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The Use of Deuterium in the Analysis of Vibrational Spectra

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INTRODUCTION

THE discovery of the isotope of hydrogen of mass 2 and the attendant development of methods for separating isotopes have enabled the chemist to prepare chemical compounds containing isotopes substituted almost at will (499).* These isotopic compounds afford valuable as-

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* References to the bibliography at the end of the article are given in ( ).

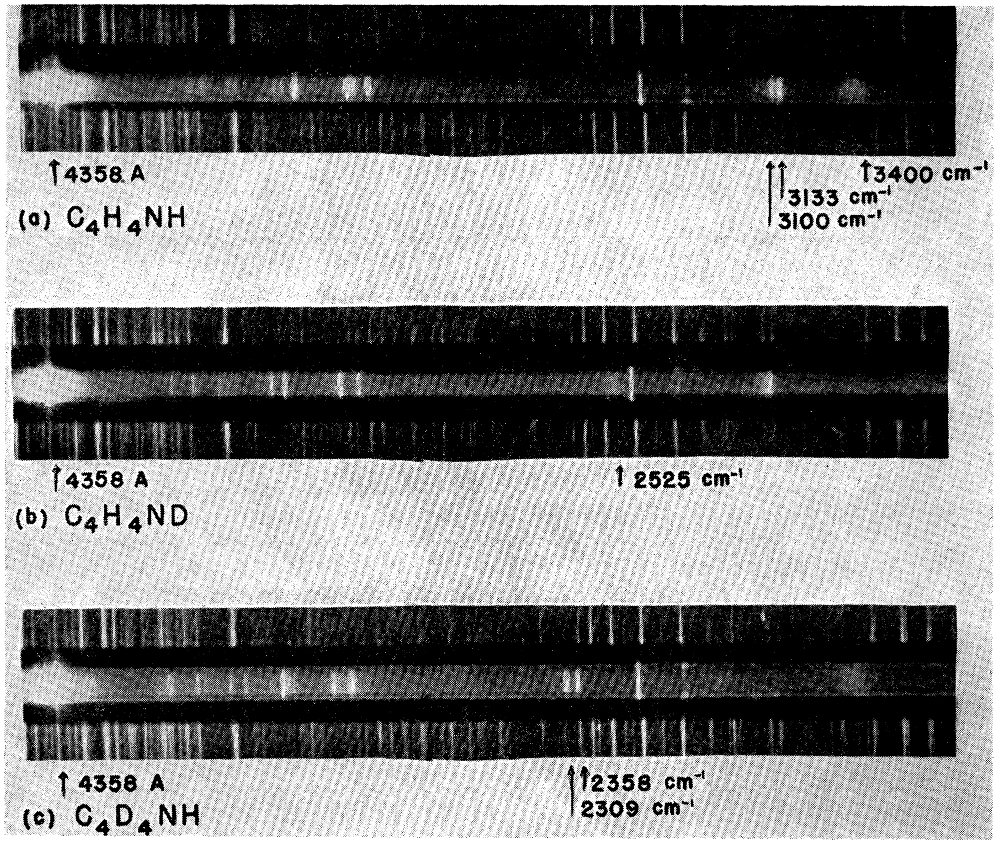

FIG. 1. Raman spectra of pyrrole (a) C_4H_4NH, (b) C_4H_4ND, (c) C_4D_4NH.

sistance in the analysis of molecular spectra of various kinds. Because the spectroscopic changes occasioned by isotopic substitution are associated only with a change in mass, the molecular properties dependent primarily on electronic structure are unaffected. This means that force constants, electronic energy levels, and similar properties are unchanged by isotopic substitution. On the other hand, vibration frequencies, moments of inertia, and those molecular properties dependent on mass may be quite considerably altered.

Deuterium is not only the most readily obtainable isotope, but also the most helpful from the standpoint of spectroscopic analysis of molecular structure. Not only is hydrogen present in nearly all compounds of carbon, but in addition, the fact that deuterium has twice the mass of hydrogen gives rise to especially pronounced effects of deuterium substitution on molecular spectra. These effects can be utilized in several ways in the analysis of the spectra of molecules containing hydrogen.

For example, deuterium substitution can be used to distinguish between those vibrations of a molecule which are "hydrogen" vibrations and those which are "heavy atom" vibrations. A molecule can be considered more or less as an assembly of interacting oscillators,* some of the various normal vibration frequencies being not far removed from those of the component oscillators. Some vibrations involve certain hydrogen atoms predominantly, whereas others are primarily determined by the heavy atoms. The former are known as "hydrogen" vibrations, and we expect a large change in frequency if one of the hydrogen atoms concerned is replaced by deuterium, (a shift to a frequency $\sim(2)^{-\frac{1}{2}}$ that

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* Reference 231, p. 194.

of the original). The latter, "heavy atom" vibrations, will be much less sensitive to the substitution. Thus one use of deuterium substitution is to indicate which frequencies belong to "hydrogen" vibrations and which to "heavy atom" vibrations. These shifts are illustrated by the Raman spectra of pyrrole* in Fig. 1. The band at 3400 cm^{-1} in (a), primarily an N – H stretching vibration, shifts to 2525 cm^{-1} in (b) when the H attached to the N is replaced by D. The lines at 3133 cm^{-1} and 3100 cm^{-1} in (a), primarily C – H stretching vibrations, shift to 2358 cm^{-1} and 2309 cm^{-1}, respectively, in (c), symmetrical pyrrole $-d_4$.

The symmetry of a molecule is very important in the determination of the normal modes of vibration and in the selection rules governing which vibrations are spectroscopically active. Isotopic substitution affords a means of changing the symmetry merely by changing the mass, without a change in the potential system. If the symmetry is such as to require certain vibrations to be degenerate, it will ordinarily be possible to lower the symmetry sufficiently by substitution to split the vibrations into non-degenerate forms.

When vibrations with the same symmetry properties have frequencies close together, interaction occurs and the frequencies are spread apart. The amount of spreading depends on the coupling and on the initial proximity of the frequencies. Overtones sometimes interact with fundamentals in this manner, the overtone gaining some of the properties of the fundamental. In particular, the overtone may show a considerable gain in intensity at the expense of the fundamental. Since isotopic substitution does not affect all vibrations by the same amount, the isotope effect can often be used to decide whether such interaction is taking place.

It may occasionally happen that two vibrations have the same frequency but are of different symmetry types and so cannot interact. Only a single frequency is observed, and the vibrations are called accidentally degenerate. Isotopic substitution, however, may affect the two vibrations by different amounts so that two frequencies can be observed, or so perturb the symmetry that the two vibrations can interact and spread apart in frequency.

Fundamentally the information obtained from a study of an isotopic molecule is a set of frequencies for a system differing from the original only in a change of mass for one or more atoms. The structures, dimensions, and potential systems of the two molecules are essentially the same. The new data can thus be used in evaluating potential constants, checking calculated frequencies, and in determining rotational constants. Unfortunately, it is only for a few polyatomic molecules that rotational structure can be resolved and interpreted, but when possible for both the original and the isotopic molecules, the latter furnishes additional data for evaluation of dimensions appearing in the constants.*

As we have remarked, isotopic substitutions do not change the electronic structure, and therefore the actual electronic energy levels, apart from the vibrational complications, are the same for the isotopic molecules (422). The vibrational effect, however, may alter the electronic spectrum considerably. In particular, since the frequencies in an excited electronic state are usually less than those in the ground state, substitution of a heavier isotope will cause the 0 – 0 band of an electronic system (band due to transition from the ground vibrational and electronic states to the ground vibrational level of the excited electronic state) to shift toward the violet. The vibrational frequencies of the ground state usually decrease more with isotopic substitution than those in the excited state, with a corresponding increase in energy between the two zero vibrational levels. The changes in symmetry occasioned by isotopic substitution also may alter the electronic and vibrational selection rules. The isotope effect in electronic spectra, although a very valuable practical help in analyzing the spectra, is essentially the effect on molecular vibrations. Inasmuch as an analysis of a molecule's vibrational spectrum is usually a necessary preliminary to the analysis of its electronic spectrum, we have in this paper paid chief attention to vibrational rather than electronic spectra. This does not

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* These pictures are reproduced through the courtesy of Dr. Foil A. Miller. See reference 295.

* There is, of course, a slight difference in the effective internuclear distances for the two molecules because of anharmonicity, which may be neglected in most cases for accuracy to ±0.01A.

mean that isotopic molecules are not useful in the analysis of electronic spectra. It means rather that up to the present time very few electronic spectra of polyatomic molecules have been studied with the help of deuterium derivatives.*

The first part of the present paper is a discussion of the general effect of deuterium substitution on vibrational frequencies. Theorems are stated without proof, but with literature references where the proofs may be found. Familiarity with molecular symmetries and with normal coordinate treatments of molecules is assumed. (An excellent discussion of these topics is given in Herzberg's book (231).) A section on the small isotope effect is included since certain vibrations of a deuterium substituted molecule can be treated by those methods.

In the second part of the paper, those molecules whose deuterium derivatives have been studied spectroscopically in some detail are discussed as illustrations of the material in the first part. Certain typical examples are considered in more detail than others. The tables and references are believed to be a complete list of all the deuterated molecules whose spectra have been reported to June 1946.

PART I. THEORETICAL CONSIDERATIONS

1. Introduction

For computational purposes, a molecule composed of N atoms can be represented by a system of N mass points held in equilibrium positions relative to each other by some force field. The complexity of the calculation of vibrational frequencies of such a system is determined by the nature of the force field, by the number and kinds of mass points, and by the geometric arrangement of their equilibrium positions. The force field in turn is determined by the electronic structure of the molecule, and the mass points by the atomic nuclei.

Since the exact analytical expression for the force field in which the nuclei oscillate is unknown, an approximation is introduced. A simple harmonic force is assumed for small amplitudes of oscillation, justified for computational purposes by general agreement between calculated and observed frequencies. Any assumed force field must satisfy the condition that the vibrational potential energy function derived from it be invariant upon application of the symmetry operations associated with the molecule.

Solution of the problem of obtaining vibrational frequencies is greatly facilitated for molecules which possess some symmetry by the introduction of symmetry coordinates (231, 246, 390, 398, 475). They are any coordinates which satisfy the symmetry requirements for normal coordinates, and are usually much simpler. There are different kinds, depending on whether they are functions of the masses and whether they indicate motions which conserve angular and linear momenta (476). By virtue of their symmetry properties, a given set of such coordinates can be classified according to the various symmetry types associated with the molecular point group. Consequently, when the kinetic and potential energies of the system are expressed in terms of symmetry coordinates, no cross products can appear involving coordinates belonging to different symmetry types (398). Thus the vibrational motions of a given symmetry type can be treated independently of those of the other types, with the corresponding reduction in degree of the equations encountered. If the transformation to symmetry coordinates is made linear, orthogonal, and independent of nuclear masses, the kinetic and potential energies for motions of type a become

$$T_a = \tfrac{1}{2} \textstyle\sum_i m_i \dot{S}_i^{(a)^2}, \quad V_a = \tfrac{1}{2} \sum_{i,j} K_{ij} S_i^{(a)} S_j^{(a)}, \quad (1.1)$$

where the summation is over the degrees of freedom of type a, m_i is the mass associated with symmetry coordinate S_i, and K_{ij} is the force constant associated with the interaction of coordinates S_i and S_j (371).

The frequencies calculated on the basis of Eq. (1.1) for a harmonic potential function, although usually in good agreement with observed frequencies, are rigorously true only for infinitesimal amplitudes of vibration. These frequencies, called the zero-order frequencies if the force constants are for the vibrationless state, are designated by the symbol ω. However, since real molecules vibrate with a finite amplitude even in the

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* For some compounds which have been studied, see reference 422, pages 114 and 115.

lowest vibrational state, the effect of anharmonicity enters in all observed frequencies. The observed frequencies are designated by the symbol ν and are the ones usually given for a polyatomic molecule, since the ω's have been determined in only a few cases. For purposes of calculation, deviations from harmonicity are introduced as perturbations in the potential energy function (146). The zero-order function is just the harmonic one expressed in terms of the normal coordinates, and the perturbing terms are cross products of third degree and higher, each one invariant with respect to the symmetry operations of the molecular point group. Then the general expression for the vibrational energy levels of a polyatomic molecule is of the form (146, 231, 496)

$$E_{\mathrm{vib}}=\sum_i hc\omega_i(v_i+d_i/2) + \sum_{i,k} X_{ik}(v_i+d_i/2)(v_k+d_k/2)+\cdots \quad (1.2)$$

where sums over i and k are sums over all the vibrational degrees of freedom. d_i is the degree of degeneracy of the ith normal vibration, and v_i is the ith quantum number for the level. The terms X_{ik} are anharmonic constants which are usually negative and small but may be positive (146). The observed frequencies (ν's) are the energy differences between any two anharmonic levels given by Eq. (1.2), divided by hc.

2. Order Rule (Limitations on Frequency Shifts)

The substitution of an isotope (or isotopes) for one (or more) of the atoms of a molecule changes the mass (masses) of the nucleus (nuclei) concerned, but does not change the electronic structure of the molecule. Hence the potential energy function in Eq. (1.1) is the same for both the original and isotopic molecules to a high order of approximation (231). The only change in Eq. (1.1) on going from one molecule to the other is in the masses of the isotopic atoms appearing in the kinetic energy expression. Since the isotope under consideration is deuterium, let the term isotopic molecule designate the one which is obtained from the original by direct replacement of hydrogen atoms by one or more deuterium atoms. For example, if dideuteromethane were considered the original molecule, trideutero and tetradeuteromethane could be considered isotopic molecules.

Courant has shown (112, 113) that for a vibrating mechanical system with a harmonic potential function, the effect of increasing the mass of one or more parts of the system without altering the potential forces (in our case, substitution by a heavier isotope) is to leave unchanged or decrease the frequencies of the normal modes of vibration. Thus if the normal frequencies of the original molecule are designated by ω and are arranged according to increasing values, that is, $\omega_r \leqslant \omega_{r+1}$, and those of the isotopic molecule designated by ω' and arranged in a similar fashion, the following relationship is obtained

$$\omega_1' \leqslant \omega_1, \quad \omega_2' \leqslant \omega_2, \quad \cdots, \quad \omega_t' \leqslant \omega_t, \quad (2.1)$$

where t is the number of vibrational degrees of freedom. Furthermore, the shift is limited by the expression

$$\omega_r/\omega_r' \leqslant (m_{\mathrm{D}}/m_{\mathrm{H}})^{\frac{1}{2}} = 2^{\frac{1}{2}}. \quad (2.2)$$

Equations (2.1) and (2.2) make no statement as to the similarity of the normal vibrations whose frequencies are being compared, but if the symmetry is not altered by the substitution, it is logical to expect close similarity. Frequencies of degenerate vibrations are included once for each degree of degeneracy.

The order rule expressed by Eqs. (2.1) and (2.2) may be more or less restrictive depending on the symmetries of the molecules to be compared. If the replacement of hydrogen atoms by deuterium replaces all members of a hydrogen point set (equivalent positions in the molecule), the isotopic molecule has the same symmetry as the original (CH_4 and CD_4; C_4H_4NH and C_4D_4NH; C_4H_4NH and C_4H_4ND) or is more symmetric (CD_3H and CD_4; HDO and D_2O). When the symmetry is the same, the same geometrical symmetry coordinates apply to both molecules, and the order rule can be applied to each symmetry type separately. Thus t in Eq. (2.1) is the number of vibrational degrees of freedom in the symmetry type under consideration. This statement does not apply to an original and isotopic molecule belonging to the same point group if the isotopic one is obtained by incomplete substitution of a hydrogen point set. For example, CH_3D and CD_3H both belong to the point group C_{3v}, but the order rule does not apply to the individual symmetry types separately. It does apply, however, if the correct combinations of symmetry types are used. The only element of symmetry in CH_3D which is preserved on going to CHD_3 is one plane. Consequently Eqs. (2.1) and (2.2) apply to the symmetry types separately of point group C_s, and it is necessary to resolve the symmetry types of the two molecules of C_{3v} symmetry into those of the C_s point group.

In general the order rule applies to the separate symmetry types of a point group whose symmetry elements are those of the original molecule preserved by isotopic substitution. Thus it is necessary to note the symmetry elements common to both molecules and resolve the symmetry types of the two molecules into those of that point group. Such a resolution is simple for non-degenerate types, but may be complex for degenerate ones. Herzberg (231, page 236) gives an excellent discussion of the method together with some tables which facilitate the procedure.

The order rule as expressed by Eqs. (2.1) and (2.2) is rigorously true only for the "normal" frequencies, or the ω's. Since amplitudes of vibration are inversely proportional to the masses involved, and the usual effect of anharmonicity is to decrease frequencies with increasing amplitude, the idealized harmonic ratio (Eq. (2.2)) is generally larger than the anharmonic one. Consequently the order rule (Eqs. (2.1) and (2.2)) may be expected to be valid in most cases even if ν's are substituted for the ω's.

By analogy with diatomic molecules, and requiring the isotopic molecule to have essentially the same symmetry as the original molecule, the anharmonic constant X_{ik}' for an isotopic molecule might be expected to bear the relationship

$$X_{ik}'=\frac{\omega_i'\omega_k'}{\omega_i\omega_k}X_{ik} \tag{2.3}$$

to the X_{ik} of the original molecule in Eq. (1.2). Thus $|X_{ik}'|\leqslant|X_{ik}|$. The observed fundamental frequencies are caused by transitions between the ground level for which all the $v_i=0$, and an excited level for which only one $v_i\neq 0$ and it has the value unity. If all $X_{ik}=0$, i.e., the harmonic case, $\nu=\omega$. For the usual case, as mentioned before, $X_{ik}<0$, and one obtains $\nu<\omega$. There is the possibility, however, that the contribution from the second sum in (1.2) is positive in a certain singly excited state (or at least contributes a smaller negative quantity than in the ground state), and consequently the observed frequency for a transition between that excited state and the ground state will be greater than the normal frequency, that is $\nu>\omega$. A similar state of affairs will hold for the isotopic molecule, but because of (2.3), ν' and ω' will be closer together, that is $\nu-\omega>\nu'-\omega'$. Hence, even if (2.2) were satisfied, the ratio of ν to ν' might conceivably be greater than $(m_D/m_H)^{\frac{1}{2}}$. Such cases are rare, however, and may have an interesting geometrical significance (146).

A combination of Eqs. (1.2) and (2.1; 2.2) indicates that a vibrational energy level never increases upon substitution of a heavier isotope into a molecule. It is necessary, however, to consider the possibility of the ground vibrational level being lowered in energy more than the first excited level (one of the normal vibrations excited with one quantum of energy). In the harmonic case, the drop in the first excited level (considering only the contributions of the excited degree of freedom) is approximately three times that in the ground level. The usual effect of anharmonicity is to make the drop in the first excited level due to the concerned vibration slightly less than three times the drop in the ground level. But the possibility of anharmonicity making the change in the upper level less than one times the change in the ground level (thus making $\nu'>\nu$) seems remote. Certainly if the substituted atom of heavier mass takes any appreciable part in the normal vibration under consideration, it will not happen. On the other hand, if the mode of motion concerned is one which in the harmonic case is unaffected by the isotopic substitution, it is possible but not probable that some of the interaction terms in (1.2) with modes which are affected, may cause the excited level to drop less on substitution than the ground level. Such cases are rarely found in practice, and in any event the difference must be small.

Thus the order rule is satisfied in general by the ν's as well as the ω's. If exceptions exist, they have some unusual explanation characteristic of the particular molecule studied.

3. Product Rule (371, 475, 239, 157, 207)

The product rule, discovered independently by Teller (12) and by Redlich (371), furnishes an expression for the ratio, τ, of the product of a set of normal frequencies in one molecule to the product of the corresponding set of frequencies in a second molecule which is an isotopic derivative* of the first. The only assumptions necessary for the derivation of the rule are: (1) invariance of the potential constants with substitution of an isotopic atom, and (2) harmonic vibrations. The first one, if indeed it can be classed as an assumption, is valid within the limits of experimental error. The second assumption is valid for the normal frequencies of the molecule, but since in actual practice it is necessary to use the observed fundamentals, an error can be introduced by the substitution of the latter. It is possible, however, to give an empirical estimation of the magnitude of this error.

