THE ENERGY LEVELS AND STATISTICAL WEIGHTS OF POLYATOMIC MOLECULES[1]

DONALD STATLER VILLARS

Research Laboratory, Standard Oil Company (Indiana), Whiting, Indiana

Received February 25, 1932

Revised to September 30, 1932

The spectroscopy of diatomic molecules has proved to be of colossal importance to the study of elementary photochemical processes. The application of the principles of this science to chemistry in general is severely handicapped, however, by the fact that most molecules are polyatomic and, until a few years ago, little had been learned towards the elucidation of their spectra. Recently remarkable advances have been made along these lines. Although the wealth of material is small when compared with that available on diatomic molecules, still it is so large in absolute amount that a review of the fundamental principles which have been so far discovered may be of great value to one wishing to enter into a thorough study of this subject for the first time. No apology need be made therefore for limiting our discussion to a few molecules which represent typical cases and for omitting from consideration a great mass of literature which is increasing daily by leaps and bounds. We shall divide the present summary of the status of polyatomic band spectroscopy into two parts: the first will be a discussion of the general principles of significance to chemistry, and the second will consist of illustrative applications of these principles to typical compounds —in general, the hydrogen compounds.

---

[1] A brief summary of Part I of this review was presented at the Symposium on The Application of Quantum Theory to Physical Chemistry held by the Physical and Inorganic Section at the 81st meeting of the American Chemical Society at Indianapolis, March 31, 1931.

PART I. GENERAL PRINCIPLES

The information derivable from the spectroscopy of molecules which is of interest to chemists is of two types: physical and chemical. Thus, a successful complete analysis of a molecular spectrum enables one to compute the physical constant, the moment of inertia, and from it, the average nuclear separation for different energy states. One can tell, for example, whether excitation of the molecule brings about a bond loosening (the usual case) or tightening, by observing whether the band is shaded towards the red or, respectively, the violet. A knowledge of the different moments of inertia of a polyatomic molecule is necessary to the elucidation of its structure and size. Further information of interest to physics and photochemistry involves transition probabilities. Vibrational transitions associated with electronic are of greatest significance to photochemical change. Rotational transition probabilities are not so important to such processes because they are zero for all but small changes in rotational energy ($\Delta K = \pm 1$ or 0), but they are essential to an understanding of selection principles which, in turn, are necessary for a successful analysis of the fine structure. The chemical information which one may obtain from molecular spectroscopy embraces heats of dissociation, bond strengths, heat contents, entropies, specific heats, free energy and equilibrium constants, and, quite recently, activation heats. It is beyond the scope of the present article (1) to go into the means whereby these constants may be derived; we shall limit ourselves to a consideration of the two things, a more or less complete knowledge of which is prerequisite to such calculations, namely, the energy levels, ϵ_i, and their statistical weights, w_i. The latter are the relative probabilities of finding a molecule having the energy, ϵ_i, and are equal to the products of the Boltzmann factor, $e^{-\epsilon_i/kT}$, into the *a priori* probabilities, p_i. The *a priori* probability may be looked upon as the number of individual levels happening to have exactly the same energy, ϵ_i, and is given in classical theory by the number of quantized orientations which an angular momentum may assume in a force field. The component of the momentum, j, along the force axis may take any of the values $+j, j - 1, j - 2, \ldots .$

$-j+1$, $-j$, making $2j+1$ in all. The *a priori* probability is therefore $2j+1$. More rigorously, in quantum mechanics, it is the number of ways of obtaining an eigenfunction completely antisymmetric[2] in the protons (2) from those characterizing the energy level in question (Pauli exclusion principle). Such an eigenfunction will be completely antisymmetric in the protons only when it is antisymmetric in the nuclei, A_N, if the latter contain an odd number of protons each (Fermi-Dirac statistics) or symmetric in the nuclei, S_N, if the latter contain an even number of protons (3) (Bose-Einstein statistics).

The energy of the level in a molecule is customarily considered as made up of separate contributions from the rotational, the vibrational, and the electronic motions. In such a case the molecular eigenfunction may be taken (4) as the product of subsidiary functions, the electronic, vibrational, rotational, and nuclear.

$$\psi = \psi_{\mathrm{el}}\,\psi_{\mathrm{vibr}}\,\psi_{\mathrm{rot}}\,\psi_{\mathrm{nuclei}} \tag{1}$$

Its symmetry follows the sign multiplication rule; $S \times S = S$, $S \times A = A$, $A \times A = S$, etc. We shall accordingly divide our discussion into these logical subdivisions.

ROTATIONAL

1. Diatomic molecules

We shall first review the case of the diatomic molecule in order to be better prepared for the polyatomic molecule. The former has two equal moments of inertia, the third being negligible (except it be due to electronic momentum with a component along the line joining the nuclei (figure axis)—$\Lambda > 0$—in which case it is properly considered under electronic energy levels). Each moment of inertia corresponds to one rotational degree of freedom and the rotational specific heat at high temperatures is consequently $2R/2$.

a. Energy levels. The energy levels are given by the general formula

$$\epsilon_K = K(K+1)h^2/8\pi^2 I \tag{2}$$

where K is the rotational quantum number and may take on positive integral values starting with zero, h is Planck's constant, and I is the moment of inertia. Figure 1 illustrates this energy level sequence.

