry treatment as follows:

$$z_4 = z_1,\ z_3 = z_2 = -\frac{M+2m}{M+m} z_1,\ y_4 = -y_1,\ y_3 = -y_2. \quad (1)$$

This then requires the solution of only a third order determinant.

Under these conditions the terms in the potential energy expression are

45. Herzberg, Op. Cit., p. 195

$$|\Delta r_{12}|^2 = \sqrt{\left\{ (y_2-y_1+a)^2+(-\mu z_1+b)^2 \right.} - \left. |r_{12}^o| \right\}^2 \qquad (2)$$

$$|\Delta r_{23}|^2 = \left\{ -2\ y_2+C - |r_{23}^o| \right\}^2 \qquad (3)$$

$$|\Delta r_{34}|^2 = \left\{ \sqrt{(-y_1+y_2+a)^2+(\mu z_1-b)^2} - |r_{34}^o| \right\}^2 \qquad (4)$$

$$|\Delta\theta_1|^2 = \frac{1}{\sin^2\theta_1^o} \left\{ -\left[\frac{(y_2-y_1+a)(-2y_2+c)}{\sqrt{[(y_2-y_1+a)^2+(-\mu z_1+b)^2][(-2y_2+c)^2]}} \right] - \cos\theta_1^o \right\}^2 \qquad (5)$$

$$|\Delta\theta_2|^2 = \frac{1}{\sin^2\theta_2^o} \left\{ -\left[\frac{(-2y_2+c)(-y_1+y_2+a)}{\sqrt{[(-2y_2+c)^2][(-y_1+y_2+a)^2+(\mu z_1-b)^2]}} \right] - \cos\theta_2^o \right\}^2 \qquad (6)$$

where

$$\mu = 1 - \frac{M - 2M}{M - M}$$

The expansion of the secular equation gives a third order equation in λ which is then solved by Horner's method to give the three roots. The three roots for this equation give three normal frequencies of vibration which, expressed in wave numbers, are

$$\frac{1}{\lambda_1} = 289\text{cm}^{-1}, \quad \frac{1}{\lambda_2} = 1140\text{cm}^{-1}, \quad \frac{1}{\lambda_3} = 1450\text{cm}^{-1}. \qquad (7)$$

Now to obtain the frequencies associated with the hydrogen motion the carbon masses are considered infinite which means that all corrdinates associated with motion of the carbon atoms disappear.

The only remaining coordinates from the symmetry conditions are then

$$z_\eta = z_\alpha,\ z_\sigma = z_\beta,\ y_\eta = -y_\alpha,\ y_\sigma = -y_\beta.$$

$$y_\delta = -y_\gamma, \; z_\delta = z_\gamma = -(z_\alpha + z_\beta). \tag{8}$$

This leaves five coordinates and requires the solution of a fifth order secular equation. The five roots of the secular equation again give five normal frequencies of vibration which are

$$\frac{1}{\lambda_1} = 882\text{cm}^{-1}, \; \frac{1}{\lambda_2} = 1350\text{cm}^{-1}, \; \frac{1}{\lambda_3} = 2840\text{cm}^{-1}$$

$$\frac{1}{\lambda_4} = 2920\text{cm}^{-1}, \; \frac{1}{\lambda_5} = 3630\text{cm}^{-1}. \tag{9}$$

For species B_1 when the hydrogen bond constants are considered infinite, the coordinates remaining from the symmetry treatment are:

$$y_2 = -\eta y_1 \text{ and } z_2 = Ry_1 - Hz_1$$

where

$$\eta = \frac{M+2m}{M+m}, \; R = \frac{\lambda + \rho + \mu - \eta}{1+x}, \; H = \frac{\xi + \zeta + \nu}{1+x}$$

and

$$\lambda = \frac{2(b+h)}{M+m}, \; \rho = \frac{2(b+e+h)}{2g+c}, \; \xi = \frac{2a+2f+c}{2g+c}, \; \zeta = \frac{2a-2d+c}{2g+c},$$

$$x = \frac{Mc}{m(2g+c)}, \; \mu = \frac{2M(b+h)}{m(2g+c)}, \; \nu = \frac{M(2a+c)}{m(2g+c)}. \tag{10}$$