The general product rule formula for any molecule, if we assume substitution of only one kind of isotope, is

$$\Pi_j \omega_j/\omega_j' = [(m'/m)^n (M/M')^t (I_x/I_x')^{s_x} \times (I_y/I_y')^{s_y} (I_z/I_z')^{s_z}]^{\frac{1}{2}}. \quad (3.1)$$

Here primes refer to the isotopic molecule; ω's are the zero-order frequencies, and j runs over the normal vibrations of the symmetry type under consideration. m' over m is the ratio of the mass of the isotopic atom to the mass of the atom it replaced. M is the total mass of the molecule and t is the number of translations of the symmetry type considered. I_x, I_y, I_z are the moments of inertia about the x, y, and z axes through the center of mass; s_x, s_y, s_z are 1 or 0 depending on whether the rotation about the x, y, z axis is of the symmetry type being considered. n is the number of degrees of freedom contributed by the substituted point set to the symmetry type. The value of n can be determined readily by means of equations given by Herzberg (231, pp. 136–7). Frequencies of degenerate vibrations are entered only once on the left side of (3.1) with the corresponding values of n, t, and s on the right.

Equation (3.1) applies to each symmetry type of the point group whose elements are the symmetry elements common to the two molecules being compared. Thus if all members of one or more hydrogen point sets of the original molecule are replaced by deuterium, all symmetry elements are preserved and the product rule applies to each symmetry type of the original point group. For example, in comparing the $D_{\infty h}$ molecules acetylene and acetylene-d_2, Eq. (3.1) can be applied to each symmetry species Σ_g, Σ_u, Π_g, and Π_u. If only part of a hydrogen point set is replaced by deuterium, it is necessary to resolve the symmetry types of the two molecules into the symmetry types of the point group whose elements are the symmetry elements preserved by deuterium substitution (as was also the case for the order rule). For example, if only one hydrogen in acetylene is replaced by deuterium, the infinite fold axis is preserved but the center of symmetry is lost. The point group whose elements are those remaining after substitution is $C_{\infty v}$ (which incidentally is also the point group of the isotopic molecule, mono deutero acetylene) and so the product rule applies to the symmetry types Σ and Π of point group $C_{\infty v}$. The resolution of symmetry types of $D_{\infty h}$ into those of $C_{\infty v}$ shows that Σ_g and Σ_u go over into Σ, and Π_u and Π_g go over into Π. Therefore, in applying Eq. (3.1) to type Σ, j in the numerator on the left-hand side runs over the σ_g and σ_u vibrations of acetylene, and in the denominator runs over the σ vibrations of monodeuteroacetylene. An analogous statement holds for the application to type Π.

It is not necessary to limit the isotopic substitution to one kind of isotope. If two kinds of isotopes are considered, the product rule has the form

$$\Pi_j \omega_j/\omega_j' = [(m_1'/m_1)^{n_1} (m_2'/m_2)^{n_2} (M/M')^t \times (I_x/I_x')^{s_x} (I_y/I_y')^{s_y} (I_z/I_z')^{s_z}]^{\frac{1}{2}} \quad (3.2)$$

with the same interpretation for the symbols as in Eq. (3.1). This form of the product rule is often more useful than Eq. (3.1) if the original molecule contains some deuterium. As an illustration, consider CH_3D and CD_3H. Let the isotopic substitution designated by subscript 1

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* The previous restriction (page 91) on isotopic molecule is not necessary here.

be replacing the H_3 point set by deuterium, and the one designated by subscript 2 be replacing the D point set by H. Then $m_1'/m_1=2$, $m_2'/m_2=\frac{1}{2}$, and all symmetry elements are preserved by the substitution. Consequently Eq. (3.2) can be applied to each symmetry type of point group C_{3v}. Equation (3.2) is given by Eq. (3.1) if n is replaced by n_1-n_2.

The values of n, t, and s for a given symmetry type are readily determined from symmetry conditions alone, and therefore the value of the right-hand side of Eq. (3.1) or (3.2) can be calculated without any reference to frequencies. It is denoted by τ_c, and is exactly equal to the ratio of the zero order frequency products on the left side of the equation. In practice, however, the zero-order frequencies are rarely known, and it is the observed fundamentals which are available. From the discussion in connection with the order rule, we expect observed "hydrogen" frequencies to deviate more from their normal frequencies than "deuterium" frequencies do from theirs. In the ratio on the left-hand side of Eq. (3.1) or (3.2), original molecule frequencies are in the numerator, and so if we replace the ω's by the corresponding ν's, calling the ratio obtained τ_0 (observed), we expect $\tau_0<\tau_c$. Empirically, Redlich (374) has found τ_0 to be about 1.3 percent less than τ_c for each aliphatic "deuterium-stretching" frequency, and 1.1. percent less for each aromatic "deuterium-stretching" frequency. For the bending vibration he found no regular deviation—the correction sometimes was even negative. However, it was rarely over 2 percent. If the third-order coefficient of the potential energy for the bending normal coordinate vanishes because of symmetry, the anharmonicity factors are very small (375). Therefore, using observed fundamentals for getting τ_0, we find that τ_0 cannot deviate very much from τ_c.*

There are various ways in which we can put the product rule to use in deciding questions of molecular structure. For example, when complete spectroscopic data are available, τ_0's can be calculated on the basis of tentative frequency assignments for various possible structures. Comparison with the τ_c's can then show which possible structure gives the closest agreement. However, in practice the application is more often in the nature of a confirmation of a decision made on other grounds. Usually when the spectroscopic data are sufficiently extensive, other considerations (selection rules, for example) enable a clear-cut decision to be made regarding the proposed molecular structures.

It can also be used to check frequency values calculated on the basis of an assumed potential function. With the exception of a few molecules for which the data are very extensive, it is necessary to make all the assumptions underlying the product rule, and usually additional, much more doubtful, assumptions about the special nature of the molecular potential system in order to calculate the frequencies of isotopically related molecules. The product rule, however, must be obeyed by all such calculations irrespective of the special nature of the potential system. It thus serves as a numerical check on these calculations.

The assignment of observed frequencies in various isotopic molecules is usually made with the help of selection rules, polarization measurements, intensity considerations, etc. When an assignment has been completed, it may be checked by the product rule. Agreement with the product rule does not necessarily mean that the assignment is correct, but disagreement extending beyond the narrow limits allowed by anharmonicity and experimental error definitely shows that the assignment must be reconsidered.

Occasionally all the frequencies in a given symmetry type are observed for one isotopic molecule but not for another. If only one frequency is missing we can use the product rule to calculate it, making an empirical correction for anharmonicity. Such calculated values indicate where to look for the missing frequency, and often are sufficiently accurate for spectroscopic calculations of thermodynamic functions.

Since the molecular moments of inertia appear in the product rule, it would appear at first sight that it should be possible to use the expression for obtaining some of the molecular dimensions. However, the moments of inertia appear in the form of a ratio which is not far different from unity, and so a relatively large error in dimen-

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* In Monats. f. Chemie **72**, 268 (1939), Kohlrausch and Paulsen have ascribed a rather large error to the product rule. However, the τ_c which they apparently have used is incorrect, being about 4 percent larger than the true τ_c and thus accentuating the difference between τ_c and τ_0.

sions would have only a small effect on τ_c. It is for that reason we do not have to know the molecular dimensions with a high degree of accuracy in order to use the product rule. On the other hand, a small error in τ_c would make a large error in the dimensions calculated therefrom. Unfortunately τ_0 is too inaccurate to be used for such calculations, as we shall illustrate by an example later. If sufficient overtones and combination tones have been observed, it is possible to extrapolate to the normal frequencies (the ω's) by means of (1.2). By (3.1) we know that τ_c is precisely determined by the ω's, and so under favorable conditions it is possible to use the product rule in this manner (39). As an illustration, consider the water molecule. The normal vibration ω_3 (page 119) appears in type B_1 with a translation and a rotation, the rotation being around an axis perpendicular to the plane of the molecule. Applied to H_2O and D_2O, the product rule for type B_1 has the form

$$(\omega_3/\omega_3')^2=\tau_c^2 = (m_D/m_H)^2(M_{H_2O}/M_{D_2O})(I_z/I_z'). \quad (3.6)$$

Assuming constancy of equilibrium internuclear distances and bond angles in isotopic molecules, one can reduce (3.6) to the equation

$$\left(\frac{\omega_3}{\omega_3'}\right)^2=\tau_c^2=\frac{m_D}{m_H}\left(\frac{m_0+2m_H\sin^2\varphi}{m_0+2m_D\sin^2\varphi}\right) \quad (3.7)$$

where 2φ is the HOH angle. From observed data, Dennison (146) has calculated $\omega_3=3935.59$ cm^{-1} and $\omega_3'=2883.79$ cm^{-1}. Using these values for the normal frequencies, we calculate $2\varphi=105°$ from (3.7), which compares favorably with the infra-red value of 104°31′ given by Dennison. The observed fundamental frequencies are

$$\nu_3=3755.41 \text{ cm}^{-1} \quad \text{and} \quad \nu_3'=2784 \text{ cm}^{-1}.$$

Using these values to get τ_0^2 and equating to (3.7) we get $2\varphi=137°$. Thus it is apparent that quite careful corrections to the ν's are necessary in order to get information concerning the dimensions of the molecule.

It is only in a few cases that sufficient observed data are available for the evaluation of the anharmonic constants. A method for estimating these constants, which in certain instances possesses some degree of precision, has been described by Dennison (146). It involves expressing the relationship between the normal frequency and the fundamental in the following manner,

$$\omega_i=\nu_i(1+\alpha_i),$$

and assuming that the corresponding quantities for the isotopic molecule obey the equation

$$\omega_i'=\nu_i'(1+\alpha_i\omega_i'/\omega_i)\cong\nu_i'(1+\alpha_i\nu_i'/\nu_i).$$

(The anharmonic term X in (1.2) in the diatomic case contains a factor which will give this shift in α_i.) The product rule now furnishes a precise relationship between the normal frequencies, and it is possible to derive an expression connecting several α's from these equations. There will be other relationships depending on the molecule being studied which will permit an evaluation of the α's. The procedure is given in detail for ammonia by Dennison.

It has also been found useful in certain instances to use an approximate product rule (475). In practice it is found that each vibrational frequency is chiefly determined by the values of a few force constants and much less affected by others. If the frequencies are well separated from each other, the interaction constants are particularly small. In the calculation of frequencies from assumed potential functions, it has been found that the error in neglecting the non-diagonal elements in the secular determinant in the row and column associated with the "hydrogen-stretching" symmetry coordinate is usually not over 1 percent (116, 426). If there is more than one high frequency in the symmetry class, row and column are to be interpreted in the broad sense, such that we obtain one factor containing only high frequencies and another containing the low ones. The "high" frequencies should be over 2800 cm^{-1}, and experience has shown that if the "low" frequencies are less than 2000 cm^{-1}, the error introduced by the approximation is small. Doing this for both the original and isotopic molecules, we can get an approximate product rule from the two factors, one over the "high" frequencies and one over the "low" frequencies. τ_c also splits up into two factors, and we get

$$\begin{aligned}\Pi_j\frac{\omega_j}{\omega_j'}&=2^{n/2},\\ \Pi_k\frac{\omega_k}{\omega_k'}&=\left[2^l\left(\frac{M}{M'}\right)^t\Pi_i\left(\frac{I_i}{I_i'}\right)\right]^{\frac{1}{2}},\end{aligned}\tag{3.8}$$

where j runs over the "high" frequencies, k over the "low" frequencies, n is the number of deuterium-substituted "hydrogen-stretching" frequencies, and $n+l$ is the total number of degrees of freedom contributed by the substituted point sets to the symmetry type. (The expression given by Wilson (475) in place of Eq. (3.8) is more accurate, but is not always as readily obtained.)

4. Ratio Rule (341, 156, 157a)

A method for the calculation of vibrational frequencies of isotopic molecules from the vibrational frequencies of closely related molecules has been proposed by Noether (341) and termed the "ratio rule." This rule assumes that, for corresponding normal vibrations, the ratio of the vibrational frequency of the isotopic molecule to that of the original molecule is a constant for a series of closely related molecules. In a group of molecules such as the methyl halides, the ratio rule is of the form

$$\nu_n\mathrm{CD}_3Y/\nu_n\mathrm{CH}_3Y=\nu_n\mathrm{CD}_3X/\nu_n\mathrm{CH}_3X,\tag{4.1}$$

where ν_n refers to frequencies of corresponding vibrations, and where X and Y are any of the halides. If three of the quantities in Eq. (4.1) are known, the fourth may be calculated.

Edgell (157a) has discussed the ratio rule from the point of view of small perturbations of the kinetic energy of the original molecule on going to the isotopic molecule. He found the ratio rule satisfied if, in the two pairs of molecules discussed, there were like perturbations of the kinetic energy, and the original molecules had essentially the same normal coordinates. In view of that, he proposes using certain terms in the kinetic energy expression for obtaining the ratio; this, however, involves picking symmetry coordinates which are almost normal coordinates. The agreement, as might be expected, between calculated and observed frequencies is best when the pairs of molecules are very closely related.

5. Small Isotope Effect

Although deuterium has twice the mass of hydrogen, the substitution of deuterium for hydrogen has an effect on certain normal vibrations resembling that due to substitution of one isotope by another, differing only a few percent in mass. If in a given normal vibration certain groups of atoms move essentially as a unit, the replacement of a hydrogen atom by deuterium may make only a small percentage change in the mass of a group, with a correspondingly small isotope effect. In such a case it is possible to calculate the frequency shift for the normal vibration by using expressions derived for a small percentage mass change.

An excellent discussion of the small isotope effect, together with certain sum rules and their applications, is given by Teller in reference 437. We shall give only the results obtained by Teller, and others, in discussing the effect of small mass changes on normal vibrations and normal frequencies. Here also as with the previous discussions, if the isotopic substitution does not preserve all the symmetry elements of the original molecule, the comparison of vibrational frequencies of isotopic molecules must be made according to the symmetry types of the point group composed of the common elements.

The alterations introduced in the vibrational motions of a molecular system by substitution of an isotope can be calculated, where the change in atomic mass is small, by treating the change in mass as a perturbation of the kinetic energy. Wilson has given the expression (cited in reference 119)

$$|\lambda_k{}^0\delta_{kr}-\lambda[\delta_{kr}+\textstyle\sum_i\Delta m_i\mathbf{l}_{ik}\cdot\mathbf{l}_{ir}]|=0\tag{5.1}$$

for the frequencies, where k and r refer to normal vibrations of approximately the same frequency and of the same symmetry type. $\mathbf{l}_{ik}$ is the vector displacement of atom i in the kth normal vibration; Δm is the difference in mass between the original atom and the isotope which replaced it; and the summation with respect to i is over the substituted atoms. λ is related to the frequency by the formula $\lambda=4\pi^2\omega^2$; the superscript zero refers to the original molecule; and the λ without a superscript to the isotopic molecule. δ_{kr} is one for $k=r$, and zero for $k\neq r$. It is assumed that normalized coordinates are used, that is $\sum m_i l_i^2 = 1$.

A first approximation to the solution of Eq. (5.1) obtained by neglecting non-diagonal elements, is

$$\lambda_k = \lambda_k^0 (1 + \sum_i \sigma_i \eta_i^k)^{-1}, \tag{5.2}$$

where $\sigma_i = \Delta m_i / m_i$ (the fraction by which the mass of atom i is changed) and $\eta_i^k = m_i l_{ik}^2 / l$ (the fraction of the total kinetic energy of the kth normal vibration contributed by atom i). In terms of the frequencies, Eq. (5.2) may be written (437)

$$\Delta\omega_k^0 / \omega_k^0 = -\tfrac{1}{2} \sum_i \sigma_i \eta_i^k, \tag{5.3}$$

where $\Delta\omega$ is the amount by which the frequency shifts in going from the original to the isotopic molecule.

From the definition of η_i^k it is apparent that a knowledge of this quantity gives direct information as to how actively atom i participates in the kth mode of motion. η_i^k is a pure number, and there are several sum rules which facilitate its use (437). An obvious one is that the sum of the η_i^k values for the kth normal vibration over all atoms in the molecule is unity, that is

$$\sum_{i=1}^{N} \eta_i^k = 1. \tag{5.4}$$

Another theorem of similar nature holds for the summation over the various modes of motion k of a given atom i, namely

$$\sum_{k=1}^{3N} \eta_i^k = 3. \tag{5.5}$$

Note that the summation in Eq. (5.5) is over both internal and external degrees of freedom. This sum rule can be made more restrictive, however, by summing over the degrees of freedom in a given symmetry type rather than over all $3N$ degrees. A sum is obtained which is dependent only on the symmetry properties of the molecule. It takes the form

$$\sum_{k=1}^{t} \eta_i^k = \zeta_i, \tag{5.6}$$

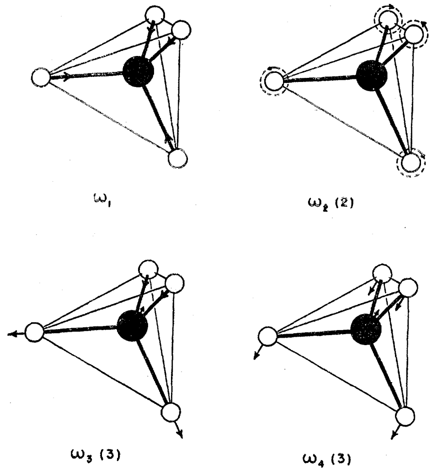
where t is the number of degrees of freedom of the symmetry type under consideration, and ζ_i is a pure number characteristic for the symmetry type and atom i. In order to obtain ζ_i, determine the number of degrees of freedom which the point set, of which atom i is a member, contributes to the symmetry type, and divide it by the number of atoms in the point set.

6. Miscellaneous

If a molecule has a threefold or higher axis of symmetry, certain of the normal vibrations are necessarily degenerate. On the other hand, two or more normal vibrations may have the same frequency because of an accidental numerical agreement of potential constants, the degeneracy then being termed accidental. If these accidentally degenerate vibrations have the same symmetry properties, however, in all known cases they interact and yield vibrational modes with distinct frequencies. Interactions between normal vibrations of different symmetry types are usually negligible (except possibly for fine structure interpretation and are present as small couplings between angular momenta of degenerate vibrations).

Since necessary degeneracy of normal vibrations is a function of molecular symmetry, isotopic substitution may afford a means of removing the requirement. In general there are two effects to be considered when a substitution releasing requirements for necessary degeneracies of certain normal vibrations has been made: (1) the shift of frequencies caused by the mass effect, and (2) the splitting caused by interactions. Replacing an atom by a heavier isotope decreases some frequencies, but the decrease cannot be to a frequency which is less than $(\text{mass ratio})^{\frac{1}{2}}$ times the original one. The normal vibrations into which a degenerate vibration may split upon isotopic substitution need not have the same frequency and may be of different symmetry types. However, the frequencies of the original and isotopic molecules must still satisfy the product rule.

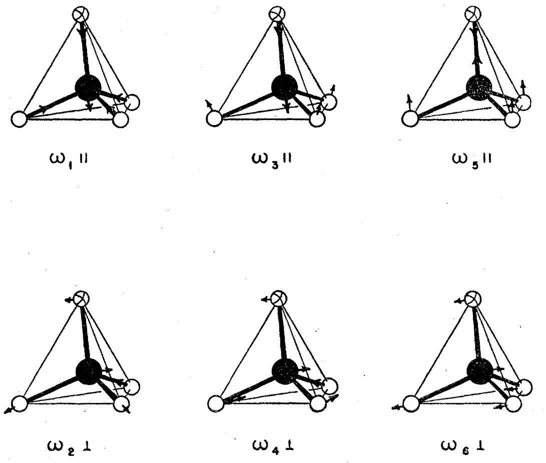
It is important to consider the symmetry of the molecule rather carefully, since some perturbations may not be large enough to release a necessary degeneracy. If the isotopic substitution is made in a portion of the molecule not directly affected by the degenerate vibration, it conceivably could have a negligible influence.



ω_1 ω_2 (2)

ω_3 (3) ω_4 (3)

FIG. 2. Schematic description of vibrations of T_d molecule XY_4.



$\omega_1 \parallel$ $\omega_3 \parallel$ $\omega_5 \parallel$

$\omega_2 \perp$ $\omega_4 \perp$ $\omega_6 \perp$

FIG. 3. Schematic description of vibrations of C_{3v} molecule ZXY_3.

In this paper only general discussions of isotopic shifts have been given. Various authors (108, 124, 231, 395, 407, 457, 496) have treated individual molecules, using special potential systems, and have given expressions for frequency shifts in the individual cases. Some of these are valid only for small changes in mass, whereas others also include deuterium substitution. References to such treatments will be made in the discussions of specific molecules.