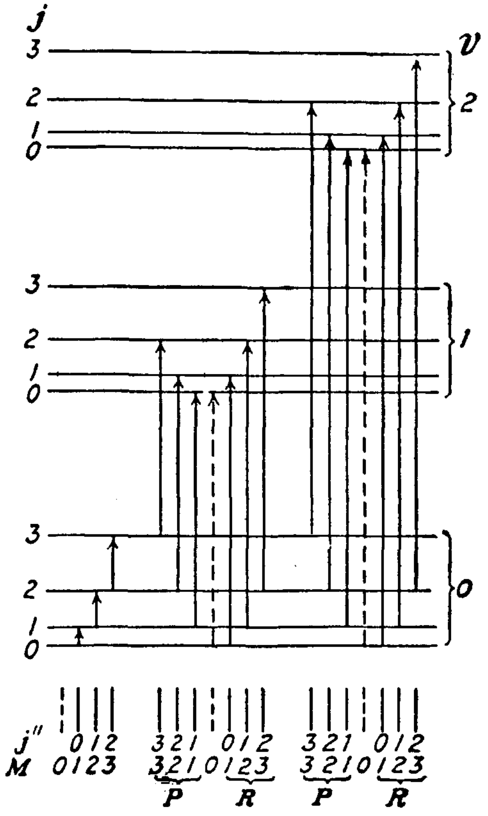


Fig. 1. The Vibrational and Rotational Energy Levels of HCl

The rotational levels are plotted on ten times the scale of the vibrational levels. (From Ruark and Urey: Atoms, Molecules and Quanta. McGraw-Hill Book Co., New York (1930). Reproduced by courtesy of the publishers.)

b. Statistical weights. The *a priori* probability of the K'th level is

$$p_K = 2K + 1 \tag{3}$$

since the rotation of the nuclei has associated with it K units of angular momentum. The statistical weight of the state is therefore

$$w_K = (2K + 1)e^{-K(K+1)h^2/8\pi^2IkT} \tag{4}$$

These weights are to be multiplied by the nuclear spin statistical weight which is

$$\begin{aligned} w_n &= (2i_1 + 1)\,(2i_2 + 1)\,\ldots\ldots\,(2i_\nu + 1) \\ &= \prod_\nu (2i_\nu + 1) \end{aligned} \tag{5}$$

The Boltzmann factor does not appear in this expression, since the energy difference between levels of different nuclear spin orientations is negligible (coupling very slight).

A modification of this rule usually occurs if both of the nuclei in the molecule are the same. In this event, the rotational eigenfunctions, ψ_{rot}, are, starting with the lowest level, alternately S_N and A_N (the subscript referring to changes in designation of the *nuclei*). The lowest vibrational (S_N) and lowest electronic (S_N) states can therefore combine alternately with only A_N and S_N eigenfunctions of the nuclear spin, ψ_{nuclei}, if the number of protons in each nucleus is odd (Fermi-Dirac statistics) or alternately with only S_N and A_N nuclear spin eigenfunctions if the number is even (3) (Bose-Einstein statistics).

The nuclear weight, 5, is therefore divided into two parts, each of which applies separately to a separate set of rotational levels. If the nuclear spin is zero, this means the exclusion of a whole set of levels (either all odd or all even) because ψ_{nuclei} is S_N only. If the spin is 1/2, three S_N spin functions may be formed from those available (call spin in one direction α, in the other β) (5), namely,

$$\left.\begin{array}{ll} \left.\begin{matrix}\alpha_1\alpha_2\\ \alpha_1\beta_2 + \alpha_2\beta_1\\ \beta_1\beta_2\end{matrix}\right\} & S_N \\ \text{but only one } A_N & \\ \alpha_1\beta_2 - \alpha_2\beta_1 & A_N \end{array}\right\} \tag{6}$$

and the nuclear spin statistical weights are respectively 3 and 1. The weights for other nuclear spins are given in table 1. Note that the sum of the two types of weights must equal $(2i_N + 1)^2$. The nuclear spins are thus seen to contribute an additional statistical weight of their own. This holds as well when the nuclei are different, but in this case all rotational weights are multiplied indiscriminately by the factor $(2i_1 + 1)(2i_2 + 1)$.

TABLE 1

Nuclear spin statistical weights

i_N	s_N	A_N	EXAMPLE
Fermi-Dirac statistics			
0	1	0	
1/2	3	1	H_2
1	6	3	
3/2	10	6	
Bose-Einstein statistics			
0	0	1	O_2
1/2	1	3	
1	3	6	N_2
3/2	6	10	

2. Polyatomic molecules

The polyatomic molecule in general has three moments of inertia. Each moment of inertia corresponds to one rotational degree of freedom and the rotational specific heat at high temperatures is consequently $3R/2$. The *a priori* probability associated (6) with each value of the total angular momentum, j, (or rotational angular momentum, K) of a molecule is $2j + 1$ if it is collinear, or $(2j + 1)^2$ if it is not. In the latter case, if all three moments of inertia are equal, all $(2j + 1)^2$ terms fall together.

---

[2] An eigenfunction is an equation, the square of the absolute value of which gives the probability of finding the particle to which it refers in a prescribed position in space. An antisymmetric eigenfunction, A, is one which becomes multiplied by -1 when the numbers designating two like particles are interchanged. A symmetric eigenfunction, S, becomes multiplied by $+1$ (i.e., is unchanged) by such an interchange.

If only two of the moments of inertia are equal (symmetrical top), these terms fall into $(2j + 1)$ groups of quantum number

$$\tau = j, j - 1, \ldots\ldots - j + 1, - j$$

Each τ group has the degeneracy $(2j + 1)$ and, moreover, those groups of $+ \tau$ coincide with those of $- \tau$. If all three moments of inertia are different (asymmetrical top), the + and $- \tau$ groups are separated, each having its own degeneracy of $(2j + 1)$.

Three cases of the polyatomic molecule may be distinguished.

Case I—Collinear molecule. Two moments of inertia are equal and the third is negligible. These are exactly the same conditions governing the diatomic molecule, and the energy relations and *a priori* probabilities therefore obey the same laws. The rotational specific heat at high temperature is of course only $2R/2$. From the rotational line sequence one may determine the moment of inertia as before, but additional information is necessary to estimate the nuclear separations.