The process of solving for the roots is the same as that outlined for species A_1. In this case the solution of a second order secular equation is required which gives the frequencies

$$\frac{1}{\lambda_1} = 1600\text{cm}^{-1} \quad \text{and} \quad \frac{1}{\lambda_2} = 678\text{cm}^{-1}. \tag{11}$$

In species B_1 when considering the frequencies due to the motion of the hydrogen atoms the same terms disappear in the potential function and the kinetic energy function as for A_1 but the relations between the remaining

cartesian coordinates are as follows:

$$z_\eta = -z_\alpha,\ z_\sigma = -z_\beta,\ y_\eta = y_\alpha,\ y_\sigma = y_\beta,$$
$$y_\delta = y_\gamma = -(y_\alpha + y_\beta) \text{ and } -z_\delta = z_\gamma = \lambda y_\beta + \rho y_\alpha - \xi z_\beta - \zeta z_\alpha. \quad (12)$$

This then requires the solution of a fourth order secular equation which gives the frequencies

$$\frac{1}{\lambda_1} = 1620\text{cm}^{-1},\ \frac{1}{\lambda_2} = 2050\text{cm}^{-1},\ \frac{1}{\lambda_3} = 2770\text{cm}^{-1},\ \frac{1}{\lambda_4} = 2830\text{cm}^{-1}. \quad (13)$$

First of all, it is noticed in Table IV that in the process of making the approximation three roots disappear. The remaining roots, while having a similar overall pattern to those determined by the exact solution, differ from them by about 200 wave numbers in the case of the carbon oscillations and by a greater amount in the case of the hydrogen oscillations. The wave numbers in the approximation method are smaller in general than in the exact determination as would be expected from the general theory of oscillations.

TABLE IV.
Comparison of Frequencies, in Wave Numbers From Approximate and Exact Calculations

A_{1*}	A_{1c}	A_{1h}	B_{1*}	B_{1c}	B_{1h}
434	289	...	894	678	...
1180	...	882	1230	...	...
1320	1140	...	1400	...	...
1640	1450	...	1730	1600	...
1640	...	1350	2430	...	1620
2060	...	...	2960	...	2050
2860	...	2840	3020	...	2770
2990	...	2920	4930	...	2830
2990	...	3630			

(* indicates exact calculations, the subscript c indicates carbon vibrations, and h indicates hydrogen vibrations)

6. Calculation of Heat Capacity

From a knowledge of the fundamental frequencies of a molecule it is possible to calculate its thermodynamic quantities. It is generally best to calculate the partition function first since all of the other thermodynamic quantities can be determined from it. The partition function is given by[46]

$$Q = \sum g_n e^{-\frac{\epsilon_n}{kT}} \tag{1}$$

where ϵ_n is the total energy of the atoms or molecules in a given equilibrium distribution, k is Boltzmann's constant, T is the absolute temperature and g_n is the statistical weight or degeneracy. This can be separated into a translational part and an internal part. The internal partition function, which is the part of interest here, is given by

$$Q_{int} = \sum g_{int} e^{-\frac{\epsilon_{int}}{kT}} \tag{2}$$

This part, again, is composed of contributions from electronic, vibrational and rotational energy, but in most cases the electronic contribution is negligible. Thus, there are only two parts remaining, the vibrational and rotational energy contributions. The partition function can then be written

$$Q_{int} = \sum_v \left(g_v e^{-G_0(v_1, v_2, \cdots)\frac{hc}{kT}} \sum g_r e^{-F_v(J, \cdots)\frac{hc}{kT}} \right) \tag{3}$$

where

$$\epsilon_{int} = [G_0(v_1, v_2, \cdots) + F_v(J, \ldots)]hc$$

46. Herzberg, Op. Cit., p. 501 ff.

and F (J) is the rotational term value, J is the rotational quantum number, G_o is the vibrational term value, and v_i are the vibrational quantum numbers. If the interaction between vibration and rotation is neglected, this can be written as the product of the vibrational and rotational partition functions, and each part can be separately evaluated. Then

$$Q_v = \sum_v g_v e^{-G_o(v_1, v_2, \cdots)\frac{hc}{kT}}, \quad Q_r = \sum_r g_r e^{-F_v(J, \ldots)\frac{hc}{kT}} \tag{4}$$