There are also a number of isotopic relationships involving even powers of the frequency shifts in going from one molecule to its isotopic derivative, but they include some of the potential constants of the molecule. Unfortunately, the determination of potential constants is not easy, and once determined, they may not carry over very well from one compound to another. A method for getting these relationships is given by Redlich and Tompa (390, 444) and is applied to benzene.

PART II. APPLICATIONS TO OBSERVED SPECTRA

In this section those molecules will be considered for which a complete vibrational analysis for both the original and isotopic molecules have been made. In addition, since much of the previous discussion is applicable to the set of vibrations belonging to each symmetry type individually, some illustrations will be given of molecules in which only part of the fundamental vibration frequencies are known.

References to individual papers concerning a certain molecule are given at the beginning of the discussion of that molecule, and only those of special interest repeated in the discussion. No attempt has been made to make the reference list complete for the hydrogen derivative, but it is believed to be complete for the deuterium derivatives up to June 1946. The water, ammonia, methyl halide, and methane molecules are discussed in detail in a review article by Dennison (146), and these and certain others are discussed by Herzberg in his book on polyatomic molecules (231). In the following there is as little duplication of these two references as possible except for preservation of continuity, and insofar as the discussion relates to the effect of deuterium substitution on molecular vibrations. In general, fundamental vibrational frequencies will be the only ones considered.

TABLE I. (CH_4, CD_4) Symmetry elements and types for T_d molecules (352a).

Column 1 lists symbols for types; columns 2, 3, 4, 5 list behavior with respect to symmetry operations (352a); columns 6, 7 list the degrees of freedom of the deuterium point sets for each symmetry type; column 8 lists the classification of the degrees of freedom; columns 9, 10 list the selection rules for the Raman effect and for infra-red absorption.

					D contributions		Degrees of	Selection rule	
T_d	C_2^z	C_2^y	C_3	S_4	CH_4	CD_4	freedom	*R*	*IR*
A_1	+	+	+	+	0	1	ω_1	+	−
A_2	+	+	+	−	0	0		−	−
E	+	+	$\epsilon^{\pm}$	±	0	1	ω_2	+	−
F_1	K	K	K	$-K$	0	1	R	−	−
F_2	K	K	K	K	0	2	ω_3, T, ω_4	+	+

Normal modes of motion will be diagrammed in some cases; and in others, just a reference to where they may be found will be given. The notation usually will correspond to that used by Herzberg. We use his convention of denoting the fundamental *vibrational* type or species by the small letter corresponding to the capital letter representing the general symmetry species.* For example, an a_{1g} vibration has the symmetry A_{1g}. The molecules are arranged according to the symmetry of the unsubstituted form, starting from tetrahedral and proceeding to lower symmetries. The observed frequencies are for the vapor state unless otherwise specified, and are given in terms of wave numbers.

1. T_d

(*a*). CH_4 (31, 49, 100, 101, 102, 103, 111, 126, 146, 147, 188, 189, 252, 253, 255, 297, 298, 318, 332, 333, 334, 395, 405, 406, 446, 455, 457a)

The methane molecule possesses a very high degree of symmetry, being tetrahedral, and therefore offers the possibility of numerous changes in symmetry by isotopic substitution. All four hydrogen atoms in CH_4 are members of the same point set, and replacement by deuterium yields the following set of molecules (with symmetries): CH_3D (C_{3v}); CH_2D_2 (C_{2v}); CHD_3 (C_{3v}); and CD_4 (T_d). The modes of harmonic vibration of these molecules, insofar as they are determined by symmetry, are reproduced schematically in Figs 2–4. A diagram of CH_2D_2 referred to a system of Cartesian coordinates is given in Fig. 5, since it is the only molecule for which the arbitrariness in the choice of symmetry planes has any effect in the later discussion. For CH_4 (or CD_4), the hydrogen (or deuterium) nuclei oscillate in phase along the radii of the tetrahedron in ω_1, the carbon nucleus remaining stationary. In ω_2 the hydrogen nuclei move upon the surface of a sphere circumscribed about the tetrahedron, the motion being isotropic in two dimensions and consequently doubly degenerate.

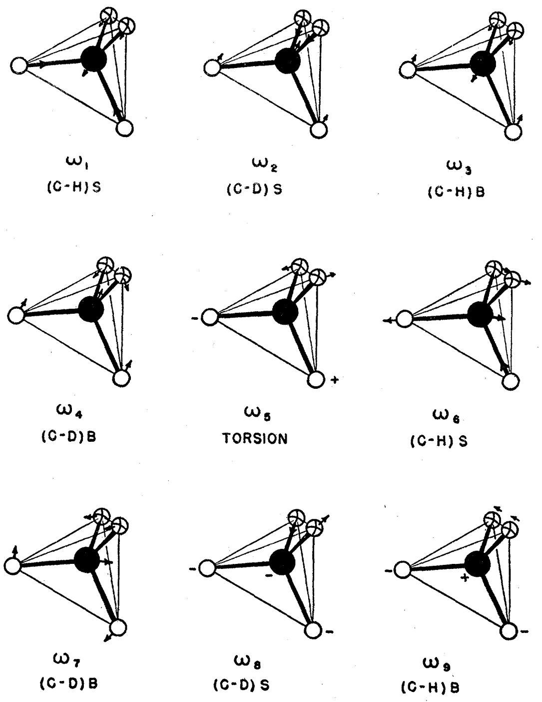


FIG. 4. Schematic description of vibrations of C_{2v} molecule CH_2D_2.

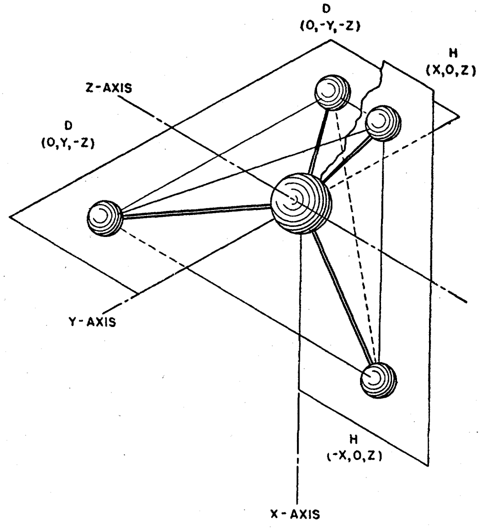


FIG. 5. Coordinate system for CH_2D_2.

TABLE II. (CH_3D, CD_3H) Symmetry elements and types for C_{3v} molecules (352a).

C_{3v}	C_3	σ_v	*D* contributions CH_3D	*D* contributions CHD_3	Degrees of freedom	Selection rule *R*	Selection rule *IR*
A_1	+	+	1	2	ω_1, ω_3, ω_5, $T_{\parallel}$	+	+
A_2	+	−	0	1	$R_{\parallel}$	−	−
E	$\epsilon^{\pm}$	±	1	3	ω_2, ω_4, ω_6, $R_{\perp}$, $T_{\perp}$	+	+

---

* Sponer and Teller (422) proposed using Greek letters to represent the classical vibrations.

TABLE III. (CH_2D_2) Symmetry elements and types for C_{2v} molecules (352a).

C_{2v}	C_2^z	σ_{yz}	σ_{xz}	D contributions CH_2D_2	Degrees of freedom	Selection rule R	IR
A_1	+	+	+	2	ω_1, ω_2, ω_3, ω_4 T_z	+	+
A_2	+	−	−	1	ω_5, R_z	+	−
B_1	−	+	−	2	ω_8, T_y, R_x, ω_9	+	+
B_2	−	−	+	1	ω_6, R_y, T_x, ω_7	+	+

ω_3 and ω_4 are linear combinations of two limiting vibration forms, one a vibrating hydrogen tetrahedron with no central particle, and the other a central carbon atom oscillating against a rigid hydrogen tetrahedron. They are both triply degenerate.

The normal vibrations of the T_d and C_{3v} isotopic molecules have been treated by a number of authors (144, 395, 457, 458) on the basis of assumed potential functions and expressions derived for the frequencies. Dennison and Johnston (147, 255) have evaluated the five constants for the most general harmonic potential function consistent with tetrahedral symmetry from the observed data for methane and have used them to calculate the fundamental frequencies for CH_3D, CH_2D_2, CHD_3, and CD_4. Calculations of the constants using more data have also been made by Dennison (146).

The classifications of vibrations under molecular symmetries for the five molecules are given in Tables I, II, and III. The tables contain a column for each molecule giving the degrees of freedom contributed to each symmetry type by the deuterium point sets. The selection rules for Raman and infra-red spectra are also given, + denoting active and − inactive, in order to indicate the changes in selection rules brought about by deuterium substitution. However, even though the symmetry restriction forbidding the spectroscopic appearance of a frequency may have been removed by isotopic substitution, the intensity with which the frequency should appear may be so low as to prevent its being observed. Nevertheless, many of the newly allowed frequencies are observed.

Table III contains three symmetry elements although only two are essential. The twofold axis is included since that is one of the conventional elements of C_{2v} symmetry, and both planes are included since it is possible to pick either plane as the common element in a comparison with CH_3D and CHD_3. However, the choice of plane removes all arbitrariness in the comparison, and the types corresponding to that element must be used. (For methods of determining what symmetry types one can compare in the general case for isotopic molecules of different symmetry, see reference 231, page 235.)

The observed values of the fundamental frequencies of the methanes are listed in Table IV. They are essentially the same as those given by Herzberg (231, page 309). Values enclosed in parentheses, however, are not observed fundamentals, but values calculated by Dennison (146) with corrections for anharmonicity. In both CH_4 and CD_4 the frequency of the vibration ω_2 has not been observed as a fundamental, but the first overtone $2\nu_2$ has been observed. We prefer to give Dennison's calculated values, rather than $\frac{1}{2}(2\nu_2)$, since his calculations take into account the positive contribution of the second sum in (1.2) of Part I. Thus in the expression $\omega_2=(1+\alpha)\nu_2$, the anharmonicity constant α has a negative value which is a reversal of the usual effect. The observed $2\nu_2$ therefore is greater than $2\times\nu_2$. A plausible explanation frequently given for the negative sign of α is that in ω_2 the hydrogen nuclei when displaced from their equilibrium positions approach the other hydrogen nuclei, with a corresponding rise in the potential which is steeper than a parabola, making the anharmonic correction to the energy positive.

The measured moments of inertia are the following (146):

$$
\begin{aligned}
&CH_4 && I= 5.328\times10^{-40}\text{ g cm}^2,\\
&CH_3D && I_\perp= 7.215\times10^{-40}\text{ g cm}^2,\\
&CD_4 && I=10.57\times10^{-40}\text{ g cm}^2.
\end{aligned}
$$

TABLE IV. Fundamental frequencies of the methanes.

	CH_4		CH_3D	CHD_3		CH_2D_2
ν_1	2914.2	ν_1	2982.2	2141.1	ν_1	2974.2
ν_2	(1499)	ν_2	3030.2	2268.6	ν_2	2139.0
ν_3	3020.3	ν_3	2204.6	2992.0	ν_3	1450
ν_4	1306.2	ν_4	1476.7	1299.2	ν_4	1034.4
		ν_5	1306.4	1046	ν_5	1285.6
	CD_4	ν_6	1156.0	982	ν_6	3020.0
ν_1	2084.7				ν_7	1090.0
ν_2	(1036)				ν_8	2255.0
ν_3	2258.2				ν_9	1235.0
ν_4	995.6					

Assuming a regular tetrahedral structure, one calculates from the moments of inertia of CH_4 and CH_3D the most probable value of the C–H distance to be 1.093A. With this information one can readily calculate I_x, I_y, and I_z for the CH_2D_2 molecule of Fig. 5, and $I_\perp$ for CHD_3. For the C_{3v} molecules, of course, $I_{\parallel}$ is the same as for the corresponding tetrahedral molecule.

Table V contains a comparison of the fundamental frequencies for molecules which can be obtained from each other by substitution of a single isotope. The comparison is by symmetry types of a point group whose elements are the common symmetry elements of the two molecules. The comparison of Column 1 with Column 4 (or 6 or 8) is implicit in the comparison of 1 with 2, and 3 with 4, and so forth. For C_{2v} and C_{3v} molecules, the choice of a common plane now depends on the individual C_{3v} molecule, since we limited ourselves to a single substitution, and thus the C_{2v} types combined for comparison with CH_3D are different from those for comparison with CHD_3. There are three places in the table where the fundamental frequency of the isotopic molecule is 10 cm^{-1} or more larger than that of the corresponding original one. If ν_5 of CH_2D_2 were assigned the Raman frequency 1332.9 cm^{-1} (ν_5 being allowed only in the Raman spectrum), one of these violations would drop out. A ν_5 for CH_2D_2 may be calculated by using the product rule and the symmetry types indicated in Table V. Values for ν_5 calculated in this way range from 1300 cm^{-1} to 1315 cm^{-1}, and because of the peculiar anharmonicities encountered in methane it is difficult to say whether they are high or low. Thus the product rule in this case does not permit an unambiguous decision, since the frequencies under question bracket the calculated value.

TABLE V. Order rule comparisons for some isotopic methanes.

CH_4 a_1f_2	CH_3D a_1
3020.3	2982.2
2914.2	2204.6
1306.2	1306.4
ef_1f_2	e
3020.3	3030.2
(1499)	1476.7
1306.2	1156.0
CH_3D a_1e	CH_2D_2 a_1b_1
3030.2	2974.2
2982.2	2255.0
2204.6	2139.0
1476.7	1450
1306.4	1235.0
1156.0	1034.4
a_2e	a_2b_2
3030.2	3020
1476.7	1285.6
1156.0	1090.0
CH_2D_2 a_1b_2	CHD_3 a_1e
3020	2992.0
2974.2	2268.6
2139.0	2141.1
1450	1299.2
1090.0	1046
1034.4	982
a_2b_1	a_2e
2255.0	2268.6
1285.6	1299.2
1235.0	982
CHD_3 a_1	CD_4 a_1f_2
2992.0	2258.2
2141.1	2084.7
1046	995.6
e	ef_1f_2
2268.6	2258.2
1299.2	(1036)
982	995.6

TABLE VI. Product rule ratios for some methanes.

T_d	$CH_4:CD_4$		C_{3v}	$CH_4:CH_3D$		C_{3v}	$CHD_3:CD_4$	
a_1	τ_c τ_0	1.41 1.40	a_1f_2/a_1	τ_c τ_0	1.37 1.34	a_1/a_1f_2	τ_c τ_0	1.38 1.37
e	τ_c τ_0	1.41 1.45	ef_1f_2/e	τ_c τ_0	1.18 1.14	e/ef_1f_2	τ_c τ_0	1.25 1.25
f_2	τ_c τ_0	1.79 1.75						
C_{3v}	$CH_3D:CHD_3$		σ_{yz}	$CH_3D:CH_2D_2$		σ_{xz}	$CH_2D_2:CHD_3$	
a_1	τ_c τ_0	1.34 1.33	a_1e/a_1b_1	τ_c τ_0	1.67 1.67	a_1b_2/a_1e	τ_c τ_0	1.68 1.62
e	τ_c τ_0	1.75 1.78	a_2e/a_2b_2	τ_c τ_0	1.18 1.22	a_2b_1/a_2e	τ_c τ_0	1.25 1.24

The type of anharmonicity encountered in ν_2 of CH_4 and CD_4 is that discussed in Section 2 of Part I and results in a violation of Eq. (2.2). In going from CH_4 to CD_4, ν_2 shifts from 1499 cm^{-1} to 1036 cm^{-1}, giving a ratio of 1:1.447. A geometrical explanation of this anharmonicity has been mentioned already, the effect being less in CD_4 than in CH_4 because of the smaller amplitudes of vibration.

The product rule can be applied, of course, to the frequencies of any arbitrary pair of the isotopically related molecules. We can illustrate its applicability, however, by considering only a few of the possible combinations. In Eq. (3.1), n will represent the difference between the number of degrees of freedom contributed to the symmetry type by the deuterium point sets of the molecule whose frequencies are in the denominator of τ_0, and the number contributed by the deuterium point sets of the molecule represented in the numerator. The τ's obtained are given in Table VI, using Dennison's calculated value for ν_2 in CH_4 and CD_4. Notice that in a few cases $\tau_0 > \tau_c$ because of the special type of anharmonicity in some vibrations. The agree-

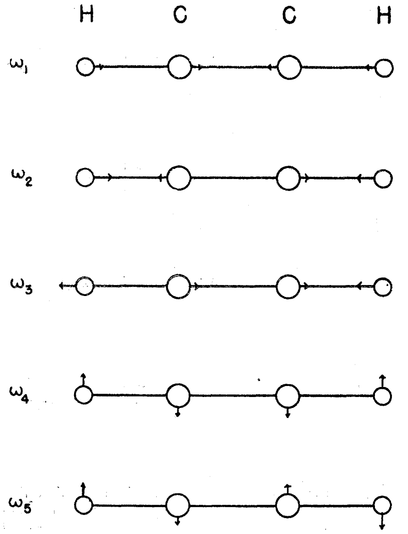


FIG. 6. Schematic description of vibrations of $D_{\infty h}$ molecule X_2Y_2.

ment between r_0 and r_c, however, is good, and deviations are within the limits mentioned in Section 3 of Part I.

2. $D_{\infty h}$

(*a*). C_2H_2 (59, 61, 76, 77, 79, 108, 131, 191, 193, 194, 232, 233, 234, 235, 289, 307, 308, 319, 320, 321, 359, 391, 427, 429, 455, 494, 497)

Acetylene has been studied rather thoroughly spectroscopically, and so furnishes an excellent illustration of some of the isotope effects. Substitution of one hydrogen yields a $C_{\infty v}$ molecule, whereas replacement of both gives back the original symmetry. The displacement forms and symmetry types are given in Fig. 6 and Table VII, respectively, and since the normal vibrations for C_2HD are similar to those for the $D_{\infty h}$ molecules, we use the same notation for both. For the $D_{\infty h}$ symmetry, types Σ_g and Π_g are Raman active, and Σ_u and Π_u are infra-red active, whereas for $C_{\infty v}$ symmetry all types are active in both Raman and infra-red spectra. The degeneracy of the π-vibration is associated with the axis which cannot be removed by deuterium substitution, so that there is no possibility of splitting these frequencies.

Potential functions have been assumed by Colby (108) and by Wu and Kiang (496, 497), the frequency expressions calculated, and the constants evaluated from the observed C_2H_2 spectra. The expressions were then used to calculate the frequencies for the deuterium substituted molecules. The results all lie within 3 percent of the experimental values. Wu and Kiang (494, 497) have also attempted a normal coordinate perturbation treatment, introducing the first- and second-order anharmonic potentials consistent with the symmetry of the molecule, and also the interactions between vibration and rotation for such a linear molecule. However, sufficient experimental data are not available for a complete determination of the constants, or even for all the normal frequencies of C_2H_2.

The observed frequencies for the gaseous state are given in Table VIII, arranged in symmetry types to indicate the shifts on going from one molecule to the other. The largest shift, from C_2H_2 to C_2D_2, has the ratio $\nu/\nu' = 1.354$. The frequency ν_5 for C_2D_2 has not been observed, presumably because of too low intensity in the Raman effect.

If we neglect the interaction between vibration and rotation, the structure of a band will consist merely of the rotation frequencies superimposed on the vibrational transition. A vibration in which the change of electric moment is along the molecular axis will thus give rise to a $\|$-band in exactly the same way as the vibration of a diatomic molecule. If the change in electric moment is perpendicular to the axis, however, the corresponding band has a *Q*-branch and is called "perpendicular." The *Q*-branch is just the vibrational frequency itself spread out by vibration-rotation interactions. For values of J, the rotational quantum number, not too high, we have the expression for a rotational-vibrational energy level of a linear molecule,

$$W = W_v + B_v J(J+1) - D_v J^2(J+1)^2, \quad \text{(a.1)}$$

TABLE VII. Symmetry elements and types for $D_{\infty h}$ and $C_{\infty v}$ molecules (352a).