The rotational *a priori* probabilities are also more complicated. If all atoms are different, each weight is multiplied by the spin product, $\prod\limits_{\nu} (2i_\nu + 1)$. If the molecule has a symmetrical form, the effects of the symmetry characteristics of the eigenfunctions must be worked out for each case. For example, suppose we have a rod-shaped molecule of the form XYYX. The radical XY may be considered as a unit of a diatomic molecule. When the nuclear spins of the left XY radical have the same resultant as those of the right one, the rotational weights may be computed from table 1, and one may expect alternate weak and strong levels. But when the resultant spin of the left XY radical differs from that of the right one, the molecule is no longer symmetrical and all rotational weights will be multiplied by the same nuclear spin factor $(2j_{\text{left}} + 1)\ (2j_{\text{right}} + 1)$ where j is, in this instance, the resultant of the two nuclear spins, i_X and i_Y. In other words, the states are no longer divisible into symmetric and antisymmetric. This case is exactly analogous to that of a diatomic molecule composed of isotopes of differing weights.

Case II—Symmetrical top. Here two moments of inertia (A) are equal and the third (C) is unequal but greater than zero.

Each moment of inertia corresponds to one rotational degree of freedom and the rotational specific heat at high temperature is therefore $3R/2$.

(a) Energy levels. The energy levels of the symmetrical top are given by the formula,

$$\epsilon_{j,\tau} = (h^2/8\pi^2)\,[j(j+1)/A + (1/C - 1/A)\tau^2] \qquad |\tau| \leq j \tag{7}$$

where $j = 0, 1, 2, 3 \ldots$ and τ is a positive or negative integer, the absolute value of which cannot be greater than j. The first half of the formula gives an energy level sequence similar to that characteristic of the diatomic molecule, but the second half requires that each successive level have built on it a satellite system which grows ever larger and larger. The unequal moment of inertia, C, may be greater or less than the others, A, and this determines whether the satellite system builds up or down. A picture of the relations involved in ammonia ($C > A$) is given in figure 2.

(b) Statistical weights. The *a priori* probability of one (associated with definite τ) of the j levels is

$$p_{j,\tau} = 2j + 1 \tag{8}$$

and the statistical weight is

$$w_{j,\tau} = (2j+1)e^{-j(j+1)\sigma_1}\,e^{-\tau^2\sigma_2} \tag{9}$$

where

$$\sigma_1 = h^2/8\pi^2AkT \tag{10}$$

$$\sigma_2 = (h^2/8\pi^2kT)\,(1/C - 1/A) \tag{11}$$

It is interesting to trace out two limiting cases. If $C = A$, $\sigma_2 = 0$ and the $(2j + 1)$ levels, one for each possible value of τ, are completely degenerate. The total *a priori* probability is

$$p_j = (2j+1)^2 \tag{12}$$

If, on the other hand, $C = 0$, then $\sigma_2 = \infty$ and the statistical weights are zero for all values of τ but $\tau = 0$. This gives as the total weight only, $p_j = 2j + 1$, in complete agreement with equation 3 for the diatomic molecule, which this contingency represents.

The statistical weights given by equations 8 and 9 must be multiplied by the product of the nuclear degeneracies $\prod_{\nu} (2i_{\nu} + 1)$, if the component nuclei have spin. If the molecule is symmetrical, the effects of the symmetry characteristics of the eigenfunctions must here also be worked out for each case. We shall review those for three and four equal nuclei, as they have been presented in detail by Hund (4).

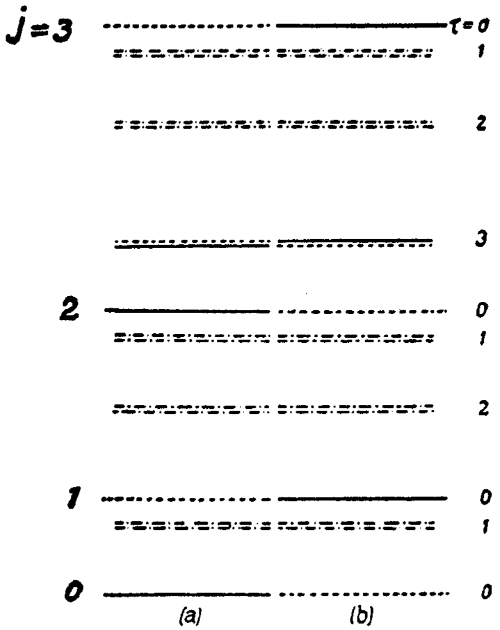


FIG. 2. ROTATIONAL ENERGY LEVEL DIAGRAM OF DOUBLE GROUND VIBRATIONAL STATE OF NH_3 TYPE MOLECULE

(Taken from Badger and Cartwright (46))

——— = symmetric term, $S(3)$.
—·—·— = degenerate symmetry term, $S(2 + 1)$.
.... = antisymmetric term, $S(1 + 1 + 1)$.

The symmetry characteristics of eigenfunctions of more than two like particles are not so clear cut, in contrast with those of two which are either completely S or completely A. The functions may have mixed symmetry character.[3] Thus, A (3) is an eigenfunction, A, in the interchange of two of any three particles, A (2 + 1) is A in a certain pair but not for any other, and A (1 + 1 + 1) is A in none. The last eigenfunction, Hund has shown, is completely symmetrical, S (3), the first is symmetrical in no pair, S (1 + 1 + 1), and the second is reciprocal to itself, i.e., is likewise S (2 + 1). Of the characters of mixed symmetry, S (2 + 1) is found to be doubly-, S (2 + 2) to be doubly-, and S (3 + 1) to be triply-degenerate. But it has been found, in multiplying together two degenerate characters, that the symmetry characters of the products are different, and are distributed among the various possible kinds by definite predetermined fractions. Thus, only one-fourth of the combinations between the S (2 + 1) rotational and S (2 + 1) nuclear spin characters may be combined to form a completely symmetrical product, S (3), and one-fourth to form a completely antisymmetrical S (1 + 1 + 1), the residual half remaining degenerate, S (2 + 1). The same is true of combinations between two S (2 + 2) functions. Only one-ninth of the products of two S (3 + 1) functions may form an S (4) function, and another ninth may form S (1 + 1 + 1 + 1) functions.