Now, in the usual harmonic oscillator approximation we have

$$G_o(v_1, v_2, \ldots) = \sum \omega_i v_i \tag{5}$$

where ω_i are the frequencies in cm^{-1} for infinitesimal amplitudes. Then

$$Q_v = \left(\sum_{v_1} e^{-\omega_1 v_1 \frac{hc}{kT}}\right)\left(\sum_{v_2} e^{-\omega_2 v_2 \frac{hc}{kT}}\right)\cdots \tag{6}$$

which can be written

$$Q_v = \left(1 - e^{-\omega_1 \frac{hc}{kT}}\right)^{-1}\left(1 - e^{-\omega_2 \frac{hc}{kT}}\right)^{-1}\cdots \tag{7}$$

by making use of the relation

$$\sum_{v_i} e^{-\omega_i v_i \frac{hc}{kT}} = \frac{1}{1 - e^{-\omega_i \frac{hc}{kT}}}.$$

If degeneracy exists and d_1, d_2, d_3,... represent the degrees of degeneracy of ω_1, ω_2, ω_3,..., the partition function can be written

$$Q_v = \left(1 - e^{-\omega_1 \frac{hc}{kT}}\right)^{-d_1}\left(1 - e^{-\omega_2 \frac{hc}{kT}}\right)^{-d_2}\cdots \tag{8}$$

In actual calculations the wave numbers ν_i are used instead of the ω_i.

For the rotational partition function the expression varies depending upon whether the molecule is linear, symmetric top or asymmetric top. For a linear molecule[47]

47. Herzberg, Op. Cit., p 505.

$$Q_r = \frac{kT}{hcB} + \frac{1}{3} + \frac{1}{15}\frac{hcB}{kT} + \frac{4}{315}\left(\frac{hcB}{kT}\right)^2 + \frac{1}{315}\left(\frac{hcB}{kT}\right)^3 + \cdots, \quad (9)$$

for a rigid symmetric top molecule

$$Q_r = e^{\frac{Bhc}{4kT}}\sqrt{\frac{\pi}{B^2A}\left(\frac{kT}{hc}\right)^3}\left[1 + \frac{1}{12}\left(1-\frac{B}{A}\right)\frac{Bhc}{kT} + \frac{7}{480}\left(1-\frac{B}{A}\right)^2\left(\frac{Bhc}{kT}\right)^2 + \cdots\right] \quad (10)$$

and for asymmetric top molecules

$$Q_r = e^{\sqrt{BC}\frac{hc}{4kT}}\sqrt{\frac{\pi}{ABC}\left(\frac{kT}{hc}\right)}\left[1 + \frac{1}{12}\left(1-\frac{\sqrt{BC}}{A}\right)\frac{\sqrt{BC}\,hc}{kT} + \cdots\right] \quad (11)$$

where A, B and C are the rotational constants.

Other thermodynamic quantities can then be calculated in terms of the partition function. For example, the specific heat at constant pressure is given by

$$C^\circ_{p,int} = R\frac{d}{dT}\left[T^2\frac{d(\ln Q_{int})}{dT}\right] . \quad (12)$$

Again, if the interaction of rotation and vibration is neglected, then

$$C^\circ_{p,r} = R\frac{d}{dT}\left[T^2\frac{d(\ln Q_r)}{dT}\right] \quad (13)$$

and

$$C^\circ_{p,v} = R\frac{d}{dT}\left[T^2\frac{d(\ln Q_v)}{dT}\right] . \quad (14)$$

For almost all gases the rotational contribution is practically equivalent to the classical values for ordinary temperatures. By substituting the value for Q_v in the above equation the value for the specific heat is

$$C^\circ_{p,v} = R\left(\frac{hc}{kT}\right)^2\sum_i \frac{d_i\omega_i^2 e^{-\frac{\omega_i hc}{kT}}}{\left(1-e^{-\frac{\omega_i hc}{kT}}\right)^2} . \quad (15)$$