$D_{\infty h}$	$C_{\infty v}$	C_∞	i	$D_{\infty h}$	$C_{\infty v}$
Σ_g	Σ	$+$	$+$	ω_1, ω_2	ω_1, ω_2
Σ_u		$+$	$-$	ω_3, T	ω_3, T
Π_g	Π	$\epsilon^{\pm}$	$+$	ω_5, R	ω_4, ω_5
Π_u		$\epsilon^{\pm}$	$-$	ω_4, T	R, T

where W_v is vibrational energy level, $B_v = h/4\pi^2 I_v$, $1/I_v$ being the mean value of $1/I$ during the vibrations of the level, and D_v is a constant dependent on the vibrational state which corrects for centrifugal stretching. Equation (a.1) can be applied to the parallel vibrations of acetylene using the expressions for B_v and D_v from diatomic theory.

$$B_v = B_e - \alpha(v+\tfrac{1}{2}) - \cdots,$$
$$D_v = D_e + \beta(v+\tfrac{1}{2}),$$

where e indicates the unobtainable state in which the atoms are at rest, and v is the vibrational quantum number. The J selection rules for the infra-red for the parallel bands are $\Delta J = \pm 1$, and for the perpendicular bands $\Delta J = 0, \pm 1$.*

The photographic infra-red spectra of C_2H_2 and C_2HD have been studied by Herzberg, Patat, Spinks, and Verleger (233, 235, 237), and analyzed on the basis of linear molecules. The bands studied were $\nu_1+\nu_2+\nu_3 = 8512$, $3\nu_3 = 9640$, and $2\nu_2+\nu_3 = 9835$ cm^{-1} for C_2H_2, and for C_2HD, $3\nu_2 = 9706$ cm^{-1}, $2\nu_2+\nu_3 = 9139$ cm^{-1}, $2\nu_2+\nu_1 = 8409$ cm^{-1}, $3\nu_3+\nu_1 = 9405$ cm^{-1}, $3\nu_2+\nu_3 = 12{,}263$ cm^{-1}, and $4\nu_2 = 12{,}747$ cm^{-1}. The constants B_0 and B_e were evaluated for each molecule and yielded the moments of inertia for the two states. For C_2H_2, $I_0 = 23.502\times10^{-40}$ g cm^2, and $I_e = 23.365\times10^{-40}$ g cm^2, whereas for C_2HD, $I_0 = 27.899\times10^{-40}$ g cm^2, and $I_e = 27.753\times10^{-40}$ g cm^2. Assuming the same internuclear distances in corresponding states, we have two equations for each state and can solve for the two unknowns. The values obtained are:

$$r_e(C-H) = 1.057A, \quad r_0(C-H) = 1.057A,$$
$$r_e(C-C) = 1.199A, \quad r_0(C-C) = 1.204A.$$

The rotational lines are regularly spaced, as is characteristic of linear molecules, and in C_2H_2 show an intensity alternation of 1:3, corresponding to the spin $\frac{1}{2}$ of the hydrogen nucleus. However, in C_2HD the intensity variations disappear. Thus the isotopic molecule corroborates the theory of relative population of rotational levels, as well as furnishing an additional relationship for the determination of molecular dimensions.

TABLE VIII. Fundamental frequencies of the acetylenes.

	C_2H_2	C_2HD	C_2D_2
ν_2	3372	3335	2700
ν_1	1974	1851	1762
ν_3	3288	2585	2428
ν_4	730	679	539
ν_5	612	519	(512)

TABLE IX. Product rule ratios for the acetylenes.

$D_{\infty h}$		$C_2H_2:C_2D_2$	$C_{\infty v}$		$C_2H_2:C_2HD$	$C_2HD:C_2D_2$
σ_g	τ_c	1.41	σ	τ_c	1.39	1.39
	τ_0	1.40				
σ_u	τ_c	1.36		τ_0	1.37	1.38
	τ_0	1.35				
π_g	τ_c	1.20	π	τ_c	1.27	1.29
	τ_0	—				
π_u	τ_c	1.36		τ_0	1.27	—
	τ_0	1.35				

Since we have the dimensions, we can calculate the moment of inertia for C_2D_2 also, and apply the product rule. (For C_2D_2, $I_0 = 32.518\times10^{-40}$ g cm^2, $I_e = 32.352\times10^{-40}$ g cm^2.) If we were using the normal frequencies in the product rule, we should also use the I_e values; but since the moments of inertia enter as the square root of their ratio, τ_c is quite insensitive to small variations in the dimensions. The τ's are given in Table IX, with the exception of τ_0 for types involving ν_5 of C_2D_2, since this frequency has not been observed. However, we can use the product rule to calculate it rather accurately, since ω_5 was one of the normal frequencies obtained by Wu and Kiang for C_2H_2. Type π_g for $D_{\infty h}$ symmetry contains ω_5 and a rotation; therefore

$$\omega_5/\omega_5' = \tau_c = (2I_e/I_e')^{\frac{1}{2}}. \tag{a.2}$$

By (a.2) we find $\tau_c = 1.201$, and ω_5 for C_2H_2 is given as 622 cm^{-1}. Therefore, we calculate ω_5' for C_2D_2 to be 518 cm^{-1}. Now, using the formula $\nu = \omega(1-\alpha)$ for C_2H_2, we find $\alpha = .016$. Assuming that α' for C_2D_2 is $(\omega_5'/\omega_5)\alpha$, we calculate $\alpha' = .013$, and consequently $\nu_5' = 512$ cm^{-1}. In this particular case we would not have made much of an error in ν_5' by calculating it directly from the fundamental ν_5 and τ_c, getting the value 509 cm^{-1}.

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* For a discussion of vibration-rotation spectra consult (145, 230, 231, 437).

TABLE X. Symmetry elements and types for D_{6h} molecules.

D_{6h}	C_3^z	C_2^z	C_2^y	i	Rot. and trans.	Selection rules R	IR
A_{1g}	+	+	+	+		+	−
A_{1u}	+	+	+	−		−	−
A_{2g}	+	+	−	+	R_z	−	−
A_{2u}	+	+	−	−	T_z	−	+
B_{1g}	+	−	+	+		−	−
B_{1u}	+	−	+	−		−	−
B_{2g}	+	−	−	+		−	−
B_{2u}	+	−	−	−		−	−
E_{1g}	$\epsilon\pm$	−	±	+	$R_{x,y}$	+	−
E_{1u}	$\epsilon\pm$	−	±	−	$T_{x,y}$	−	+
E_{2g}	$\epsilon\pm$	+	±	+		+	−
E_{2u}	$\epsilon\pm$	+	±	−		−	−

TABLE XI. Symmetry elements and types for D_{3h} molecules.

D_{3h}	C_3^z	C_2^y	σ_h	Rot. and trans.	Selection rules R	IR
A_1'	+	+	+		+	−
A_1''	+	+	−		−	−
A_2'	+	−	+	R_z	−	−
A_2''	+	−	−	T_z	−	+
E'	$\epsilon\pm$	±	+	$T_{x,y}$	+	+
E''	$\epsilon\pm$	±	−	$R_{x,y}$	+	−

3. $\mathbf{D}_{6h}$

(*a*). C_6H_6 (9, 10, 11, 12, 21, 21a, 21b, 22a, 22b, 22c, 23, 38, 53, 54, 74, 99, 149, 238a, 238b, 250, 250a, 263, 266, 267, 269, 270, 271, 274, 283, 284, 294, 296, 326, 355a, 358, 363, 372, 381, 383, 384, 385, 386, 388, 389, 414, 419, 420, 421, 468, 470, 483, 484)

Benzene is a planar molecule with D_{6h} symmetry and has been studied rather extensively both by the Raman effect and infra-red absorption. Since the six hydrogen atoms all belong to one point set, it is possible to get a variety of molecular symmetries by deuterium substitution. All of these deuterium isomers have been prepared and studied, with the result that many of the uses of isotopes are displayed in this single case.

Wilson (470) and others (53, 54, 300, 312a) have worked out normal coordinate treatments of the benzene molecule, giving the selection rules and normal modes of vibration, using modified valence force potential functions. Angus, Bailey, Ingold, and co-workers (12, 22c, 238b) and Langseth and Lord (284) discuss the normal vibrations in detail and make the assignments of observed frequencies. Using ten of these assignments, Miller and Crawford (312a) evaluated the force constants appearing in their normal coordinate treatment of the non-planar vibrations of benzene and its deuterium derivatives, and calculated forty-nine additional frequencies. These were in good agreement with observed data where checks were available. The values for the force constants should be applicable to certain other derivatives of benzene analogous to the transfer of force constants from one aliphatic compound to another (116). Bernard, Manneback, and Verleysen (53, 54) treated the planar vibrations in a similar fashion, but the results were not as satisfactory.

The essential symmetry elements and symmetry types for point groups D_{6h}, D_{3h}, V_h, and C_s are given in Tables X to XIII. The schematic modes of vibration for a D_{6h} molecule will not be reproduced here, but the reader is referred to reference 231, page 118. Herzberg's notation for the vibrations will be used.

In a molecule such as C_6H_6 and C_6D_6, there should be seven fundamental vibrations active in the Raman effect and four in infra-red absorption. However, the Raman spectrum of C_6H_6 shows eight rather strong lines, indicating that an overtone or combination tone is appearing. Presumably it is gaining sufficient intensity to appear by interacting with a fundamental

TABLE XII. Symmetry elements and types for D_{2h} molecules.

D_{2h}	C_2^y	C_2^z	i	Rot. and trans.	Selection rules R	IR
A_{1g}	+	+	+		+	−
A_{1u}	+	+	−		−	−
B_{1g}	−	+	+	R_z	+	−
B_{1u}	−	+	−	T_z	−	+
B_{2g}	+	−	+	R_y	+	−
B_{2u}	+	−	−	T_y	−	+
B_{3g}	−	−	+	R_x	+	−
B_{3u}	−	−	−	T_x	−	+

TABLE XIII. Symmetry elements and types for C_s molecules.

C_s	σ_{xy}	Rot. and trans.	Selection rules R	IR
A'	+	$T_{x,y}$, R_z	+	+
A''	−	T_z, $R_{x,y}$	+	+

which is Raman active. An analysis (284) shows that the frequency ν_{16} lies at about 1596 cm^{-1} in C_6H_6, and since it is of the same symmetry (e_{2g}) and accidentally close to the combination tone $\nu_2+\nu_{18}$ ($\nu_2=991.6$ cm^{-1}, $\nu_{18}=605.6$ cm^{-1}), there is resonance between them, giving rise to the 1584.8−1606.4 cm^{-1} doublet in the Raman spectrum. On going to C_6D_6, however, ν_{16} shifts downward by a larger amount than does the combination tone, with the result that the accidental degeneracy is removed. Thus for C_6D_6 only seven Raman frequencies are observed.

The observed fundamental vibrational frequencies for benzene and some of its deuterium derivatives as given by Bailey, Ingold, *et al.* (21a, 21b, 22a, 22b, 22c, 238a, 238b) are listed in Tables XIV–XVI. Because it would involve a great deal of repetition, the compounds are not arranged to demonstrate the order rule. The frequencies in square brackets were calculated by means of the product rule, and those in parentheses were obtained by indirect methods.

TABLE XIV. Fundamental frequencies of C_6H_6, symmetrical $C_6H_3D_3$, and C_6D_6 (238b). (Columns labelled *W* and *H* are Wilson's (470) and Herzberg's (231) numbering systems.)

D_{6h}	D_{3h}	*W*	*H*	C_6H_6	sym. $C_6H_3D_3$	C_6D_6
a_{1g}	a_1'	1	2	991.6	956.2	943.2
		2	1	3061.9	3052.7	2292.6
b_{1u}		12	6	[1010]	1003.6	[963]
		13	5	[3060]	2281.9	[2290]
a_{2g}	a_2''	3	3	(1326)	(1230)	(1037)
b_{2u}		14	9	(1648)	(1600)	(1571)
		15	10	(1110)	(920)	(825)
a_{2u}	a_2''	11	4	671	533	496.5
b_{2g}		4	8	[703]	691	(601)
		5	7	985	915	(827)
e_{2g}	e'	6	18	605.6	593.0	577.4
		9	17	1178.0	1101.8	867.3
		8	16	1596	1573.1	1551.5
		7	15	3046.8	2292	2264.9
e_{1u}		19	13	1485	1407	1333
		18	12	1037	833.5	813
		20	14	3080	3084	2294
e_{2u}	e''	16	20	405	372.7	352
		17	19	[970]	947	[793]
e_{1g}		10	11	848.9	710.2	661.7

TABLE XV. Fundamental frequencies of p-$C_6H_4D_2$ and p-$C_6H_2D_4$ (21a, 238a).

D_{2h}	p-$C_6H_4D_2$	p-$C_6H_2D_4$
a_{1g}	596.6	589.0
	978.0	862.2
	1173.4	960.9
	1587.0	1572.1
	2280.0	2285.0
	3055.0	3045.0
a_{1u}	405	352
	970	793
b_{2g}	849.5	663.6
b_{2u}	992	819
	1033	977
	1469	1353
	2275	2280
	3060	3078

D_{2h}	p-$C_6H_4D_2$	p-$C_6H_2D_4$
b_{1g}	600.9	585.8
	908.5	954
	1309.0	1255.3
	1569.3	1564
	3042	2272
b_{1u}	367	383
	597	548
	876	925
b_{3g}	634.1	615.1
	736	767.1
	967	929.7
b_{3u}	814	812
	1106	1057
	1413	1439
	3079	2280

TABLE XVI. Fundamental vibrational frequencies for C_6H_5D (22a)

	C_{2v}		
a_1	b_1	a_2	b_2
3066	3079	970	995
3060	3041	849.9	922
3054.8	1292	405	778
2269	1158.2		698
1591.1	1076		608
1480	858		380
1175.6	——		
1031	——		
1006.8	——		
980	——		
601			

The mode of vibration designated by ν_2 is totally symmetrical with the C−H groups moving essentially as units. Therefore, replacement of the hydrogen atoms by deuterium atoms should affect this vibration in much the same way as replacement of all the C^{12} atoms by C^{13} atoms, making the discussion of the small isotope effect applicable. Treating the CH group as a unit and applying Eq. (5.3), $\sigma_i=1/13$, $\eta_i=1/6$, and the sum is over all six units. Thus one obtains $\Delta\nu_2=-(1/26)\nu_2$ for the shift in going from C_6H_6 to C_6D_6. Since $\nu_2=991.6$ cm^{-1}, $\Delta\nu_2=-38$ cm^{-1}. The observed shift is a little larger, −48 cm^{-1}, indicating that the C−H group does not act quite as a unit. Nevertheless the approximation is not bad, and so one might expect the substitution of each deuterium atom to produce the same downward shift in ν_2, namely one-sixth of the benzene-benzene-d_6 shift. Thus the value of ν_2 should change in a regular fashion, and should be a constant for the various isomers of a given

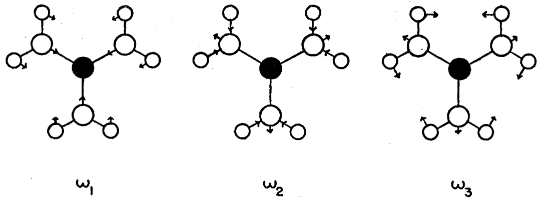

FIG. 7. Schematic description of a_1' vibrations of $C(NH_2)_3^+$.

isotopic species. In the Raman spectra of ortho- and para-$C_6H_4D_2$, and ortho- and para-$C_6H_2D_4$, intense lines are found at the predicted positions. However, for the other derivatives, ν_2 is found near enough to its predicted point to confirm its identity, but far enough away to indicate a perturbing effect. The perturbation arises from the presence of a vibration ν_6 on the high frequency side of ν_2, slightly over 1000 cm^{-1}, which can interact with ν_2 in the derivatives of symmetry D_{3h}, C_{2v}, and C_s. Furthermore, it is just for those symmetries that the disagreement between estimated and observed values of ν_2 is found. ν_6 is not actually observed either in benzene or benzene-d_6, but it is found in some of the derivatives and so values for the others can be obtained by means of the product rule.

Lord and Teller (296) calculated the intensities of some of the Raman lines in benzene and benzene-d_6 using only the assumption that a harmonic force field was involved. The intensity changes of the a_{1g}, a_{2u}, and e_{1g} vibrations on going from C_6H_6 to C_6D_6 are calculated in detail and agree quantitatively with observed data. In some cases the intensity changes are rather striking.

Wilson's potential function (470) describes the potential energy of the planar vibrations in terms of only four constants, but it gives good agreement with observations for the a vibrations of C_6H_6, sym-$C_6H_3D_3$, and C_6D_6. It was used by Langseth and Lord to calculate the approximate amplitudes of the atoms in the a_1' vibrations of sym-$C_6H_3D_3$, and from them the approximate theoretical intensity ratios in the Raman effect. The agreement with observations is good.

The C−C distance in benzene has been determined by electron diffraction (348) to be 1.390A, and the C−H distance is taken to be 1.08A. Thus the necessary moments of inertia can be calculated and the product rule applied. The calculated and observed τ's are given in Table XVII. Not all of the possible comparisons have been made, since many of them would be redundant.

TABLE XVII. Product rule ratios for some benzenes.

$C_6H_6:C_6D_6$			$C_6H_6:p\text{-}C_6H_4D_2$		
a_{1g}	τ_c	1.41	$a_{1g}e_{2g}/a_{1g}$	τ_c	1.41
	τ_0	1.40		τ_0	1.39
a_{2g}	τ_c	1.29	e_{1g}/b_{2g}	τ_c	1.00
	τ_0	1.28		τ_0	1.00
a_{2u}	τ_c	1.36	$a_{2g}e_{2g}/b_{1g}$	τ_c	1.37
	τ_0	1.35			—
b_{1u}	τ_c	1.41	$b_{1u}e_{1u}/b_{2u}$	τ_c	1.40
	τ_0	(1.40)		τ_0	1.40
			$p\text{-}C_6H_4D_2:p\text{-}C_6H_2D_4$		
b_{2g}	τ_c	1.41	a_{1g}	τ_c	1.41
	τ_0	(1.39)		τ_0	1.42
b_{2u}	τ_c	1.41	b_{2g}	τ_c	1.29
	τ_0	(1.41)		τ_0	1 28
e_{2g}	τ_c	2.00	b_{1g}	τ_c	1.37
	τ_0	1.97		τ_0	1.37
e_{2u}	τ_c	1.41	b_{3g}	τ_c	1.03
	τ_0	1.41		τ_0	1.03
e_{1g}	τ_c	1.29	b_{1u}	τ_c	0.99
	τ_0	1.28		τ_0	0.99
e_{1u}	τ_c	1.93	b_{2u}	τ_c	1.40
	τ_0	1.91		τ_0	1.38

4. D_{3h}

(a). $C(NH_2)_3^+$ (159, 260, 344)

The structure of the guanidinium ion is not unambiguously determined, but it appears to be more symmetrical than the closely related C_{2v} molecule urea. In agreement with the form pro-

TABLE XVIII. Observed frequencies for $C(NH_2)_3^+$ and $C(ND_2)_3^+$.

	$C(NH_2)_3^+$ in H_2O			$C(ND_2)_3^+$ in D_2O		
	Frequency	In	P	Frequency	In	P
ν_1	1015	8	P	921	8	P
ν_2	3290	3	—	2433	6	P
ν_3	1670	1	?	1278	1	P
e''	536	4	D	459	5	D
	1462	0	?			
e'	1565	2	D	1193	1	D
				2127	0	—
H_2O?	3212	3	—	2374	6	P

TABLE XIX. Symmetry elements and types for D_{3d} molecules.

D_{3d}	C_3	C_2	i	Rot. and trans.	Selection rules R	IR
A_{1g}	+	+	+		+	−
A_{1u}	+	+	−		−	−
A_{2g}	+	−	+	$R_{\parallel}$	−	−
A_{2u}	+	−	−	$T_{\parallel}$	−	+
E_g	$\epsilon\pm$	±	+	$R_{\perp}$	+	−
E_u	$\epsilon\pm$	±	−	$T_{\perp}$	−	+

posed by Pauling, Brockway, and Beach (349), we consider $C(NH_2)_3^+$ to be a planar ion with a C_3 axis perpendicular to it, and 3 planes of symmetry through the axis, making the total symmetry D_{3h}. This picture also is compatible with the x-ray diffraction patterns obtained by Theilacher (440).