With these working rules (the reader is referred to the original references (7,8) for the complete set), one is in a position to calculate the *a priori* probabilities of the different symmetrical varieties of molecules containing three or four equal nuclei. If the latter have only two orientation possibilities (spin = 1/2) one may set up α and β values as above in equations 5 and 6 and get as a final result

$$\left.\begin{array}{ll} 4 & S\,(3) \\ 2 & S\,(2+1)\text{ doubly degenerate} \end{array}\right\}\text{ Three nuclei}$$

$$\left.\begin{array}{ll} 5 & S\,(4) \\ 3 & S\,(3+1)\text{ triply-degenerate} \\ 1 & S\,(2+2)\text{ doubly-degenerate} \end{array}\right\}\text{ Four nuclei}$$

eigenfunctions of nuclear spin.

Hund has shown that symmetry characters with more than two

---

[3] Terminology introduced by Hund (7).

terms in the argument may occur only when the spin can take on more than two values. Since there is very little coupling force between the nuclear spins and the outer forces of the molecule, these different symmetry systems are practically non-combining and form distinct molecular varieties in exactly the same way that the two symmetry varieties of hydrogen are formed. We shall designate them as nuclear quartet, nuclear doublet and nuclear quintet, nuclear triplet, and nuclear singlet. The corresponding forms of hydrogen are nuclear triplet ("ortho") and nuclear singlet ("para").[4]

The *a priori* weight and character of the rotational eigenfunctions of a triatomic symmetrical molecule are given in table 2 (from Hund (4)); those of a molecule of tetrahedral symmetry[5] are given in table 3 (from Elert (8)).

If the number of protons in the equal nuclei is odd, the Fermi-Dirac statistics (if even, the Bose-Einstein) must be obeyed, and it is a comparatively simple matter now, to count the total number of completely A_N (or respectively, S_N, for Bose-Einstein statistics) functions which can be formed from all of those available. The further discussion of this topic will be continued in Part II.

Case III—Asymmetrical top. The most general case of the polyatomic molecule is exemplified by the asymmetrical top, whose three principal (mutually perpendicular) moments of inertia, (A, B, and C, arranged in order of increasing value) are all different. The high temperature rotational specific heat of this type of molecule is the same as that of the symmetrical top, $3R/2$, the distribution of the moments of inertia having no effect, provided, of course, sufficiently high temperatures are used in the comparison.

---

[4] That the nomenclature, ortho- and para-hydrogen, is perverted has been pointed out by Eucken and Hiller (Z. physik. Chem. **4B**, 142 (1927), footnote 4) and by Mulliken (Trans. Faraday Soc. **25**, 638 (1929), footnote 16).

[5] Elert (8) demonstrated this distribution to hold for the first few j states and believed it to be general but was unable to prove it. The author has recently received a personal communication from Professor Hund stating that he has been informed by Mr. van der Waerden that it is indeed general.

TABLE 2

Rotational weights in NH_3 *type molecule* (1e)

	τ	NUCLEAR QUARTET $S(3)$	NUCLEAR DOUBLET $S(2 + 1)$
0	0	4 × 1	4 × 0
1	0	3	0
1	1	0	3
2	0	5	0
2	1	0	5
2	2	0	5
3	0	7	0
3	1	0	7
3	2	0	7
3	3	7 × 2	0
4	0	9	0
4	1	0	9
4	2	0	9
4	3	9 × 2	0
4	4	0	9
		4 $(2j + 1)$ for $\tau = 0$ 8 $(2j + 1)$ for τ divisible by three	4 $(2j + 1)$ for τ indivisible by three

TABLE 3

Rotational weights in CH_4 *type molecule* (1f)

j	NUCLEAR QUINTET $S(4)$	NUCLEAR TRIPLET $S(3 + 1)$	NUCLEAR SINGLET $S(2 + 2)$
0	5 × 1	0	0
1	0	3·3	0
2	0	5·3	5·2
3	7	7·6	0
4	9	9·6	9·2
5	0	11·9	11·2
6	13·2	13·9	13·2
7	15	15·12	15·2
8	17	17·12	17·4
9	19·2	19·15	19·2
10	21·2	21·15	21·4

(a) Energy levels. The energy levels of the asymmetrical top have been given by Kramers and Ittmann (9)

$$\epsilon_{j,\tau} = (h^2/8\pi^2)\, j(j+1)\, H_{j,\tau} \tag{13}$$

where $H_{j,\tau}$ must lie between

$$c < H_{j,\tau} < a \tag{14}$$

The small letters, a, b, and c shall be the reciprocals of the corresponding moments of inertia. For large j and values of τ approaching

$$\tau_0 = (j + 1/2)\,[(4/\pi) \operatorname{arc\,tan}(b - c)^{1/2}/(a - b)^{1/2} - 1] \tag{15}$$

$H_{j,\tau}$ is given by

$$H_{j,\tau} = b + \frac{\tau - \tau_0}{j + 1/2}\, \frac{\pi(a - b)^{1/2}\,(b - c)^{1/2}}{\ln\,[(j + 1/2)16\, e^{0.577} \sin 2 \operatorname{arc\,tan}(b - c)^{1/2}/(a - b)^{1/2} \pm \pi/2]} \tag{16}$$

where alternate values of the plus or minus sign are to be chosen for successive values of τ. The fine structure spacing within a j group of levels is thus seen to be constant near the center of the group.

$$\underset{\text{center}}{\Delta H_\tau} \cong \pi(a - b)^{1/2}\,(b - c)^{1/2}/(j + 1/2)\ln\,(j + 1/2) \tag{17}$$

$$j \text{ large} \quad \tau \cong \tau_0$$

This is no longer true when $H_{j,\tau}$ differs appreciably from b, in which event the sublevels pair together (splitting decreasing inversely as j), two pairs being separated by the energies

$$H_{\text{pairs}} = 2(a - c)^{1/2}\,(a - b)^{1/2}/(j + 1/2) \quad \text{for} \quad (a - H) \ll (a - c) \tag{18}$$

$$= 2(a - c)^{1/2}\,(b - c)^{1/2}/(j + 1/2) \qquad (H - c) \ll (a - c) \tag{19}$$