The calculations for the value of the vibrational contributions to the heat capacity are simplified by the

use of a table published by Wilson[48] where the vibrational contributions to the heat capacity are given as a function of $\frac{\omega}{T}$. The calculated value for Butadiene determined for a temperature of 25°C with the aid of this table is

$$7.26 \ ^{cal}/mol \ deg.$$

By adding this to the translational and rotational contributions as given by Wilson the heat capacity turns out to be

$$15.21 \ ^{cal}/mol \ deg.$$

The best experimental value available obtained by comparison of the results published by Astor, Moessan, Gustave, Hardy, and Szasz[49] and Scott and Mellors[50] is

$$19.16 \ ^{cal}/mol \ deg.$$

The difference between the observed value and the calculated value is due to internal rotation and could aid in establishing the height of the potential barrier in the molecule.

7. Evaluation of Results

The results obtained in this calculation indicate again the fact that it is possible to transfer force constants from parts of one molecule to another where similar structure exists. The fairly reasonable check of the pattern of the observed spectra with the calculated lines demonstrates that the force constants as chosen in the potential function probably agree favorably with the correct

48. Wilson, E. B. Jr., Chem. Rev. 27, 17 (1940)
49. Astor, John G. Moessan, Gustave W., Hardy, Howard C., and Szasz, George J., J. Chem. Phys. 12, 458 (1944)
50. Scott, Russell B. and Mellors, Jane W., J. Res. Nat. Bu. Stand. 34, 243 (1945)

values. The characteristic frequencies of various groups within molecules and of the motion within these groups as given by Herzberg[51] check fairly well with calculated frequencies which serves as an aid in identifying certain motions in the molecule. Exact agreement between observed and calculated lines is, of course, not possible because the valence force model is an approximation, and there may also be complications due to impurities in the experimental samples and because of the prescence of combination and overtone bands.

Probably of greater significance in this work is the method used for expanding the secular equation. This part of the problem has always been the most tedious and laborious of all the work involved. By the use of this method, not only is it uneccessary to make use of approximations, but the exact expansion can in general be accomplished in less time and with less effort than previous approximation schemes required. Furthermore, a continuous check is provided on the numerical work thereby reducing the chance of error. Since the method is also readily adaptable to I.B.M. calculation, an additional saving in time and labor can be accomplished without the use of iteration or approximation schemes with their attendent loss or shift of frequencies.

51. Herzberg, Op. Cit., p. 195

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A B S T R A C T

The study of infra-red and Raman spectra and their relationship to the vibrations and rotations of atoms in molecules has become more and more a matter of interest to the physicist and chemist within the past several decades. The study of the vibrations of the atoms which give rise to the broad band spectra in the near infra-red has led to a more thorough understanding of the forces in the molecules including a theoretical explanation of valence. The study of the rotation of groups of atoms within a molecule as well as the rotation of molecules as a whole which give rise to the band spectra in the far infra-red and to fine structure in the near infra-red has led to a rather accurate means for determining the structure of molecules.

This paper deals with the theoretical determination of the vibrational frequencies of 1, 3- butadiene. As is well known, the frequencies obtained from a quantum mechanical treatment of the problem are the same as those resulting from a classical determination; consequently, though the quantum mechanical methods are outlined, the actual calculations are carried out by the classical method of treating small oscillations. The normal frequencies of vibration determined for an oscillating system having particles of masses equal to those of the masses of the atoms with force constants of magnitude equal to the forces actually existing in a molecule will be the same as the infra-red and Raman frequencies

emitted or absorbed by the molecule.

In general the force constants are unknown so that the problem essentially has to be worked backward by carrying it out algebraically and then, by making use of observed spectra, determining the force constants. For a large molecule, such as butadiene, this is not easy nor even feasible. Consequently, force constants determined by others for smaller molecules where the structure of part of the molecule is similar to a part of butadiene are used for a determination of the normal frequencies. The force constants in this work were transferred from the work on propylene by Wilson and Wells[1] and from a paper on force constants in organic molecules by Crawford and Brinkley[2].