The symmetry types for the D_{3h} point group were given in Table XI. For the guanidinium ion there should be three vibrations of type a_1', one of a_1'', two of a_2', two of a_2'', six of e', and two of e''. Approximate modes of displacement of type a_1' are given in Fig. 7. Assuming that frequencies of totally symmetric vibrations appear with the stronger intensities in the Raman effect, and knowing that a_1' frequencies should be polarized, we can make a plausible assignment of the three frequencies ν_1, ν_2, ν_3. Otvos and Edsall (159, 344) have studied the Raman effect of a solution of guanidinium chloride in H_2O, and of the deuterated chloride in D_2O, and have obtained the polarizations of some of the lines. The observed frequencies are given in Table XVIII with a tentative assignment to types. Unfortunately no infra-red data are available, and so the assignments are necessarily incomplete.

Kellner (260) has given a calculation of frequencies on the basis of an assumed potential function, but used only C_{3h} symmetry which would hardly be present without the ion also having the twofold axes perpendicular to the threfold axis. The data are not sufficient for a very rigid check on the calculations.

Assuming our assignments of the a_1' frequencies are correct, we can apply the product rule as a check. We find $\tau_c = 2.00$, and $\tau_0 = 1.95$, a deviation of 2.5 percent. However, there are three frequencies of that type, and so the deviation is less than 1 percent per frequency.

TABLE XX. Fundamental frequencies for ethane and ethane-d_6 (1. Estimated fundamental frequency from resonance doublet. 2. Calculated from overtone and combination band. 3. Given in (231)).

D_{3h}'	D_{3h}	D_{3d}		C_2H_6	C_2D_6
a_1	a_1'	a_{1g}	ν_1	2925[1]	2115[2]
			ν_2	1375[2]	1158
			ν_3	993	852
$\bar{a}_1$	a_1	a_{1u}	ν_4	(275)	[200]
$\bar{a}_2$	a_2''	a_{2u}	ν_5	2925[2]	2100[1]
			ν_6	1379	1072
e	e'	e_u	ν_7	2994[3]	2237
			ν_8	1486[3]	1102
			ν_9	821	601
$\bar{e}$	e''	e_g	ν_{10}	2960	2225
			ν_{11}	1460	1055
			ν_{12}	[1170]	970

5. D_{3d}

(*a*) C_2H_6 (27, 43, 49, 55, 98, 115, 171, 195, 197, 202, 204, 244, 256, 265, 291, 318, 327, 356, 426, 438, 472, 473)

The ethane molecule has at least D_3 symmetry for the equilibrium positions of the atoms, and possibly has D_{3d} (staggered form) or D_{3h} (eclipsed form) symmetry. Howard (244, 245) has shown, however, that the potential energy has a special D_{3h} symmetry for an arbitrary angle of orientation of one methyl group with respect to the other, which makes the selection rules more stringent than for a D_3 symmetry. This special D_{3h}' (a prime is used to distinguish it from the usual notation) group represents the molecule with free internal rotation of the methyl groups, and its selection rules are the same as those of the usual D_{3h} symmetry. When a potential restricting internal rotation is introduced, the vibrational selection rules are unchanged except for the staggered form. It has a center of symmetry, and one of the degenerate types becomes inactive in the Raman effect. The types for D_{3d} symmetry are given in Table XIX.

The heat capacities (264, 265) for gaseous C_2H_6 and C_2D_6 at low temperature show quite conclusively that there is a potential barrier restricting internal rotation in ethane with a magnitude of about 2750 calories per mole. Therefore one must consider C_2H_6 as having a D_{3h} or D_{3d} structure, with a potential barrier

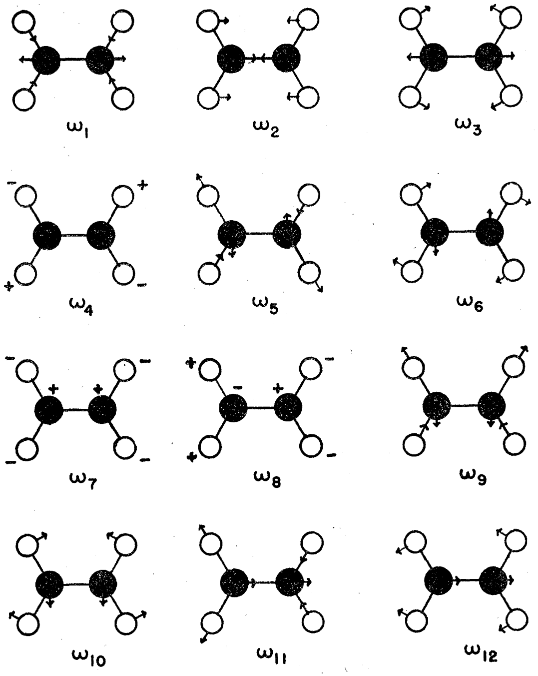

FIG. 8. Schematic description of vibrations of D_{2h} molecules X_2Y_4. (The notation is that given by Herzberg (231, page 326).)

restricting rotation from one form to the other, and a torsional oscillation ω_4 as one of the normal vibrations. The position of the first excited level of ν_4 is determined from specific heats to be 275 cm^{-1} above the ground level. Wilson (473) has calculated the first three levels assuming a cosine shape barrier of 2750 cal./mole, and the agreement is good. Using the same barrier for C_2D_6, the value $\nu_4' = 200$ cm^{-1} was obtained.

As has been pointed out by several writers, (115, 426), the spectroscopic data can be interpreted either on the basis of a D_{3h} or a D_{3d} structure. Therefore we have arbitrarily listed it as a D_{3d} molecule, deriving slight support from the report that heats of hydrogenation indicate it is the more stable form (265).

The fundamental frequencies for C_2H_6 and C_2D_6 are listed in Table XX as given by Crawford, Avery, and Linnett (115) and by Stitt (426). The frequencies for C_2D_6 are for the liquid. (The notation used is that given by Herzberg (231).) In the column for C_2H_6, the frequency in the bracket, $\nu_{12} = [1170]$, is one calculated by using the product rule and making an approximate correction for anharmonicity. The ν_4 frequencies are put in parentheses since they are determined indirectly as mentioned previously. If the symmetry is D_{3h}, ν_{12} of C_2H_6 and ν_{10}, ν_{11}, ν_{12} of C_2D_6 are not definitely determined from the vibrational spectra, but ν_{12} for C_2H_6 and ν_{11} for C_2D_6 must have values close to those assigned in order to get agreement with specific heat curves (251).

TABLE XXI. Product rule ratios for C_2H_6 and C_2D_6.

D_{3d}	a_{1g}	a_{2u}	e_u	e_g	a_{1u}
τ_c	2.00	1.82	2.58	2.35	1.41
τ_0	1.91	1.79	2.47	—	—

Assuming $r(C-H) = 1.013$A, $r(C-C) = 1.55$A, and $\angle HCH = 109°28'$, one can calculate the moments of inertia and the product rule τ's. The τ's are given in Table XXI. The deviations of τ_0 from τ_c in some cases are somewhat larger than we expect, but some of it can be assigned to uncertainties in the frequency values. The order rule is satisfied in every case, however.

6. $D_{2h}(V_h)$

(*a*). C_2H_4 (52, 57, 70, 84, 109, 110, 143, 171, 184, 197, 214, 215, 288, 301, 302, 303, 357, 431, 432, 436, 438, 442, 456, 492, 493, 496)

Ethylene is a planar molecule with a center of symmetry and two twofold axes perpendicular to each other. Substitution of one or of three of the hydrogen atoms by deuterium yields a C_s molecule, whereas replacement of two hydrogens can give rise to three different forms—symmetric $C_2H_2D_2$ and *cis*-$C_2H_2D_2$ which have C_{2v} symmetry, and *trans*-$C_2H_2D_2$ which has C_{2h} symmetry. C_2H_4 and C_2D_4, of course, have D_{2h} symmetry. The schematic vibrational modes for the D_{2h} molecules are given in Fig. 8, and the types for C_{2h} symmetry in Table XXII.

TABLE XXII. Symmetry elements and types for C_{2h} molecules.

C_{2h}	C_2^z	σ_{xy}	i	Rot. and trans.	Selection rules R	IR
A_g	+	+	+	R_z	+	−
A_u	+	−	−	T_z	−	+
B_g	−	−	+	R_x, R_y	+	−
B_u	−	+	−	T_x, T_y	−	+

TABLE XXIII. Fundamental frequencies for some ethylenes. (Numbers below symmetry designations indicate number of normal vibrations of that type.)

	C_2H_4	C_2D_4		C_2H_3D		C_2HD_3
ν_1	3019.3	2251.6		3104.8		2272
ν_2	1623.3	1514.7		3015.0		2215
ν_3	1342.4	981	a_1	2963.2	a_1	1545
ν_4	825	[585]	9	2266.3	9	1289
ν_5	3069	2304		1599.1		996
ν_6	1055	860		1395.7		919
ν_7	949.2	720.0		1284.2		
ν_8	950	780				
ν_9	3105.5	2345				
ν_{10}	995	740				
ν_{11}	2989.5	2200.2				
ν_{12}	1443.9	1077.9				

	cis-$C_2H_2D_2$		*trans*-$C_2H_2D_2$		asym. $C_2H_2D_2$
	3033		3046		2221
	2290		2276		1581
a_1	1567.3	a_g	1567.3	a_1	1379
5	1214	5	1282	5	
	763		863		
b_2 1	[845]	b_g 1	[870]	a_2 1	[715]

TABLE XXIV. Product rule ratios for some ethylenes.

	$C_2H_4:C_2D_4$						
D_{2h}	a_{1g}	a_{1u}	b_{1g}	b_{1u}	b_{2g}	b_{2u}	b_{3u}
τ_c	1.99	1.41	1.65	1.32	1.22	1.87	1.87
τ_0	1.92		1.63	1.32	1.22	1.78	1.82

$C_2H_4:a_1$ *cis*-$C_2H_2D_2$		$C_2H_4:a_g$ *trans*-$C_2H_2D_2$	
τ_c	1.93	τ_c	1.81
τ_0	2.02	τ_0	1.77

(Types for D_{2h}, C_{2v}, and C_s have been given in the discussion of benzene.) The plane of the molecule is taken as σ_{xy}, with the x axis along the C=C bond. Thus *cis*-$C_2H_2D_2$ has the elements $C_2{}^y$ and σ_{xy}; asymmetric $C_2H_2D_2$, $C_2{}^x$ and σ_{xy}; and C_2H_3D and C_2HD_3 have only σ_{xy}. For D_{2h} symmetry, ω_1, ω_2, ω_8, are a_{1g}; ω_4 is a_{1u}; ω_5, ω_6, are b_{1g}; ω_7 is b_{1u}; ω_8 is b_{2g}; ω_9, ω_{10} are b_{2u}; and ω_{11}, ω_{12} are b_{3u}. In comparing the symmetry types of some of these molecules, one finds the following have the same behavior with respect to common symmetry elements:

$$\begin{array}{lcl} D_{2h} & & cis\ C_{2v} \\ A_{1g}B_{2u} & \longleftrightarrow & A_1 \\ A_{1u}B_{2g} & \longleftrightarrow & A_2 \\ B_{1g}B_{3u} & \longleftrightarrow & B_1 \\ B_{1u}B_{3g} & \longleftrightarrow & B_2 \end{array} \qquad \begin{array}{lcl} D_{2h} & & trans\ C_{2h} \\ A_{1g}B_{1g} & \longleftrightarrow & A_g \\ A_{1u}B_{1u} & \longleftrightarrow & A_u \\ B_{2g}B_{3g} & \longleftrightarrow & B_g \\ B_{2u}B_{3u} & \longleftrightarrow & B_u \end{array}$$

$$\begin{array}{lcl} D_{2h} & & \text{asymmetric } C_{2v} \\ A_{1g}B_{3u} & \longleftrightarrow & A_1 \\ A_{1u}B_{3g} & \longleftrightarrow & A_2 \\ B_{1g}B_{2u} & \longleftrightarrow & B_1 \\ B_{1u}B_{2g} & \longleftrightarrow & B_2 \end{array}$$

By the selection rules, ν_4 for D_{2h} symmetry is forbidden to appear either in the Raman or infra-red spectrum as a fundamental. It is a torsional vibration of the two CH_2 groups about the C–C double bond and is expected to have a low frequency. Therefore it should make a noticeable contribution to the specific heat of ethylene. From a comparison of the experimental specific heat curve with calculated curves, Burcik, Eyster, and Yost (84) found good agreement using 828 cm^{-1} for ν_4. This is in substantial agreement with the earlier result of Eucken and Parts (171) who placed it in the interval 750–800 cm^{-1}, using less reliable values for the fundamentals. Another argument for a value near 825 cm^{-1} is the observed Raman line at 1654 cm^{-1} (67) which must represent the overtone of ν_4. There is no fundamental in C_2H_4 below 825 cm^{-1}, and so the 1654 cm^{-1} line can be explained only by resonance between $2\nu_4$ and ν_2, giving the overtone sufficient intensity to appear. ν_4 appears alone in its type and so can combine only with itself in order to interact with an a_{1g} vibration. No corresponding overtone is observed in C_2D_4 since no a_{1g} vibration is sufficiently close to $2\nu_4'$ for a noticeable interaction to take place. However, it is possible to get a reasonably accurate value of ν_4' by using the product rule, and $\nu_4=825$ for C_2H_4. This calculated value for ν_4' is 585 cm^{-1}.

The spectra of the partially deuterated ethylenes are not complete, and so we shall merely list the observed liquid frequencies (215) in probable symmetry types in Table XXIII, along with the assigned fundamentals for C_2H_4 and C_2D_4 (184). If a vibration of $C_2H_2D_2$ appears alone in its symmetry type, its frequency can be calculated from the known value for C_2H_4 by the use of the product rule. Such values are given in Table XXIV in brackets. Since the *cis*- and *trans*-isomers of $C_2H_2D_2$ have not been separated, and each preparation gives a mixture of both, only the spectrum of the mixture is observed. Therefore the assignment of frequencies to a given form is somewhat arbitrary. However,

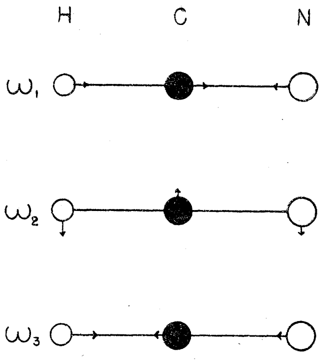

FIG. 9. Schematic description of vibrational forms for $C_{\infty v}$ molecules XYZ.

assuming that a_1 frequencies appear with the greater intensity in the Raman effect, it is possible to propose a tentative assignment by considerations of the product rule. Comparing C_2H_4 with *cis*-$C_2H_2D_2$, for a_1, $\tau_c = 1.932$, and with *trans*-$C_2H_2D_2$, for a_g, $\tau_c = 1.812$. Inserting the known values for the frequencies of C_2H_4 in τ_0 in each case, one arrives at the expression (215),

$$\frac{cis\text{-(product of frequencies of } a_1)}{trans\text{-(product of frequencies of } a_g)} = \frac{1.812(b_{2u}\nu\text{'s})}{1.932(b_{1g}\nu\text{'s})} = 0.89474.$$

There are five frequencies of type a_1 and five of type a_g. Assuming that the ten a frequencies appear with the highest intensity, and that the very intense line at 1567.3 cm^{-1} is a coincidence of frequencies for the oscillation of the CHD groups toward and away from each other, the assignment in Table XXIII is consistent with the data at hand. However, it must be emphasized that it is only tentative.

Potential functions for ethylene have been proposed by a number of writers (288, 303, 432, 436, 442, 496), and the frequencies for the deutero compounds calculated. The agreement is fair, but is not sufficiently close to decide which frequencies of the *cis-trans*-mixture belong to which molecule.

The rotational structure for several bands of both C_2H_4 and C_2D_4 has been resolved by Gallaway and Barker (184), and they obtained the following moments of inertia: $(\times 10^{40})$

$$C_2H_4\begin{cases} I_x = 5.750 \\ I_y = 28.09 \\ I_z = 33.84 \end{cases};\quad C_2D_4\begin{cases} I_x = 11.49, \\ I_y = 37.92, \\ I_z = 49.41. \end{cases}$$

These values determine the molecular dimensions to be: $r(C-H) = 1.071 \pm 0.010A$, $r(C-C) = 1.353 \pm 0.010A$, and $\angle HCH = 119° \; 55' \pm 30'$. With these dimensions one can calculate the moments of inertia for the partially deuterated compounds for the product rule applications. The calculated and observed τ's are given in Table XXIV. (Values for C_2H_4:C_2D_4 are from Gallaway and Barker (184).) The order rule is obeyed where it can be applied.

7. $C_{\infty v}$

(*a*). HCN (3, 25a, 44, 125, 133, 235, 257, 455, 464, 496)

Hydrogen cyanide is a linear molecule with three normal vibrations, one of which is doubly degenerate. The displacement forms are given in Fig. 9, ω_1 and ω_3 being of type σ, and ω_2 of type π. Since there is only one hydrogen atom in the molecule, substitution by deuterium cannot change the symmetry.

Adel and Barker (3) have assumed a potential function containing quadratic, cubic, and quartic terms consistent with the molecular symmetry, and obtained an energy expression similar to (1.2). Using observed overtones and combination tones, they have evaluated the anharmonic constants for HCN and obtained the normal frequencies. However, there is not sufficient data to carry out a similar procedure with DCN, and so all of the constants in the potential function have not been evaluated. Other authors have used simpler quadratic functions, and have obtained fair agreement between calculated and observed values.

The fundamental frequencies for the molecule are given in Table XXV. All frequencies shift to lower values in going from HCN to DCN, and the maximum ratio of ν/ν' is 1.259.

The vibrational-rotational structure for linear molecules was mentioned in the discussion of acetylene, and what was said there applies here.

TABLE XXV. Fundamental frequencies for HCN and DCN.

	HCN	DCN
ν_1	2089	1906
ν_2	712.1	569.1
ν_3	3312.9	2630.0

This structure in the infra-red has been studied by several authors (44, 235, 236, and 455), and the results for the moments of inertia and molecular dimensions are the following:

HCN	DCN
$I_e = 18.569 \times 10^{-40}$	$I_0 = 22.872 \times 10^{-40}$
$I_0 = 18.695 \times 10^{-40}$	

$$r_e(\mathrm{H-C}) = 1.057\mathrm{A} \quad r_e(\mathrm{C-N}) = 1.149\mathrm{A}$$
$$r_0(\mathrm{H-C}) = 1.057\mathrm{A} \quad r_0(\mathrm{C-N}) = 1.154\mathrm{A}.$$

Applying the product rule to the observed frequencies one gets the results given in Table XXVI. The deviation between the τ's is in the direction we expect, and is less than 1 percent. Since the normal frequencies for HCN have been determined, one can calculate ω_2 and the product $(\omega_1\omega_3)$ for DCN merely by using the product rule, as it then is an exact relation.

(*b*). $(\mathrm{FHF})^-$ (80, 85, 192, 261, 262, 489)

A very brief report* (261) on the infra-red reflection and absorption curves for $\mathrm{KHF_2}$ and $\mathrm{KDF_2}$ has appeared, and although we are not in agreement with the interpretation given in that paper, the data are interesting. The $\mathrm{KHF_2}$ crystal is composed of $\mathrm{K^+}$ and $\mathrm{HF_2^-}$ ions, the vibration of the latter giving rise to certain of the infra-red frequencies. X-ray diffraction studies (75, 209) have given the crystal structure of $\mathrm{KHF_2}$ as that in Fig. 10. The positions of the hydrogen atoms are not determined by the diffraction patterns, and so are not indicated in the diagram. A treatment of the $[\mathrm{FHF}]^-$ ion by Pauling (347) from an ionic H−F bond point of view led to a symmetrical linear equilibrium configuration of the three atoms. Although the F−H−F distance calculated was in fair agreement with the experimental values, the assumptions were perhaps a little too strong to correspond to the actual case. Nevertheless, it seems very likely that the ion is linear with the H atom some place in the vicinity of the symmetrical position.

Table XXVI. Product rule ratios for HCN and DCN.

$C_{\infty v}$	σ	π
τ_c	1.39	1.26
τ_0	1.38	1.25

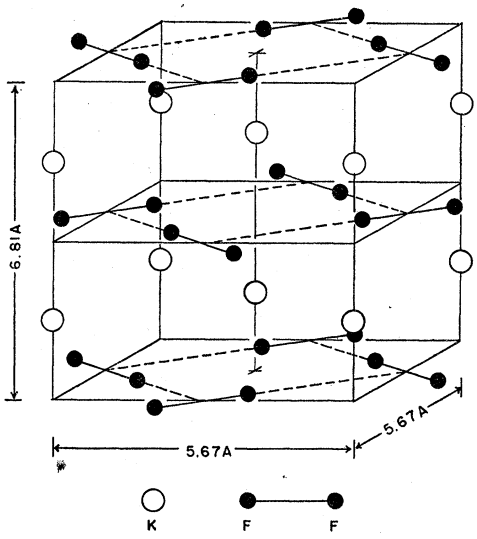

Fig. 10. Crystal structure of $\mathrm{KHF_2}$ (as given by Bozorth).