These asymptotic formulas are valid only for large j. The energy levels for small j have been worked out by Kramers and Ittmann up to $j = 4$ and are given in table 4. Dennison (10), in a valuable discussion of this subject, has recently extended the computation to $j = 9$ and Nielsen (11) to $j = 10$, but their equations are not

TABLE 4

Energy levels of asymmetrical top

Kramers and Ittmann (9a, I)

j	τ	$\frac{8\pi^2 E}{h^2}$		
0	0	0		
1	1	$a + b$		
	0	$a + c$		
	-1	$b + c$		
2	2	$4(a + b + c) - 6\Theta_1$		
	1	$4a + b + c$		
	0	$a + 4b + c$	$\Theta_1 < \Theta_2$	$\frac{1}{a - \Theta_r} + \frac{1}{b - \Theta_r} + \frac{1}{c - \Theta_r} = 0$
	-1	$a + b + 4c$		
	-2	$4(a + b + c) - 6\Theta_2$		
3	3	$9a + 9b + 4c - 10\Theta_1$	$\Theta_1 < \Theta_2$	$\frac{1}{a - \Theta_r} + \frac{1}{b - \Theta_r} + \frac{3}{c - \Theta_r} = 0$
	2	$9a + 4b + 9c - 10\Theta_1'$		
	1	$4a + 9b + 9c - 10\Theta_1''$		
	0	$4(a + b + c)$	$\Theta_1' < \Theta_2'$	$\frac{1}{a - \Theta_r'} + \frac{3}{b - \Theta'} + \frac{1}{c - \Theta'} = 0$
	-1	$9a + 9b + 4c - 10\Theta_2$		
	-2	$9a + 4b + 9c - 10\Theta_2'$		
	-3	$4a + 9b + 9c - 10\Theta_2''$	$\Theta_1'' < \Theta_2''$	$\frac{3}{a - \Theta_r''} + \frac{1}{b - \Theta_r''} + \frac{1}{c - \Theta_r''} = 0$

4	4	α_1	$\alpha_1 > \alpha_2 > \alpha_3$ $\alpha_r^3 - 20\,\alpha_r^2\,(a + b + c) + 16\,\alpha_r\,\{4\,(a + b + c)^2 + 13\,(ab + bc + ca)\}$ $-\,320\,\{7\,abc + 2\,(a + b + c)\,(ab + bc + ca)\} = 0$ $\eta_r + \zeta_r = -\,\tfrac{1}{14}\,\{-\,\alpha_r + 16\,(a + b + c)\}$ $\eta_r\zeta_r = \tfrac{1}{280}\,\{-\,\alpha_r + 16\,(a + b + c)\}\,\{-\,\alpha_r + 4\,(a + b + c)\}$ $+\,\tfrac{3}{5}\,(ab + bc + ca)$
	3	$16\,a + 9\,b + 9\,c - 14\,\Theta_1$	
	2	$9\,a + 16\,b + 9\,c - 14\,\Theta_1'$	
	1	$9\,a + 9\,b + 16\,c - 14\,\Theta_1''$	
	0	α_2	
	$-\,1$	$16\,a + 9\,b + 9\,c - 14\,\Theta_2$	$\Theta_1 < \Theta_2$ $\quad \dfrac{1}{a - \Theta_r} + \dfrac{3}{b - \Theta_r} + \dfrac{3}{c - \Theta_r} = 0$
	$-\,2$	$9\,a + 16\,b + 9\,c - 14\,\Theta_2'$	
	$-\,3$	$9\,a + 9\,b + 16\,c - 14\,\Theta_2''$	
	$-\,4$	α_3	$\Theta_1' < \Theta_2'$ $\quad \dfrac{3}{a - \Theta_r'} + \dfrac{1}{b - \Theta_r'} + \dfrac{3}{c - \Theta_r'} = 0$
			$\Theta_1'' < \Theta''$ $\quad \dfrac{3}{a - \Theta_r''} + \dfrac{3}{b - \Theta_r''} + \dfrac{1}{c - \Theta_r''} = 0$

reproduced here as the energy relations are not so readily visualized. Figure 3, taken from Kramers and Ittmann (9a, I, figure 3, page 562) shows the relation between the sublevels of $j = 4$ as the middle moment of inertia, $1/b$, changes from the value $1/c$ to $1/a$. The second quantum number, τ_{bc}, is that of the symmetrical top where $b = c$. It may be noted how the spacings discussed above in connection with equations 17, 18, and 19 are exemplified, especially when $b = 2c$.

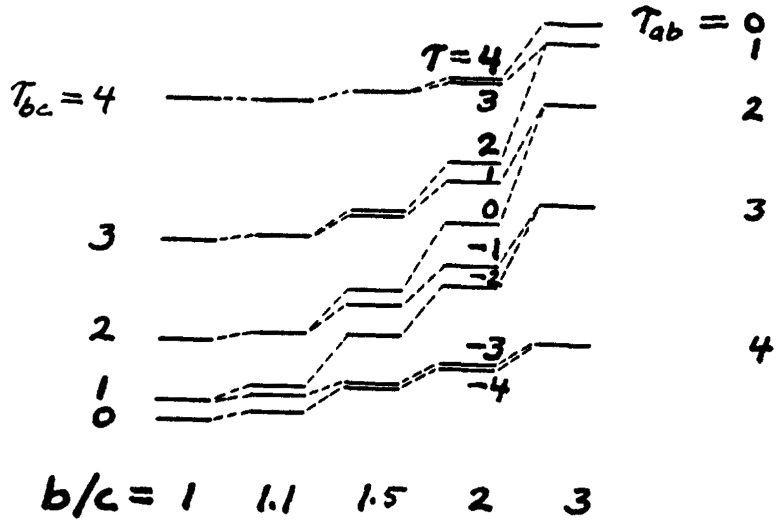


FIG. 3. ENERGY LEVELS OF ASYMMETRICAL TOP FOR $j = 4$ AND VARYING MOMENTS OF INERTIA
$a = 3c$
(From Kramers and Ittmann (9a, I))