The cis-form was selected as the normal configuration for butadiene. The force field chosen was the valence type field. This means that the changes in bond length and changes in the bond angles from the equilibrium configuration were chosen as the coordinates for the potential function. The application of group theory to the symmetry in the molecule factored the secular equation obtained from the coefficients of the variables in the kinetic and potential energy expressions from a determinant of order twenty four to four determinants of order nine, eight, four and three. Since the

1. Wilson, E.B. Jr., and Wells, A.J., J. Chem. Phy. 9, 314 (1941)
2. Crawford, B.L.Jr., and Brinkley, S.R. Jr., J. Chem. Phy. 9, 69 (1941

latter two contained only out-of-plane vibrations and would thus give zero frequencies with the type of force field chosen, only the two equations of order nine and eight had to be solved. These are, however, in determinantal form, and the process of expanding secular equations of this size is, in general, very laborious and tedious.

In order to reduce the amount of labor involved, an approximation scheme was attempted. As a first approximation, the carbon-hydrogen bond force constants, both stretching and bending, were considered infinite. This served then to increase the mass of the carbon atoms slightly while eliminating the hydrogen frequencies. Two secular equations of order three and two had to be expanded, which yielded an approximate value for the carbon skeletal vibrational frequencies. Secondly, the carbon masses were considered infinite and then the motions of the hydrogen atoms with respect to the carbon atoms were determined. This required the expansion of two secular equations of order five and four.

In the process of making these approximations, three frequencies disappeared, which should have or would have been determined by an exact expansion of the original secular equations. A method was then used for an exact expansion of the secular equations which was due to J. G. Bryan[3] and was developed for expanding matrix characteristic

3. Bryan, J.G., A Method for the Exact Determination of the Characteristic Equation and Latent Vectors of a Matrix with Applications to the Discriminant Function for More than Two Groups, Harvard Graduate School of Education Dissertation (1950)

equations and determining the latent vectors or characteristic vectors of a characteristic equation. The characteristic equation of a matrix is defined by

$$|A - \lambda I| = 0$$

where A is the original matrix and I is the unit matrix. While the secular equation is not, in general, in the form defined above, it can be put into this form by adding and subtracting rows and columns or multiples of rows and columns until the variable terms appear only on the diagonal and then dividing each column by the coefficient of the variable in that column. Since the secular equation will then be in the form as defined above, it is possible to make use of Bryan's method for an exact expansion of the characteristic equation. The method is described completely and the expansion of the eighth order secular equation is carried out in detail as an illustration of the method. The actual expansion of the secular equations by this process requires less time and effort, in general, than the approximation scheme. This method has an additional advantage in that a continual check is provided on the numerical work as the expansion proceeds. Furthermore, the method is readily adaptable to I.B.M. automatic punch card computors which can result in an additional saving in time and effort while at the same time carrying out an exact expansion rather than an approximation with its attendent loss or shift of frequencies.

After the equations were expanded, they were solved by

Horner's method yielding the seventeen required roots. These roots were proportional to the normal frequencies of vibration of the molecule and after solving for the frequencies in terms of wave numbers, they were compared with observed frequencies. The comparison showed a fairly good agreement between the observed and calculated frequencies. A comparison was also made between the frequencies obtained by the exact expansion and the approximation. This showed that the carbon vibrations in the approximation were all fairly uniformly displaced by about two hundred wave numbers toward lower frequencies as is to be expected from the general theory of small oscillations. The hydrogen frequencies were displaced by an even larger amount as also was to be expected but not in as regular a manner as the carbon oscillations.

The results of this paper again indicate that it is possible to transfer force constants from parts of one molecule to another where they exist in similar surroundings. The fairly good correlation between the observed and calculated frequencies indicates that the force constants as chosen are very nearly the correct values.

Probably of more significance in this paper is the application of Bryan's method to the exact expansion of the secular equation. This eliminates the necessity of introducing approximations, and the expansion can be carried out with less work and more of a check on the work than previously. This expansion as well as the solution of the expanded equation can be carried out on I.B.M. computors. Furthermore, the deter-

mination of the normal modes, which requires the solution of the ratios of the minors of any row of the secular equation with a given value for the frequency substituted, was performed by Crout's[4] method for the solution of determinants which is also readily adaptable to I.B.M. computors.

4. Crout, P.D., Trans. Am. Inst. Elec. Eng., LX (1941)

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