The internuclear distance in the hydrogen fluoride molecule is 0.9166A, and the fundamental frequency is $\nu = 3960\ \mathrm{cm^{-1}}$ (230). In the $[\mathrm{FHF}]^-$ ion, the F−H−F distance is 2.26±0.01A, and a symmetrical position would be 1.13A from either F atom. That is an increase of 0.21A in the H−F distance which seems quite large even for very strong hydrogen bonding. However, it would not seem improbable for two potential functions with minima 0.92A from the two fluorine atoms to combine to give a single potential function with two minima separated by a small potential barrier. Such a double minimum would tend to split the various frequencies, in particular that of the hydrogen vibration along the axis of the molecule.

In a study on liquid water (123), it was found that hydrogen bonding of the type occurring in $\mathrm{HF_2^-}$ perturbed the O−H frequency downward by about 6.7 percent. Assuming a similar shift in HF going to $\mathrm{HF_2^-}$, we will expect a frequency in the neighborhood of $3700\ \mathrm{cm^{-1}}$. If there is a double potential minimum in the ion, we will expect this frequency to be double. A band has been observed (85) in the absorption spectrum of $\mathrm{KHF_2}$ at $3745\ \mathrm{cm^{-1}}$, with a doublet structure whose two components have maxima at 3775

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* Reference (262) has not been available.

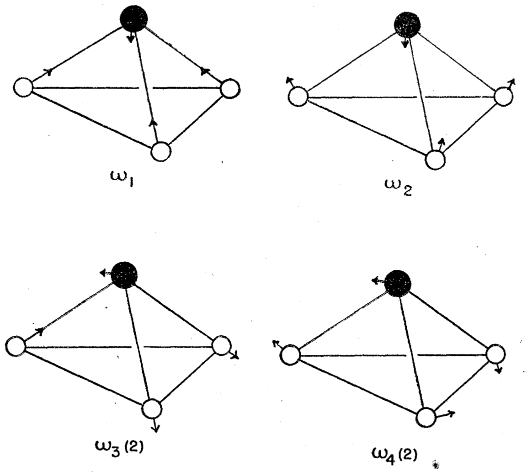

FIG. 11. Schematic description of vibrations for C_{3v} molecule XY_3.

cm^{-1} and 3664 cm^{-1}. This would seem to indicate a $C_{\infty v}$ structure for the ion.

Although the data at hand are not sufficiently complete to justify any extensive statements concerning a double minimum in [FHF]$^-$, one might try to find out if there is anything on the quantitative side which would rule out such a possibility. The problem of a particle moving in a potential field containing two equal minima has been treated by a number of authors (146, 249, 283, 323, 462). The application to the bifluoride ion has been made independently by Glockler and Evans (192) and by Halverson* using slightly different methods, but the results are the same. Using the method developed by Dennison and Uhlenbeck (148), and assuming the potential curve to be given by two equal intersecting parabolas, one can calculate the distance between the minima of these parabolas from the splitting of any one of the energy levels. However, the infra-red selection rules allow only transitions between levels of different symmetry ($s \leftrightarrow a$) with respect to inversion of coordinates, and so the observed splitting of ν is the sum of the splitting of the ground level and the first excited level. Since no other data are available (the Raman effect apparently being very weak (489)), the ground state splitting is assumed negligible compared to that of the first excited state, and the separation of potential minima calculated on that basis. An unperturbed $\nu = 3745$ cm^{-1}, with a splitting of 111 cm^{-1}, yields a minima separation of 1.0A. That would make the H$-$F distance 0.88A which seems rather small compared to 0.92A which we might expect. However, it does not exclude the possibility of a double minimum, particularly because of the assumptions made and because of the negative charge on the ion which has some effect on the bonding.

A $C_{\infty v}$ ion should have a doubly degenerate vibration corresponding to a motion of the hydrogen toward and away from the axis, with a frequency in the region of 1400 cm^{-1}. However, Ketelaar reports two frequencies for the crystal in this region, one at 1222 cm^{-1}, and the other at 1450 cm^{-1}, both very strong bands and therefore presumably fundamentals. In order to explain the presence of two fundamental bands, it is necessary to assume a perturbation of the original cylindrical symmetry (with respect to the forces acting on the nuclei) giving rise to preferred directions for perpendicular vibrations. The solution is immediately apparent when we consider the crystal structure (the spectra being for the crystal), since the inter-ionic H$-$F distance in the fluorine plane is ~2.1A, whereas in a direction perpendicular to that plane it is ~3.5A. Because of inter-ionic hydrogen bonding, the cylindrical symmetry is gone, and the degenerate vibration splits to give a frequency 1222 cm^{-1} in the fluorine plane, and one at 1450 cm^{-1} perpendicular to that plane. Ascribing a $C_{\infty v}$ structure (or also for $D_{\infty h}$ symmetry) to the [FHF]$^-$ ion in free space, the motion of the H atom perpendicular to the F$-$F axis can be described by a plane isotropic oscillator. Using this as a zero-order approximation, the effect of crystal forces on this normal vibration can be approximated by adding a perturbing potential of the form $-kr^2\cos^2\varphi$. The plane isotropic oscillator has been discussed in detail by Dennison (145), who has also tabulated the wave functions for the lower states. First-order perturbation theory for the doubly degenerate first excited level gives the expression

$$W^{\pm}/hc = W_1^0/hc \pm \epsilon/hc,$$

$$\epsilon = \int \psi_{+1}[-kr^2\cos^2\varphi]\psi_{-1}d\tau$$
$$= -hk(4\pi^2\mu c\nu)^{-1}, \quad (b.\ 1)$$

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* Dissertation, The Johns Hopkins University.

where ϵ is the energy perturbation term, W_1^0 is the unperturbed energy, and W is the perturbed energy. Since the transitions originate from the same ground level, the difference between the two frequencies 1222 cm^{-1} and 1450 cm^{-1} corresponds to the split in W_1^0, that is

$$(W^+ - W^-)/hc = 2\epsilon/hc = 228\ \text{cm}^{-1}.$$

From (*b*. 1) we find that $k = 0.09 \times 10^5$ dynes per cm which is certainly of the right order of magnitude.

Ketelaar infers a fundamental frequency ~560 cm^{-1} from various combination bands in the region he studied, which he assigns to the oscillation of the fluorine atoms toward and away from each other. In the spectrum of KDF_2 the frequencies 1222 cm^{-1} and 1450 cm^{-1} shift to 880 cm^{-1} and 1020 cm^{-1},* respectively, and the combination frequencies shift in such a fashion as to indicate little or no change in the 560 cm^{-1} frequency. The shift of the perpendicular frequencies is about what one would expect, 1.38:1.

8. C_{3v}

(*a*). NH_3 (28, 32, 36, 37, 48, 106, 134, 146, 148, 151, 152, 198, 243, 304, 310, 311, 390, 416, 435, 446, 455, 462, 490)

Ammonia has a symmetrical pyramidal structure giving it C_{3v} symmetry. Substitution of one or two hydrogen atoms by deuterium yields a C_s structure, whereas replacement of all three retains the original symmetry. The displacement forms for the C_{3v} molecule are given in Fig. 11. Of these, ω_1 and ω_2 are of type a_1, and ω_3 and ω_4 of type e in Table II. The loss of the threefold axis causes ω_3 and ω_4 in NH_3 to split into nondegenerate forms in the C_s molecules.

Potential functions for the pyramidal C_{3v} molecule, together with vibrational frequency calculations, have been discussed by several authors (146, 243, 246, 394, 397), and Howard (243) has calculated a set of frequencies for NHD_2. A more accurate method for calculating these values has been outlined by Dennison (146), but has not been carried out.

In ammonia the N-atom has two equilibrium positions which are physically indistinguishable from one another—one on either side of the H-triangle. Although the normal vibrations are for motions in an infinitesimal region surrounding a given equilibrium position, the presence of the double minimum affects them due to the "tunnel effect." There is a potential hill of height V_0 impeding the motion of the N-atom in going from one minimum to the other, which is a function of the normal coordinates, and no doubt depends chiefly on the coordinate corresponding to ω_2 in which the H-triangle widens out. The effect of ω_1 in which the H-triangle closes up as the N-atom approaches it, and of the perpendicular vibrations ω_3 and ω_4, must be very small. The problem has therefore been treated as a one-dimensional system having a double minimum (148). In such a system each vibrational state is split into two states, one symmetric and the other antisymmetric with respect to reflection in the H-plane. Transitions giving rise to infra-red absorption are allowed only between levels of different symmetry, and so a doubling of the original single band is observed, with a separation between the two components equal to the sum of the splitting separations of the two original states involved. This explanation was first given qualitatively by Hund (236) to interpret the doubling of the parallel bands in NH_3 (ω_1 splits only very slightly) and has since been treated quantitatively by a number of writers (148, 304, 323, 462).

The fundamental frequencies as listed by Dennison (146) in his review paper are given in Table XXVII. This table also serves as a comparison of frequencies of isotopic molecules. For NH_2D and NHD_2 the ν_2 infra-red doublets are 874–894 and 808–818 cm^{-1}, respectively (311).

The pure rotational structure of ammonia has been investigated by several people (20, 36, 37, 490). Because of the selection rule allowing

TABLE XXVII. Fundamental vibrational frequencies [NH_3 and ND_3 from (146, 311); PH_3 and PD_3 from (287); AsH_3 and AsD_3 from (287)].

	NH_3	ND_3	PH_3	PD_3	AsH_3	AsD_3
ν_1	3336	2419	2327	1694	2122	1534
ν_2	933 966	745.8 749.2	990.0 992.4	730	906	660
ν_3	3414	2555	(2421)	[1730]	(2185)	[1560]
ν_4	1627.5	1191	1121.4	806	1005	714

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* Reflection corrected approximately to absorption.

TABLE XXVIII. Product rule ratios.

C_{3v}		NH_3:ND_3	PH_3:PD_3	AsH_3:AsD
a_1	τ_c	3.39	1.92	1.96
	τ_0	3.08	1.87	1.90
e	τ_c	3.50	1.95	1.98
	τ_0	3.34	—	—

transitions only between levels of opposite symmetry, the rotational lines are doublets with a separation equal to twice the splitting of the ground state. The doublet separation observed is 1.33 cm^{-1}, giving the splitting of the normal state as 0.67 cm^{-1}. From these lines the moment of inertia about an axis perpendicular to the symmetry axis is determined to be 2.814×10^{-40} g cm^2. Barnes (36) also measured the pure rotational lines for ND_3, from which $I_\perp=5.447\times10^{-40}$ g cm^2 is obtained. The moment of inertia about the symmetry axis cannot be found from these lines, but there are a number of ways to get it, which are discussed by Dennison (146). The values obtained are: NH_3, $I_{\parallel}=4.452\times10^{-40}$ g cm^2; ND_3, $I_{\parallel}=8.898\times10^{-40}$ g cm^2. The $\parallel$ bands show the fine structure expected for a symmetrical rotator, with the calculated intensity alternations. The dimensions of the molecule are: (146)

$$r(\mathrm{N-H})=1.014\mathrm{A},\quad \angle\mathrm{HNH}=107°3',$$
$$\text{Height of pyramid}=0.377\mathrm{A}.$$

The transition from the symmetric ground state to the antisymmetric one has been measured by Cleeton and Williams (106) who found good agreement with $\nu=0.67$ cm^{-1}. The splitting of the levels indicates a potential barrier of 1700–2000 cm^{-1}.

The calculated and observed product rule τ's are given in Table XXVIII. We have used the average value of ν_2 in getting τ_0. The double minimum potential greatly affects ν_2, however, and makes it far more anharmonic than would normally be the case. As a result, τ_0 deviates by about 9.3 percent from τ_c for the symmetry type a_1. In e we also have a relatively large deviation, 4.7 percent, whereas we would expect about 2 percent by analogy with C–H vibrations.

(*b*). PH_3 (149, 182, 211, 212, 213, 243, 278, 287, 383, 393, 424, 430, 433, 490, 496, 498)

Phosphine has the same structure as ammonia, and so Fig. 11 and Table II apply equally well to it. However, much less data are available. The potential functions for a pyramidal C_{3v} molecule are applicable and have been applied by Howard (243) and by Hemptinne and Delfosse (212). The frequencies for the ω_1, ω_2, and ω_4 vibrations are quite well known and were used for the evaluation of potential constants. ν_3 was then calculated to be somewhat higher than ν_1, which is what we expect for an antisymmetrical hydrogen valence vibration compared to the symmetrical one. Lee and Wu (287) list the frequency 2421 cm^{-1} for ν_3 in PH_3, which is of the right order of magnitude, but we have not been able to find any reference explicitly giving that as an observed frequency. Therefore, in Table XXVII, which contains the observed fundamentals, we put that frequency in parentheses.

One expects phosphine, like ammonia, to have a double minimum, and the question arises whether the energy levels will have an observable splitting. The height of the pyramid in PH_3 will be larger than in NH_3 and conceivably can increase the potential barrier to such an extent that no observable splitting takes place. There are two strong bands, however, observed at the position for ν_2, one at 990.0 cm^{-1} and the other at 992.4 cm^{-1}. Since no other fundamental should fall that close to ν_2, it seems logical to assign the doublet to ν_2. There is a complicating factor. Fung and Barker (182) resolved the rotational structure of the doublet and give as the average spacing of the 990 cm^{-1} band $\Delta\nu=8.5$ cm^{-1}, and for the 992 cm^{-1} band, $\Delta\nu=11$ cm^{-1}. The first spacing is characteristic of a parallel band, and the second of a perpendicular band, whereas for a split frequency we expect both to have a parallel band structure. It might be argued that one of these is the ν_3 fundamental, but the success of the potential functions in predicting the observed frequencies of PD_3 discounts such an error in ν_3. Therefore it seems necessary to account for the anomalous rotational spacing on the basis of interactions.

The pure rotational spectrum of phosphine has been studied by Wright and Randall (490), but they found no doubling of the lines such as occurred in ammonia. This is to be expected since the sum of the splitting of the ground and first excited levels is only 2.4 cm^{-1}. The average spacing of the lines was about 8.7 cm^{-1}, giving as the perpendicular moment of inertia of PH_3, $I_\perp = 6.221\times10^{-40}$ g cm^2. There are not sufficient data available for an accurate determination of the moment of inertia around the symmetry axis. From the absence of the expected intensification of every third line in the vibrational-rotational spectrum of the perpendicular bands for such a molecule, Fung and Barker suggested that it might be a spherical top with an $\angle H-P-H = 88\frac{1}{2}°$. However, chemical bond theory prefers an angle of 90° or larger. Stevenson (424) has suggested an $\angle H-P-H = 93° \pm 2°$ from considerations of ionic radii and $I_\perp = 6.221\times10^{-40}$ g cm^2. Assuming an angle of 93°, and $r(P-H) = 1.415A$, one calculates $I_{\parallel}$ for PH_3 to be 6.95×10^{-40} g cm^2. By using these values for the molecular dimensions, the product rule may be applied, with the results given in Table XXVIII. The frequency ν_3 for PD_3 has not been observed, and the value given in brackets in Table XXVII is the one calculated by the product rule.

(*c*). AsH_3 (141, 212, 213, 243, 287, 342, 393, 424, 433)

The structure of arsine is completely analogous to that of phosphine and ammonia. The same potential functions with a re-evaluation of constants are valid, and have been used to calculate frequencies for the deuterated molecule. Using ν_1, ν_2, and ν_4 to evaluate the constants, the calculated ν_3 is slightly larger than ν_1 (212, 243), as was the case in phosphine also. Lee and Wu (287) list the frequency 2185 cm^{-1} for ν_3 in AsH_3, which again is of the right order of magnitude, but we have not been able to find any reference explicitly giving that as an observed frequency. Therefore, that frequency is put in parentheses in Table XXVII, which contains the observed fundamentals.

Since arsine has the same structure as ammonia one might expect a doubling of the parallel vibrations owing to the double minimum. However, no splitting has been observed, and it is necessary to conclude that the potential barrier is too high for the double minimum to have any significant effect on the energy levels.

TABLE XXIX. Fundamental frequencies for the chloroforms (379) and the bromoforms (383).

	$CHCl_3$	$CDCl_3$	$CHBr_3$	$CDBr_3$
ν_1	669	650.5	538.6	519.3
ν_2	761	738	656	628.5
ν_3	365	365	222.3	221.6
ν_4	261	261	153.8	153.4
ν_5	3019	2253	3023	2247
ν_6	1218	909	1142	848

The rotational structure of several vibrational bands of AsH_3 has been resolved, but when interpreted on the basis of simple theory, there is no agreement among the moments of inertia obtained (342). A value 7.4×10^{-40} g cm^2 for $I_{\parallel}$ of AsH_3 is obtained by Lee and Wu (287) from the somewhat irregular structure of the 2122 cm^{-1} band, which is of the order of magnitude one expects. From considerations of related compounds, Stevenson (424) suggests an $\angle HAsH = 90°$ and $r(As-H) = 1.53A$. This $r(As-H)$ seems a little long, and so we have taken $r(As-H) = 1.51A$ as given by Pauling's table of covalent radii (347). We then obtain 7.4×10^{-40} g cm^2 for $I_\perp$ of AsH_3.

The results of applying the product rule are given in Table XXVIII. The frequency ν_3 for AsD_3 has not been observed, and the one bracketed in Table XXVII is the value calculated by the product rule.

(*d*). $CHCl_3$ (88, 129, 208, 219, 371, 378, 379, 380, 445, 487, 488, 496)

Chloroform has the same symmetry as the mono- and tri-deutero substituted methanes, and so the same notation can be used for the vibrational forms and symmetry types. The most general potential function for such a molecule, with five constants, has been employed by Voge and Rosenthal (457) to calculate frequencies, and since there are six fundamentals for $CHCl_3$, all of the constants can be evaluated. It was used to calculate the fundamentals for $CDCl_3$, but the agreement with observed values is not very good, due primarily to incomplete data as to the anharmonicity. The observed frequencies for the liquid state are given in Table XXIX,

TABLE XXX. Product rule ratios for $CHCl_3$:$CDCl_3$ and $CHBr_3$:$CDBr_3$.

C_{3v}		$CHCl_3$:$CDCl_3$	$CHBr_3$:$CDBr_3$
a_1	τ_c	1.41	1.41
	τ_0	1.38	1.41
e	τ_c	1.40	1.40
	τ_0	1.38	1.41

TABLE XXXI. Fundamental frequencies for $SiHCl_3$, $SiDCl_3$, $SiHBr_3$, and $SiDBr_3$.

	$SiHCl_3$	$SiDCl_3$	$SiHBr_3$	$SiDBr_3$
ν_1	489	489	362	360
ν_2	587	555	470	468
ν_3	250	252	166	167
ν_4	179	179	115	114
ν_5	2258	1647	2236	1616
ν_6	799	[605]	770	[560]

which also indicates the shift of frequencies on deuterium substitution. One notices that in the vibration ω_3 there is no shift in going from $CHCl_3$ to $CDCl_3$, which indicates ω_3 must be a mode of motion in which the H or D atom is essentially at rest. (Even if we consider the C−H moving as a unit, η in Eq. (5.3) of Part I must be very small if we are not to get a measurable $\Delta\omega$.) Thus ω_3 must be a symmetrical breathing vibration of the Cl_3 triangle, with the C−H group almost stationary. On the other hand, ω_1 must be a vibration of the C−H group toward and away from the chlorine triangle (in order to have orthogonal normal vibrations). Therefore the most appropriate symmetry coordinates one can choose to describe the parallel vibrations are a symmetrical breathing of the Cl_3 plane, a motion of the C−H group along the axis toward and away from the Cl_3 plane, and a motion of the H atom along the axis toward and away from the CCl_3 group. This is in agreement with the usual result that a valence force function does not describe motions of the heavy atoms very well, but is satisfactory for light atoms. If one assumes that the symmetry coordinates mentioned are good approximations to the normal coordinates, the effect of deuterium substitution on the vibration ω_1 can be readily calculated by considering the C−H group as a unit and using Eq. (5.3). Using the condition of zero linear momentum, one calculates $\eta_{C-H}^{\omega_1}$ to be between 0.8 and 0.9 for ω_1. Since $\sigma = 1/13$, $\Delta\omega_1$ indicates a drop of 20 to 22 wave numbers. From Table XXIX one notes that the observed frequency drop is 18.5 cm^{-1}, which is in good agreement with the approximate calculation. A similar discussion applies to $CHBr_3$. If one makes similar calculations for $SiHCl_3$ and $SiHBr_3$, however, the frequency shift is of the order of magnitude of 5 cm^{-1}, which is inside the possible error of measurement of the observed lines. Thus one does not anticipate a noticeable isotope shift in ω_1 for those molecules.