(b) Statistical weights. The *a priori* probability of each level is, as in the case of the symmetrical top

$$p_{j,\tau} = 2j + 1 \qquad (20)$$

and the statistical weight is

$$w_{j,\tau} = (2j + 1)e^{-\epsilon_{j,\tau}/kT} \qquad (21)$$

The energy, $\epsilon_{j,\tau}$ is given in the preceding section, equation 13. The statistical rotational weights are to be multiplied by the weights due to nuclear spin, as before. If the molecule is symmetrical, the symmetry characteristics of the eigenfunctions must be examined in detail. A principle of great value in the consummation of such an investigation of the characteristics of the rotational eigenfunctions of the asymmetrical top is that the total number of terms (*a priori* probabilities) and their symmetry characters are unchanged on going from the symmetrical to the asymmetrical top. Results obtained for the former may be immediately applied to the latter. The further discussion of this topic will be reserved for Part II (H_2O).

VIBRATIONAL

If n is the number of atoms in a molecule, the latter as a whole will have $3n$ degrees of freedom (three translational degrees to each atom). If the coördinates are now transformed to such that three may be made to represent the translatory motion of the center of gravity of the system, and two or three (depending on whether it has two—collinear—or three moments of inertia), the rotational motion of the molecule, there will be left respectively $3n - 5$ and $3n - 6$ degrees of freedom and these must of necessity represent vibrational motion.

In writing down the equations for vibrational energy, an especially simple formulation may be had if a coördinate system be chosen which allows the kinetic and potential energy of the system to be represented respectively as a sum of separate terms involving successively each coördinate alone, and no products of one coördinate into another. These coördinates are called normal coördinates and there must be as many of them as were originally started out with. The reader is referred to the articles of Dennison (10) and of Mecke (12) for a fuller discussion of this point. The important result of this representation is that small oscillations about the equilibrium points may be represented as the resultant effects of a series of different harmonic oscillators all vibrating at the same time. The final vibrational frequency is then the sum of the ground or overtone frequencies of each oscillator.

That these normal vibrations have actual physical significance, notwithstanding the mathematical mode of computing them, may be best seen by watching the Kettering, Shutts, and Andrews (13) machine for representing the dynamic properties of molecules. Any one who has seen the activating vibrations pass through one resonance frequency to another cannot fail to be struck by the radical change in character of the motion. These different modes of vibration are indeed the normal vibrations about which we are writing.

The intensity of spectral lines absorbed or emitted, in which the vibrational quantum number changes, is governed by several factors. First the (total) symmetry character of the initial and final state must be identical. If the nuclei have symmetry properties, the molecules will belong to different nuclear-multiplet varieties and the preceding statement applies to the resultant symmetry character of everything but nuclear spins. Second, the transition intensity is proportional to the square of the classical electric moment; this in turn depends on whether the coördinate associated with the particular transition under consideration may be used to define a value for the moment. Obviously, the change of a coördinate corresponding to a symmetrical motion of the molecule cannot affect the electric moment. Such a frequency is therefore termed "inactive" and cannot appear as a spectral line or band except in combination with another which is "active" (associated with a coördinate of unsymmetrical vibration).

On the other hand, "inactive" frequencies are favored as Raman lines, the latter depending for their intensity on the electric moments of interaction with intermediate states. Thus, a Raman line will be intense if its frequency is the difference between two intense optical frequencies. Van Vleck (14) has deduced that the lines scattered by a polyatomic molecule "should rank as follows in intensity: first, Rayleigh scattering (no wave length shift); second, Raman lines whose displacements equal one of the fundamental vibration frequencies; third, Raman lines whose displacements are either harmonics of a fundamental vibration frequency, or else are 'combination frequencies' equal to the sum of two different fundamentals."

The *a priori* probability of each normal vibration is unity, except in those cases where more than one vibration happens to have the same frequency (degeneracy). In that event, the *a priori* probability is equal to the number of vibrations making up the degenerate oscillation. This question will be discussed in greater detail in Part II.

1. Diatomic molecules

Since a diatomic molecule is collinear, it may have only one vibrational degree of freedom. Its energy levels are generally expressed by the power series formula[6]

$$\epsilon_v = h\nu_e\,[(v + 1/2) - x(v + 1/2)^2 - \ldots.] \tag{22}$$

If the level is expressed as a series in v (not $(v + 1/2)$) the frequency is to be designated as ν_0 (not ν_e) and proper consideration is to be taken thereof. The *a priori* probability and statistical weight of each level is

$$p_v = 1 \tag{23}$$

$$w_v = e^{-\epsilon_v/kT} \tag{24}$$

The ground frequency ν_e is equal to the classical mechanical frequency

$$\nu_e = (1/2\pi)\ (k/\mu)^{1/2} \tag{25}$$

where k is the restoring force constant and μ is the reduced mass

$$\mu = m_1m_2/(m_1 + m_2) \tag{26}$$

If both nuclei are equal, the symmetry character of each vibrational level is S (2) (completely symmetric).

2. Polyatomic molecules

Case I—Collinear molecules. The case of a collinear polyatomic molecule has been worked out by Mecke (15) and shown to be particularly simple. Of the $3n - 5$ vibrational frequencies

---

[6] This formula is not continuous in v. Birge: Trans. Faraday Soc. **25,** 707 (1929).