No spectroscopic data are available concerning the dimensions of the $CHCl_3$ molecule, but they have been determined by electron diffraction (434). In the calculation of moments of inertia for the application of the product rule, we assume $r(C-H) = 1.09A$, and use the measured values $r(C-Cl) = 1.78 \pm .03A$, $r(Cl-Cl) = 2.93 \pm .02A$, and $\angle ClCCl = 111° \pm 2°$. The calculated and observed τ's are given in Table XXX.

(*e*). $CHBr_3$ (62, 383, 387)

Bromoform is analogous to chloroform and should have six fundamentals, all active in both infra-red absorption and the Raman effect. Redlich and Stricks (383) found six frequencies in the Raman effect for liquid $CHBr_3$, but in liquid $CDBr_3$, seven frequencies were found. Two of them, 840 cm^{-1} and 856.5 cm^{-1}, are of about the same intensity, and only 16.5 cm^{-1} apart, which makes it appear that the extra frequency is perhaps the result of resonance. Therefore the observed doublet 840 cm^{-1} − 856.5 cm^{-1} is assigned to resonance between a combination band $221.6 + 628.5 = 850.1$ cm^{-1} and a fundamental at about 848 cm^{-1}, both of which are of the *e* type. The observed fundamentals in the liquid state are given in Table XXIX.

Since the frequencies for $CHCl_3$ and $CDCl_3$ are known, one could use the ratio rule and the frequencies for $CHBr_3$ to calculate the fre-

TABLE XXXII. Product rule ratios.

C_{3v}		$SiHCl_3$:$SiDCl_3$	$SiHBr_3$:$SiDBr_3$
a_1	τ_c	1.41	1.41
	τ_0	1.36	1.38
e	τ_c	1.40	1.40
	τ_0	—	—

TABLE XXXIII. Fundamental frequencies for methyl halides (ν_1 for CH_3Cl is an estimated value (317). In CD_3Cl, Nielson and Nielson found ν_1 and $2\nu_4$ very close together, hence the observed value is listed; ν_1 for CH_3Br is also an estimated value).

	CH_3Cl	CD_3Cl	CH_3Br	CD_3Br
ν_1	(2920)	2160	(2930)	2134
ν_2	3047	2300	3061	2294
ν_3	1355	1030	1305	987
ν_4	1460	1081	1450	1053
ν_5	732	701	610	577
ν_6	1020	775	957	717

TABLE XXXIV. Product rule ratios.

C_{3v}		$CH_3Cl:CD_3Cl$	$CH_3Br:CD_3Br$
a_1	τ_c	1.94	1.97
	τ_0	1.86	1.92
e	τ_c	2.40	2.47
	τ_0	2.36	2.45

quencies of $CDBr_3$. If one considers ν_1, the ratio rule becomes

$$\nu_1(CDBr_3)=\frac{\nu_1(CDCl_3)}{\nu_1(CHCl_3)}\nu_1(CHBr_3),$$

and one calculates $\nu_1(CDBr_3)=524$ cm^{-1}. The measured value is 519.3 cm^{-1}, and so the error introduced in ν_1 is about 1 percent.

For the calculation of the moments of inertia, the molecular dimensions (220, 290) used are: $r(C-H)=1.09A$, $r(C-Br)=1.91A$, and $r(Br-Br)=3.16A$. The calculated and observed τ's are given in Table XXX. The e type contains some bending frequencies, and so it is not too surprising that $\tau_0>\tau_c$.

(*f*). $SiHCl_3$ (141, 210, 217, 219, 452)

Silicochloroform has also been studied in the liquid state by means of the Raman effect. The observed fundamentals for the liquid are given in Table XXXI. The frequency ν_3 is listed as being slightly larger in $SiDCl_3$ than it is in $SiHCl_3$, which may be caused by different observers. ν_6 for $SiDCl_3$ has not been observed, and the value given in the square bracket is calculated from the product rule. Notice that within the accuracy of measurements, no shift is observed for ν_1 in going from $SiHCl_3$ to $SiDCl_3$.

Hemptinne (210) has made some calculations of the frequencies from an assumed potential function for the $-SiBr_3$ part of the molecule. The calculated values give the order of magnitude, but do not agree very closely with the observed values.

Electron diffraction studies (81) of the molecule yield the dimensions: $r(Si-Cl)=2.01\pm0.03A$, $r(Cl-Cl)=3.29\pm0.03A$, and $\angle ClSiCl=110°\pm1°$. Assuming $r(Si-H)=1.51A$, which is between the values given by Stevenson (424) and by Wu (496), and which is about 0.02A less than the Si−H internuclear distance, as one might expect on going to the tetrahedral valence state, one can calculate the moments of inertia and apply the product rule. The results are given in Table XXXII.

(*g*). $SiHBr_3$ (141, 142)

Silicobromoform, like silicochloroform, has been studied in the liquid state by means of the Raman effect. The observed fundamental vibrational frequencies of the liquid are given in Table XXXI. ν_6 has not been observed for $SiDBr_3$, and the value in the square bracket is the one obtained from the product rule.

Although no spectroscopic data concerning the dimensions of $SiHBr_3$ are available, one can arrive at values from which to calculate the moments of inertia which will not introduce much of an error in the ratio of the moments of the two isotopic molecules. Pauling's table of covalent radii (347) gives the Si−Br distance as 2.31A, but since the table gives a value 7 percent too high for $r(Si-Cl)$, we shall assume $r(Si-Br)=2.15A$. (A discussion of this deviation is given by Pauling.) The value 110°±2° for the $\angle BrSiBr$ from electron diffraction data is also given by Pauling (347). By assuming $r(Si-H)=1.51A$, the moments of inertia can be calculated and the product rule applied. The results are given in Table XXXII.

(*h*). CH_3Cl (2, 33, 50, 146, 210a, 213a, 331, 339)

The methyl halides have been studied by a number of investigators. The fundamental frequencies (using the notation in Fig. 3) for CH_3Cl and CD_3Cl as listed by Nielsen and Nielsen (338) are given in Table XXXIII. For CH_3Cl, ω_1 resonates with $2\omega_4$, giving rise to the two parallel

TABLE XXXV. Fundamental frequencies for *trans*-$C_2H_2Cl_2$ and *trans*-$C_2D_2Cl_2$.

C_{2h}		*Trans*-$C_2H_2Cl_2$	*Trans*-$C_2D_2Cl_2$
a_g	ν_1	3072	2325
	ν_2	1575	1570
	ν_3	1271	992
	ν_4	840	765
	ν_5	350	346
a_u	ν_6	820	——
	ν_7	(270?)	——
b_g	ν_8	752?	657?
b_u	ν_9	3090	——
	ν_{10}	1200	——
	ν_{11}	917	——
	ν_{12}	——	——

TABLE XXXVI. Product rule ratios for *trans*-$C_2H_2Cl_2$ and $C_2D_2Cl_2$.

	Trans-$C_2H_2Cl_2$: $C_2D_2Cl_2$	
C_{2h}	a_g	b_g
τ_c	1.97	1.20
τ_0	1.89	1.15

bands at 2967 cm^{-1} and 2878 cm^{-1} in the vapor (50), which would place ω_1 without interaction at roughly 2920 cm^{-1}. In CD_3Cl, Nielsen and Nielsen report a resonating triplet, $2\omega_4$, ω_1, $2\omega_3$, a case in which deuterium substitution increased the number of interactions. The frequency $\nu_6=775$ cm^{-1} for CD_3Cl is one reported by Noether (339), which Nielsen and Nielsen did not locate. The fine structure of the parallel bands appears to be normal in all respects, but the perpendicular bands show the variable spacing from one band to the next indicating coupling between vibrational and rotational angular momenta (146). Assuming a tetrahedral shape for the methyl group, and taking $r(C-H)=1.093A$ and $r(C-Cl)=1.72A$, one can calculate the moments of inertia and apply the product rule. The calculated and observed τ's are given in Table XXXIV. Since the product rule was derived on the basis of a harmonic potential function, perturbations involving terms of the third degree such as resonance between ω_1 and $2\omega_4$ will tend to give rise to a discrepancy between τ_c and τ_0. If the resonance is pronounced, it is perhaps advisable to estimate the unperturbed frequency and use it in the product rule check.

The general potential function consistent with the symmetry of the molecule has been treated by Voge and Rosenthal (457), but it contains twelve constants and there are only six normal frequencies (unless CD_3Cl is used). Several physically plausible functions with fewer constants have been proposed (146, 293, 339) which give reasonably good agreement where they can be checked.

(*i*). CH_3Br (2, 33, 50, 146, 210a, 213a, 339)

The fundamental frequencies for CH_3Br and CD_3Br are given in Table XXXIII as listed by Noether (339), and the calculated and observed τ's in Table XXXIV. A tetrahedral structure was assumed for the methyl group, together with $r(C-H)=1.093A$ and $r(C-Br)=1.90A$ as given by Linnett (276), in calculating moments of inertia.

9. C_{2h}

(*a*). *Trans*-$C_2H_2Cl_2$ (87, 165, 301, 351a, 447, 448, 451, 491, 492, 496)

Trans-dichloroethylene has the same symmetry as *trans*-dideuteroethylene, and so Table XXIII applies to it as well. For this C_{2h} molecule, six fundamentals are Raman active and six are infra-red active. The frequency of torsional oscillation of the two CHCl groups with respect to each other is allowed in the infra-red, but has not been assigned with certainty. Wu (492) suggests 917 cm^{-1} for the torsional oscillation, which seems high when compared to 825 cm^{-1} for C_2H_4. (In *cis*-$C_2H_2Cl_2$ a Raman frequency at 406 cm^{-1} has been observed (447) which is more of the order of magnitude one might expect.) Pitzer and Freeman (351a) suggest 270 cm^{-1} on the basis of force constant comparisons and the assignment of the infra-red band at 620 cm^{-1} to an overtone ($\nu_7+\nu_5$). Some of the overtones observed in infra-red absorption by the liquid may be interpreted as involving a fundamental of about 270 cm^{-1} (496), but they are not conclusive. Pitzer and Freeman also suggest 820 cm^{-1} for the unsymmetrical wagging of the CHCl groups (ν_6) in order to get consistent force constants for the chloroethylenes.

A schematic description of the normal modes for both *cis*- and *trans*-dichloroethylene is given by Herzberg (231, page 331) and will not be repeated here. His notation is used however.

The fundamental frequencies for the *trans*-dichloroethylenes are given in Table XXXV. The g-types are liquid frequencies, and the u-types are vapor frequencies. ν_7, the torsional frequency, has been put in parentheses because of its uncertainty. The frequency $\nu_8 = 752$ cm^{-1} has a question mark since Trumpy (448) reports the degree of depolarization to be only 0.70. He also reports the corresponding line in *trans*-$C_2D_2Cl_2$ to be 657 cm^{-1} (no polarization studies are mentioned).

Brockway, Beach, and Pauling (82) have made an electron diffraction study of the dichloroethylenes and give the following data for the *trans*-compound: $r(C-C) = 1.38A$ (assumed), $r(C-Cl) = 1.69 \pm .02A$, $r(Cl-Cl) = 4.27 \pm .02A$, and $\angle ClCC = 122.5° \pm 1°$. Using these values to calculate the moments of inertia, the product rule can be applied to the a_g and b_g types. The results are given in Table XXXVI.

10. C_{2v}

(*a*). H_2O (1, 4, 5, 6, 7, 8, 8a, 29, 34, 40, 41, 46, 56, 60, 72, 91, 92, 93, 94, 97, 104, 123, 149a, 158, 161, 162, 163, 168, 181, 183, 199, 200, 229, 238, 258, 279, 299, 306, 343, 355, 362, 364, 365, 366, 368, 407, 409, 417, 455, 478, 479, 480, 481, 482, 418, 408, 47, 367)

The water molecule has the form of an isosceles triangle with the oxygen atom at the apex, giving it C_{2v} symmetry. Substitution of one hydrogen atom by deuterium gives it a C_s structure (one plane of symmetry), whereas replacement of both restores the original symmetry. The normal modes of motion are indicated in Fig. 12, and the general symmetry types in Table III. Since the normal modes for HDO do not differ greatly from those for H_2O, the same notation is employed. For H_2O and D_2O, ω_1 and ω_2 are a_1 vibrations, and ω_3 is a b_1 vibration. The fundamental frequencies are given in Table XXXVII, with brackets around $\nu_3 = 3730$ cm^{-1} for HDO since it is a value calculated by use of the product rule.

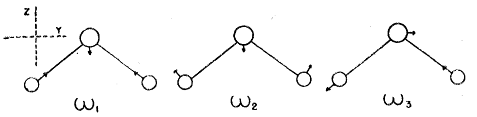

FIG. 12. Schematic description of vibrations of C_{2v} molecule XY_2.

TABLE XXXVII. Fundamental vibrational frequencies.

	H_2O	HDO	D_2O	H_2S	HDS	D_2S	H_2Se	HDSe	D_2Se
ν_1	3650	2720	2666	2615		1891	2260	1691	1630
ν_2	1595.0	1403	1179	1250	1090	934	1074	905	745
ν_3	3755.4	[3730]	2784	2685		2000	2350	2352	1696

A modified valence potential function has been suggested by Cross and Van Vleck (124, 453), who also examined the effect of cross terms, and evaluated the constants by a semi-theoretical method. Bonner (69) carried out a first and second order perturbation calculation of the vibrational energy with moderately good results except for ν_1. The discrepancy occurs because of resonance effects between overtones of ν_1 and ν_3 which are of a higher order than those entering Bonner's equation. A complete discussion of H_2O is given by Darling and Dennison (138, 146), including the normal frequencies, potential constants, rotational structure, and vibration-rotation interactions. The molecular dimensions are determined to be $r(OH) = 0.9580A$, and $\angle HOH = 104° 31'$

The calculated and observed τ's are given in Table XXXVIII. We have used the product rule to calculate a value of ν_3 for HDO, although a more accurate value could perhaps be obtained by using Dennison's equations. The values of τ_0 are for the vapor frequencies, whereas τ_c is applicable for either vapor or liquid within the harmonic approximation.

Considerable study has been made of the structure of liquid water and the interpretation of the spectra obtained for it (347). The hydrogen bonding present in the liquid and crystalline states of water causes a marked change in the Raman and infra-red spectra. Unfortunately the

TABLE XXXVIII. Product rule ratios for C_{2v} molecules XY_2.

C_{2v}		$H_2O:D_2O$	$H_2S:D_2S$	$H_2Se:D_2Se$			$H_2O:HDO$	$H_2Se:HDSe$
a_1	τ_c	3.59	1.94	1.98	a_1b_1/a_1	τ_c	1.50	1.62
	τ_0	3.43	1.85	1.99		τ_0	—	1.59
b_1	τ_c	1.36	1.39	1.41				
	τ_0	1.35	1.34	1.39				

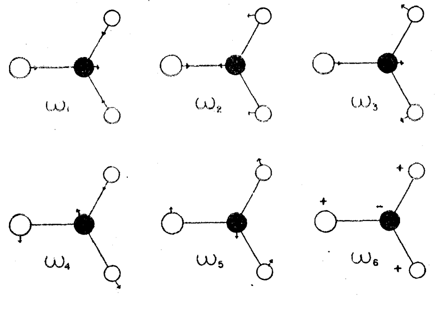

FIG. 13. Schematic description of vibrations of C_{2v} molecule XYZ_2.

frequencies are no longer sharply defined, and bands rather than lines are obtained. Attempts have been made to explain the spectra on the basis of a quasi-crystalline hypothesis, with perturbations of the vapor vibrations and addition of "restricted rotations" and "hindered translations" (51, 91, 123, 299). A band in the region 320 cm^{-1} to 1020 cm^{-1} is assigned to a "libration" of the molecule as a whole, and absorption from 60 cm^{-1} to 200 cm^{-1} to "hindered translation." Support for such an assignment is obtained from the study of liquid D_2O in which there is practically no change in the "translation" band, but the upper limit of the libration band shifts from 1020 cm^{-1} to 730 cm^{-1} (123).

Spectra have also been taken of dilute solutions of water in solvents with which it does not tend to form hydrogen bonds, and the frequencies approach those of the vapor (72, 168), but are always perturbed to some extent by liquid forces. Borst, Buswell, and Rodebush (72) observed a frequency 3659 cm^{-1} for HDO dissolved in carbon tetrachloride which is believed to be ν_3. It is somewhat lower than our calculated value, 3730 cm^{-1}, but the difference could be due to the "liquid effect."

(*b*). H_2S (24, 25, 117, 118, 121, 122, 133, 136, 263a, 324, 325, 336, 337, 423)

Hydrogen sulfide has the same structure as water, and gives a similar spectrum, but has not been subjected to such a complete analysis. The fundamental frequencies are given in Table XXXVII. There is some discussion as to the magnitude of the $\angle$HSH, the choice being between 92° 20′, and 85° 20′. Cross and Crawford (117, 118, 121, 122) have analyzed the rotational structure of a band at 10,100A and have obtained the moments of inertia $I_z=2.661\times10^{-40}$ g cm^2, $I_y=3.060\times10^{-40}$ g cm^2, and $I_x=5.856\times10^{-40}$ g cm^2. From the intensity pattern of the band, they concluded that the interchange of hydrogen nuclei took place by a rotation through 180° about the axis of intermediate moment of inertia, thus making $\angle\mathrm{HSH}=92°\,20'$. On the other hand, Sprague and Nielsen (337, 423) have investigated the structure of the ν_2 band in H_2S, which contains near the center a group of lines suggestive of a *Q*-branch for a vibration along the axis of smallest moment of inertia. This led them to suggest the $\angle\mathrm{HSH}=85°\,20'$. Using the punched card technique, King, Cross, and Thomas (263a) have calculated the appearance of the 10,100A band of H_2S on the basis of an asymmetric rotor with the electric moment along the axis of intermediate moment of inertia. The synthesized spectrum compares favorably with the observed one, and so the conclusion is that the $\angle$HSH is greater than 90°.

The calculated and observed τ's are given in Table XXXVIII. For the moments of inertia we have used $\angle\mathrm{HSH}=92°\,20'$, and $r(\mathrm{S-H})=1.35$A.

(*c*). H_2Se (89, 128, 400)

The observed fundamentals for hydrogen selenide are given in Table XXXVII. Cameron, Sears, and Nielsen (89) have resolved the fine structure for some of the bands and found that the spacing was very much like that for a symmetrical top. Assuming $I_z=I_y=I_x/2$, they obtained $I_x=7.3\times10^{-40}$ g cm^2, $I_z=3.6\times10^{-40}$ g cm^2 for H_2Se, and $I_x'=14.6\times10^{-40}$ g cm^2, $I_z'=7.3\times10^{-40}$ g cm^2 for D_2Se. These are compatible with $\angle$HSeH slightly in excess of 90°, and $r(\mathrm{SeH})=1.6$A. Stevenson (424) gives $\angle\mathrm{HSeH}=90°$ and $r(\mathrm{SeH})=1.49$A from considerations

TABLE XXXIX. Fundamental frequencies for H_2CO and D_2CO.

C_{2v}		H_2CO	D_2CO
a_1	ν_1	2780	2056.4
	ν_2	1750	1700
	ν_3	1503	1106
b_1	ν_4	2875	2160.3
	ν_5	1278	990.2
b_2	ν_6	1165	938

of covalent radii and a trend in bond angles, which are also compatible with the moments of inertia.

The calculated and observed τ's are given in Table XXXVIII, the latter set of dimensions being used for the moments of HDSe.

(*d*). H_2CO (150, 153, 154, 155, 329, 432)

Formaldehyde is a planar molecule with a twofold symmetry axis along the C−O bond. The schematic normal vibrations are given in Fig. 13. ω_1, ω_2, and ω_3 are of type a_1; ω_4, and ω_5 of type b_1; and ω_6 of type b_2 for C_{2v} molecular symmetry. The fundamental frequencies are given in Table XXXIX.