(types of vibration), $n - 1$ are in the bond directions and are called by him valence vibrations or valence frequencies. The remaining frequencies occur in pairs, $n - 2$ being different (double frequencies), and since the associated motions are perpendicular to the bond directions, he names them deformation frequencies. Dennison (10) has derived a rule which he hopes may find a useful application to the spectroscopy of many triatomic molecules. It is that when the sum of two active frequencies in a spectrum is systematically equal to a third active frequency, either (1) the molecule is not collinear or (2) if collinear, its potential energy function is not geometrically symmetrical.

(a) Energy levels. The energy levels of a collinear polyatomic molecule may be represented by a sum of as many equations similar to equation 22 as there are normal coördinates, each quantum number of vibration being capable of independent variation.

The relations between the ground frequencies of triatomic and quadratomic collinear molecules have been given by Mecke (15). If k is the restoring force constant for valence vibration of a collinear triatomic molecule, the two outside atoms of which are the same (mass, m), and d the corresponding constant for overcoming deformation (perpendicular to the valence vibration—d/k is assumed small), the two (equal) deformation frequencies are

$$\delta = (1/2\pi)\ [d(M + 2m)/Mm]^{1/2} \tag{27}$$

where M is the mass of the central atom. The valence frequencies are

$$\nu(s) = (1/2\pi)\ (k/m)^{1/2} \tag{28}$$

$$\nu(a) = (1/2\pi)\ [k(M + 2m)/Mm]^{1/2} \tag{29}$$

The first valence vibration is due to the normal coördinate representing a symmetrical oscillation (hence the descriptive letters) of the two outer atoms, each moving to and from the central atom which is stationary. It is therefore spectrally inactive. The second valence vibration is of the two like atoms moving as a unit (distance between them unchanging) in a direction opposite (asymmetrically, hence the descriptive letter a) to the motion of the central atom and parallel to the line joining the nuclei. It is active. The deformation vibration is of the two like atoms moving as a unit (distance between them unchanging) in a direction opposite to that of the central atom but perpendicular to the line joining the nuclei. Since there is a choice of two directions perpendicular to this line, the vibration is double. The deformation vibrations are active. These relationships are depicted in figure 4.

The quadratomic collinear molecule (with two pairs of similar atoms) has two double deformation frequencies and three valence vibrational frequencies (notation adopted from Mecke (12d)).

$$\delta(s) = (1/2\pi)\ [2d/(M + m)]^{1/2} \tag{30}$$

$$\delta(a) = (1/2\pi)\ [d(1/2m + 1/2M)]^{1/2} \tag{31}$$

$$\left.\begin{matrix}\nu_2(s)\\ \nu_1(s)\end{matrix}\right\} = \frac{1}{2\pi}\left\{\left(\frac{k_1}{\mu_1} + \frac{k_2}{\mu_2}\right) \pm \left[\left(\frac{k_1}{\mu_1} - \frac{k_2}{\mu_2}\right)^2 + \frac{2k_1k_2}{\mu_2^2}\right]^{1/2}\right\}^{1/2} \tag{32}$$

$$\nu(a) = (1/2\pi)\ (k_1/\mu_1)^{1/2} \tag{33}$$

where k_1 is the $M - m$ binding constant, k_2 the $M - M$ binding constant, $1/\mu_1 = 1/m + 1/M$ and $1/\mu_2 = 2/M$. The character of the normal vibrations corresponding to these frequencies is also given in figure 4. The frequencies $\nu_1(s)$ and $\nu_2(s)$ and $\delta(s)$ are inactive; $\nu(a)$ and $\delta(a)$ are active.

(b) Statistical weights. In determining which of nuclear spin statistical weights combine with which vibrational and rotational levels of symmetrical molecules, it is of importance to know the symmetry character of the different normal vibrations. These have been worked out by Hund (4). In the case of the triatomic collinear molecule considered above, the two outer atoms of which are similar, the eigenfunctions corresponding to the first valence vibration $\nu(s)$ and the deformation frequency δ are symmetric with respect to interchange of the two equal nuclei. The eigenfunctions of the second valence oscillation $\nu(a)$ which have an even quantum number are symmetric; those of odd quantum number are antisymmetric. They, as well as those of the Y_2X_2 type molecule, have been discussed in much greater

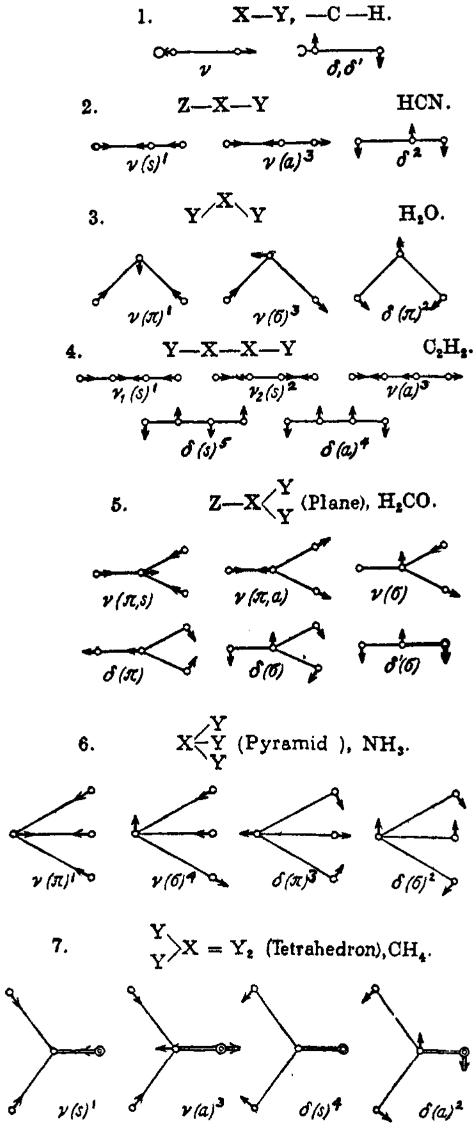


FIG. 4. FUNDAMENTAL NORMAL VIBRATIONS

(From Mecke (12d). Reproduced by courtesy of the publishers). The added superscripts designate Dennison (10) notation.

detail by Dennison (10). The reader is referred to that article for further study.