H_2CO is only a slightly asymmetric top, with one moment of inertia very much smaller than the other two. The fine structure has been resolved by Ebers and Nielsen (153, 154), and by use of the energy expressions for an asymmetrical rotator it is possible to determine the moments of inertia. However, perhaps somewhat more accurate are the values obtained by Dieke and Kistiakowsky (150) from the analysis of a number of electronic bands of the molecule. For the normal state they found $I_z = 2.941 \times 10^{-40}$ g cm², $I_x = 24.33 \times 10^{-40}$ g cm², and $I_y = 21.39 \times 10^{-40}$ g cm². The spacing of the rotational lines in the fundamental bands ν_5 and ν_6 is not what one expects from simple theory of a slightly asymmetric top. However, Nielsen has given a satisfactory explanation of this anomaly based on Coriolis interactions similar to those present in the C_{3v} derivatives of methane (328). Although there are no degenerate vibrations in formaldehyde, ν_5 and ν_6 are not very far apart, corresponding to a slightly anistropic oscillator in a plane perpendicular to the twofold symmetry axis. The smaller the separation between ν_5 and ν_6 the larger the interaction since it approaches the ideal case of twofold degeneracy.

Although the moments of inertia of H_2CO are known quite accurately, the molecular dimensions cannot be determined from the moments since only two of them are independent, and the dimensions involve three parameters. The moments for D_2CO (155) have been determined approximately, but not with sufficient accuracy for the evaluation of the bond distances and bond angle. However, electron diffraction data (425) give $r(\mathrm{C-O}) = 1.21 \pm 0.01$A, and so the moments for H_2CO are sufficient to determine the other two parameters. They are $r(\mathrm{C-H}) = 1.09 \pm 0.01$A, and $\angle \mathrm{HCH} = 120° \pm 1°$.

TABLE XL. Product rule ratios for H_2CO and D_2CO.

$H_2CO:D_2CO$	a_1	b_1	b_2
τ_c	1.94	1.67	1.22
τ_0	1.89	1.72	1.24

TABLE XLI. Fundamental frequencies for some pyrroles (295).

Type	Pyrrole	Pyrrole-*N*-*d*	sym-Pyrrole-d_4	Pyrrole-d_5
a_1	711	708	692	693
	1076	1074	812	813
	1144	1135	1094	1084
	1237	1237	919	909
	1384	1384	1319	1317
	1467	1465	1401	1389
	3100	3104	2309	2309
	3133	3131	2358	2350
	3400	2525	3410	2535
b_1	647	606	560	565
	1015	1012	793	789
	1046	1048	848	808
	(1146)	915	1163	892
	1418	1418	1415	1415
	1530	1532	1455	1455
	3111	(3104)	(2309)	(2309)
	(3133)	(3131)	(2358)	2368
a_2	[510]	[510]	[440]	[440]
	711	(708)	514	516
	868	869	769	766
b_2	565	450	(560)	450
	768	766	[610]	[590]
	838	833	730	728
	(1046)	1026	872	852

The calculated and observed τ's are given in Table XL. The deviation in the b_1 type is larger than expected.

(*e*). C_4H_4NH (63, 64, 66, 67, 95, 295, 312, 384, 388)

Pyrrole apparently is a planar C_{2v} molecule in agreement with chemical properties correlated with resonance structures. The Raman and infra-red spectra are compatible with such a configuration, and offer no evidence that the H attached to the N is out of the plane. A schematic description of the modes of vibration for such a molecule is given by Lord and Miller (295)

TABLE XLII. Product rule ratios for pyrroles (295).

Type		$C_4H_4NH:C_4D_4ND$	$C_4H_4NH:C_4D_4NH$	$C_4H_4NH:C_4H_4ND$
a_1	τ_c	5.46	3.89	1.40
	τ_0	5.21	3.75	1.37
b_1	τ_c	4.93	3.56	1.38
	τ_0	4.60	3.36	1.35
a_2	τ_c	1.80	1.80	1.00
	τ_0	—	—	—
b_2	τ_c	2.43	1.82	1.35
	τ_0	—	—	1.29
Type		$C_4H_4ND:C_4D_4ND$	$C_4H_4ND:C_4D_4NH$	$C_4D_4NH:C_4D_4ND$
a_1	τ_c	3.89	2.77	1.40
	τ_0	3.81	2.74	1.39
b_1	τ_c	3.58	2.59	1.38
	τ_0	3.41	2.49	1.37
a_2	τ_c	1.80	1.80	1.00
	τ_0	—	—	—
b_2	τ_c	1.83	1.35	1.36
	τ_0	—	—	—

together with an assignment of fundamental frequencies. Their assignment of frequencies is reproduced in Table XLI. The frequencies in parentheses are used twice, that is, they are considered coincidences. The values in brackets are calculated on the basis of the product rule. In a few instances an increase in frequency is noted on going to the heavier molecule, but the increase is small. (See Fig. 1 for Raman pictures of pyrrole.)

Schömaker and Pauling (371) have made electron diffraction studies of pyrrole, determining the angles and the C—N distance with plausible assumptions as to the various C—C distances. These dimensions are sufficiently accurate for the application of the product rule, the calculated and observed τ's being given in Table XLII.

(*f*). CH_2Br_2 (132, 165, 275, 277, 403, 447, 449 459, 495)

Dibromomethane has C_{2v} symmetry analogous to that of dideuteromethane, and so we shall use the same notation. The observed frequencies for the liquid together with a plausible assignment are given in Table XLIII. A number of authors (275, 459, 495) have discussed the change in frequencies in going from one dihalogen methane to another, but have not arrived at unambiguous assignments for all cases. The assignment for CH_2Br_2 given in Table XLIII was made with the product rule as a guide. Since both CH_2Br_2 and CD_2Br_2 have the same symmetry, relative intensities of lines were used to obtain corresponding lines. Polarization of lines and expected magnitudes also influenced the assignment. Frequencies in brackets are those calculated using the product rule.

TABLE XLIII. Fundamental frequencies for CH_2Br_2 and CD_2Br_2.

		CH_2Br_2	CD_2Br_2
a_1	ν_1	2988	2195
	ν_2	576	548
	ν_3	1183	[850]
	ν_4	173	175
a_2	ν_5	806	[575]
b_2	ν_6	3054	2235
	ν_7	1090	[870]
b_1	ν_8	638	609
	ν_9	1390	1023

Assuming the bond distances to be $r(C-H) = 1.09A$, $r(C-Br) = 1.91 \pm 0.02A$, and $\angle BrCBr = 112° \pm 2°$ (290), we can calculate the moments of inertia and apply the product rule. The calculated and observed τ's are given in Table XLIV.

11. C_s

(*a*). CH_3OH (30, 43, 45, 71, 73, 201, 205, 206, 210a, 315, 340, 378, 379, 380, 423a, 458)

Methyl alcohol consists of a methyl group to which is attached a hydroxyl group, the $\angle COH$ being somewhat larger than a right-angle. Since the C—O single bond presumably has cylindrical symmetry (or the methyl hydrogens may cause it to have slightly trigonal symmetry), the potential energy of the molecule as a function of the rotation of the hydroxyl hydrogen about the C—O axis will depend essentially on the H—H interactions. If the rotation is practically free, the molecule must be considered formally as having no symmetry; if a deep potential minimum exists, it might have a plane of symmetry. Let us consider, however, the CH_3O part of the molecule as a unit, and then attach the hydroxyl H to it. The methoxy group has C_{3v} symmetry, and it seems reasonable that the perturbation of symmetry by attaching a hydrogen to the oxygen will have only a small effect upon vibrations belonging primarily to the methyl group. We have to test by experiment to find out whether that is the case.

Borden and Barker (71) found the methyl frequencies of CH_3OH to be very close to those of CH_3F, indicating a similarity in normal vibrations. They did not find any splitting of the degenerate methyl frequencies, and so concluded that the off-axis H did not perturb the symmetry sufficiently to release the degeneracy. Noether (340), however, reports doublets for the frequencies involving the carbon-hydrogen bendings and rockings of the methyl group, indicating some asymmetry. The splittings are small—of the order 30 cm^{-1}. Because of the similarity to the methyl halides, we denote the vibrational frequencies by the same symbols as for C_{3v} symmetry, and add three to account for the hydroxyl H. ω_7 is taken to be an O−H stretching, ω_8 the hindered rotation of H around the C−O axis, and ω_9 the C−O−H bending vibration.

The rotation of the hydroxyl group around the C−O axis has been studied by Borden and Barker (71) who concluded that the motion was not entirely free. Their studies indicate that the hydroxyl group is confined within a threefold potential barrier produced by the three methyl hydrogen atoms. The barrier is estimated to be 400 to 600 cm^{-1} from considerations of the change in line spacing in the region 580 cm^{-1} assigned to ν_8. The interpretation of the region perhaps is that the low frequency end is due to oscillations in a potential minimum, and that the high frequency end is due to more or less free rotation in the upper quantum states.

The fine structure of the parallel band ν_5 has been resolved (71) for CH_3OH and CH_3OD, giving the average value of the two largest moments of inertia of the molecules. The value for CH_3OH is 34.5×10^{-40} g cm^2, and for CH_3OD it is 35.0×10^{-40} g cm^2. By assuming $r(C-H)=1.09$A, $r(OH)=.956$A, and $r(H-H)$ in the methyl group is 1.81A, the $r(C-O)$ is calculated to be 1.42–1.43A, and the ∠COH to be between 105° and 115°.

TABLE XLIV. Product rule ratios for CH_2Br_2 and CD_2Br_2.

$CH_2Br_2:CD_2Br_2$	a_1	a_2	b_1	b_2
τ_c	1.99	1.41	1.39	1.72
τ_0	—	—	1.42	—

Although substitution of the hydroxyl hydrogen by deuterium does not have much effect on the methyl frequencies, replacement of a methyl hydrogen by deuterium should make a pronounced change. Besides the increased splitting of the ν_4 and ν_6 frequencies, the degeneracy of ν_2 is released. Furthermore, assuming the presence of a threefold potential barrier toward rotation of the D around the C−O axis, there is the possibility of the existence of two forms of CH_2DOD depending upon the azimuthal position of the hydroxyl D with respect to the methyl D (30). The one form will have twice the probability of occurrence of the other. A few of the normal vibrations may have slightly different frequencies for the two forms, but most of them will be unaffected.

The observed fundamentals for CH_3OH and some of its deuterium derivatives (340, 30) are given in Table XLV, together with the most probable assignments. The shift in ν_9 in going from CH_3OH or CD_3OH to CD_3OD is too large, and it seems that a frequency of about 1030 cm^{-1} for CH_3OH would be more suitable (71). Noether (340), however, found that the 1340 cm^{-1} band of CH_3OH disappeared when the hydroxyl H was replaced by D, and that a new band appeared at 869 cm^{-1}, both having a similar fine structure.

TABLE XLV. Observed frequencies for some methanols.

	CH_3OH	CH_3OD	CD_3OH	CD_3OD	CH_2DOD
ν_1	2845	2850	2094	2081	2874
ν_2	2978	2965	2232	2227	2944 2180?
ν_3	1455	1459	1123	1121	1357
ν_4	~1430 1477	1427 1480	1055 1080	1045 1075	1330 1480
ν_5	1034	1040	990	987	1023* 1049*
ν_6	1209 1240–60	1207 1232	856 879	— —	1270?
ν_7	3683	2720	3680	2725	2718
ν_8	—	—	—	—	—
ν_9	1340?	869	1289	775	953 892 830* 810

* From different forms.

TABLE XLVI. Fundamental frequencies for CH_3NO_2 and CD_3NO_2.

	CH_3NO_2	CD_3NO_2
ν_1	2965	2160
ν_2	3048 3048	2290 2290
ν_3	1413	1090
ν_4	1449 1488	1051 1051
ν_5	921	879
ν_6	1097 1153	879 944
ν_7	1384	1384
ν_8	647	632
ν_9	—	—
ν_{10}	1582	1571
ν_{11}	476	424
ν_{12}	599	560

(*b*). CH_3NO_2 (463, 477, 353, 137)

Nitromethane has been studied by a number of investigators (463, 353, 137), and nitromethane-d_3 by T. P. Wilson (477). The CH_3N part of the molecule presumably has a C_{3v} structure, but the question arises as to how the NO_2 group is oriented with respect to the methyl group. It is like the case of CH_3OH, with a plane of symmetry corresponding to the most probable orientation if a barrier to free rotation exists. However, Crawford and Wilson (120) have shown that with some minor assumptions about interaction constants as functions of the angle of twist about the axis, these molecules may be treated as if they possessed a higher symmetry. Thus they treat CH_3NO_2 as a C_{2v} molecule for practical purposes.

The degenerate frequencies of the methyl group in the C_{3v} molecules perhaps should split due to the perturbing effect of the NO_2 group. However, vibrations which involve essentially only the CH_3 group may not be affected a great deal, such as ω_2 and ω_4. For CH_3NO_2 no splitting is reported for ν_2, but a slight splitting is reported for ν_4 (1449 cm^{-1} and 1488 cm^{-1}) (463). In CD_3NO_2 no splitting is reported for either. The vibration ω_6, however, might be more sensitive to an unsymmetrical portion attached to the CH_3 group, since it is essentially a rocking of the CH_3 group with respect to the rest of the molecule (463). Wells and Wilson (463) assign the frequency 1097 cm^{-1} to the rocking in the plane of the NO_2 group, and 1153 cm^{-1} to the rocking perpendicular to that plane.

TABLE XLVII. Product rule ratios for CH_3NO_2 and CD_3NO_2 (477).

	CH_3NO_2:CD_3NO_2		
C_{2v}	a_1	b_1	b_2
τ_c	1.94	2.61	2.50
τ_0	1.91	2.60	2.46

The fundamental frequencies for the nitromethanes are given in Table XLVI, those for CH_3NO_2 from (463) and those for CD_3NO_2 from (477). The notation used is that for the methyl halides, with the e vibrations of C_{3v} symmetry written twice. If the symmetry is C_{2v}, the first component of the e frequencies is considered of type b_1 and the second component of type b_2. The CH_3NO_2 molecule, of course, has six internal degrees of freedom in addition to those of the methyl halides. Let ω_7 represent an NO_2 symmetrical stretching, ω_8 an NO_2 symmetrical bending, ω_9 a torsion about the C−N axis, ω_{10} an unsymmetrical NO_2 stretching, ω_{11} an NO_2 rocking parallel to the NO_2 plane, and ω_{12} an NO_2 rocking perpendicular to the NO_2 plane (463). Thus for C_{2v} symmetry the a_1 vibrations are ω_1, ω_3, ω_5, ω_7, ω_8, the a_2 vibration is ω_9, the b_1 vibrations are ω_{2a}, ω_{4a}, ω_{6a}, ω_{10}, ω_{11}, and the b_2 vibrations are ω_{2b}, ω_{4b}, ω_{6b}, ω_{12}.

Electron diffraction data for CH_3NO_2 (79) yield the dimensions $r(C-N) = 1.46 \pm 0.02A$, $r(N-O) = 1.21 \pm 0.02A$ and $\angle O-N-O = 127° \pm 3°$. Wilson (477) has applied the product rule to these assignments for a C_{2v} molecule, and obtained the results given in Table XLVII.

PART III. OTHER DEUTERATED COMPOUNDS STUDIED SPECTROSCOPICALLY*

1. Acetaldehyde
   (322, 441, 485)
2. Acetic acid
   (13, 14, 127, 166, 167, 223, 224, 225, 226, 227, 399)
3. Acetone
   (45, 166, 167, 285)
4. Acetyl chloride
   (167, 177)
5. Ammonium chloride
   (7)
6. Amyl alcohol
   (240)

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* Deuterated cyclooctatetraene has been reported in preparation: Lippincott and Lord—J. Am. Chem. Soc. **68**, 1868 (1946).

7. Aniline
   (467)
8. Arsenic acid
   (176)
9. Benzoic acid
   (460)
10. Benzyldimethylmethane
    (83)
11. Butanoic acid
    (222)
12. Cobaltamine
    (254)
13. Cyclohexane
    (186, 276, 280, 369)
14. Cystine
    (221)
15. Dibromoethane
    (218, 280, 315, 317, 454)
16. Dichloroethane
    (451)
17. Dichloroethylene (*cis*)
    (448, 451, 492)
18. Dimethylamine
    (392)
19. Ethanol
    (313, 314)
20. Ethylamine
    (392)
21. Ethylbromide
    (218, 282)
22. Ethylene bromide
    (240*a*)
23. Ethylene dibromide
    (210*a*)
24. Ethylselenomercaptan
    (130)
25. Ethylthiol
    (135, 240)
26. Formic acid**
    (222, 228, 241, 242)
27. Hydrazine
    (160, 203, 351)
28. Hydrazoic acid
    (86, 169, 170, 455)
29. Hydrogen perchlorate
    (178)
30. Hydrogen peroxide
    (22, 173, 174, 175, 351)
31. Hydroxybenzaldehyde
    (15, 65, 68)
32. Indene
    (16, 17, 96)
33. Malonic acid
    (158)
34. Methylamine
    (18, 105, 160, 164, 179, 180, 345)
35. Methyldiphenylmethane
    (83)
36. Methyl iodide
    (210*a*, 213*a*)
37. Nitric acid
    (26, 377)
38. Nitrophenol
    (247, 248)
39. Paraldehyde
    (486)
40. Phenol
    (465)
41. Phenyldimethylmethane
    (83)
42. Phosphoric acid
    (354, 413, 465, 466)
43. Propanoic acid
    (227)
44. Salicylaldehyde
    (247)
45. Stearic acid
    (107)
46. Sulfuric acid
    (286, 354, 465, 466)
47. Tetrachloroethane
    (281, 448, 450, 451)
48. Tetramethylmethane
    (360, 361, 410, 411)
49. Triphenylmethane
    (83)
50. Urea
    (259, 344)

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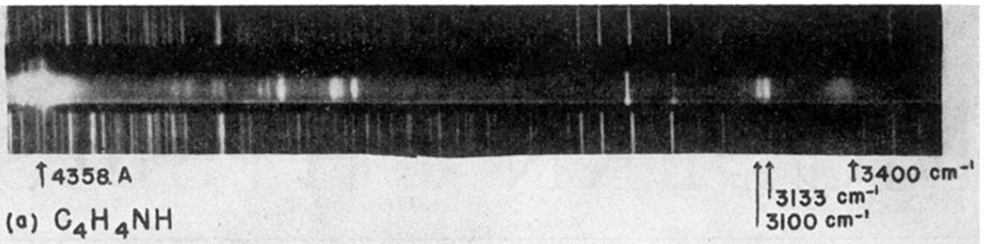
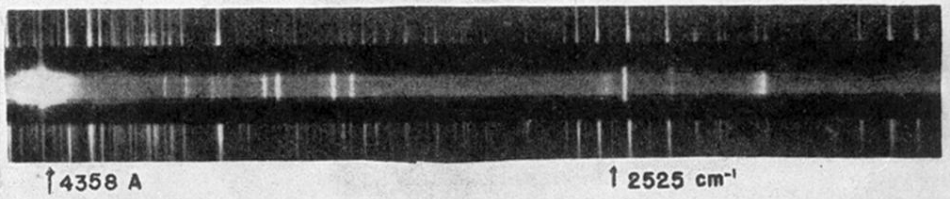
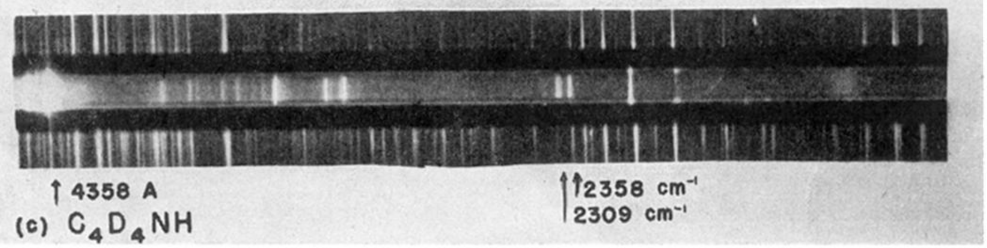


(a) C_4H_4NH



(b) C_4H_4ND



(c) C_4D_4NH

FIG. 1. Raman spectra of pyrrole (a) C_4H_4NH, (b) C_4H_4ND, (c) C_4D_4NH.