Case II—Top like molecules. A non-linear polyatomic molecule is the type most generally met with in chemistry. Table 5 gives the kinds of vibrations which these possess, as derived by Mecke (15a). Figure 4 gives the motions of the normal vibrations of this type of molecule.

TABLE 5

Normal vibrations of polyatomic molecules

TYPE MOLECULE	VALENCE VIBRATIONS	DEFORMATION VIBRATIONS
H_2O (Asymmetrical top)	2	1
NH_3 (Symmetrical top)	1 + (2)*	1 + (2)
CH_4 (Spherical top)	1 + (3)	(2) + (3)

* Parentheses indicate a multiple vibration of degeneracy indicated within.

(a) Energy levels. The fundamental valence frequencies of a symmetrically built (H_2O type) triatomic molecule which is non-linear are as follows (16),

$$\begin{matrix}\nu(\pi)\\ \text{or}\\ \delta(\pi)\end{matrix} = (1/2\pi)\left[(k + 2d)/2m + (k\cos^2\theta + 2d\sin^2\theta)/M \pm \sqrt{\{(k + 2d)/2m + (k\cos^2\theta + 2d\sin^2\theta)/M\}^2 - 2kd\,(2m + M)/M}\right]^{1/2} \quad \begin{matrix}(34)\\ \text{or}\\ (35)\end{matrix}$$

$\nu(\pi)$ goes with +, and is equation 34

$\delta(\pi)$ " " −, and is equation 35

$$\nu(\sigma) = (1/2\pi)\,[k(1/m + 2\sin^2\theta/M)]^{1/2} \tag{36}$$

where Θ is the angle between the symmetry axis and the valence bond. This reduces to the same ratio of $\nu(\sigma)$: $\nu(\pi)$ one would obtain from equations 28 and 29 by setting Θ equal to 90°, and disregarding the deformation force constant, d. (The Greek letters in parentheses indicate the direction of motion of the odd atom, π parallel, σ *senkrecht*, perpendicular, with respect to the symmetry axis.)

An unsymmetrically built molecule such as ROH where R is a heavy residue, has the following (15b) additional valence frequencies (collinear and first approximation).

$$\nu_1 = (1/2\pi)\ (k_{21}(1/m_1 + 1/m_2))^{1/2} \tag{37}$$

$$\nu_2 = (1/2\pi)\ [k_{32}\{1/m_3 + 1/(m_2 + m_1)\}]^{1/2} \tag{38}$$

where $m_3 > m_2 > m_1$. Mecke has pointed out that ν_1 is the internal O—H bond frequency and is (in the first approximation) independent of the mass of R(m_3), while ν_2 is the frequency of the R—OH bond. Equation 37 thus explains in a simple manner the well-known fact that definite infra-red or Raman frequencies may be ascribed unambiguously[7] to definite bonds (such as CH, NH, and OH) throughout a series of compounds. The normal vibrations of an ethylene type molecule have been given by Mecke in the same article (15a) which has been under discussion. The reader is referred to it for further consideration.

(b) Statistical weights. The vibrational statistical weights are determined as before from the *a priori* probabilities. The latter are equal to the number of ways of combining multiple oscillations to get the same total energy. In the case of symmetrical molecules, a knowledge of the symmetry character is also necessary in order to discover which *a priori* probabilities are ruled out by the exclusion principle. Each case is a law unto itself and will be postponed for further discussion until Part II.

In this connection it is of interest to recall a generalization of Ludloff (17) for combining functions, such as vibrational and rotational, of different symmetry character; the distribution of the rotational symmetry characters alone determines the distribution among the vibrational-rotational combined characters. Thus one-sixth of the rotational *a priori* probabilities of a symmetrical top like NH_3 are S (3), one-sixth are S (1 + 1 + 1), and two-thirds are degenerate, S (2 + 1). The distribution of these characters among the combined vibrational rotational states is the same. Rigorously speaking, this rule of Ludloff applies only to *a priori* probabilities. It is obvious that it does not necessarily

---

[7] Against this point of view, however, see Dennison (10, p. 305).

hold for the distribution of statistical weights among the different symmetry characters, since the Boltzmann energy factor is apt to cause profound changes in the relative weight of each term. The rule is therefore valid only at high temperatures, where ϵ/kT is very small.

ELECTRONIC

Energy levels

1. Diatomic molecules. A prolific literature has arisen on the electronic structure and energy levels of diatomic molecules (18). Of fundamental importance to chemistry is the potential energy curve of the electronic state under consideration. Naturally, that of the ground level is of most importance. Higher levels are usually so extremely high that their statistical weight is negligible; an exception to this general rule is a chemically unsaturated molecule[8] whose ground state is likely to be a multiplet with small energy level separation (19). The higher levels are accordingly of little interest to ordinary thermal chemistry; they are of importance to photochemistry.

Up to now there has been no completely satisfactory method of computing potential energy curves. One usually proceeds by setting the potential energy equal to an inverse power series in ρ, the fractional deviation from the equilibrium nuclear separation, and evaluating the constants by certain relations which may be derived from band spectra theory. This procedure has the disadvantage that the derived curves are valid only for small deviations from the equilibrium position. If one sets the potential energy equal to an inverse power series in r, the nuclear separation, beginning (20) with r^{-6}, he may evaluate enough of the coefficients to obtain a convergent series for large nuclear separations. But this is of no value for small separations, as the analytical form of the function makes it behave strangely, giving several minima, some of which are actually lower than the one corresponding to the stable state of the molecule. Perhaps the most satisfactory (although qualitative) way of representing potential energy functions is by the equation of Morse (21).

$$V = D\,[e^{-a(r - r_e)} - 1]^2 - W_0 \tag{39}$$

where D is the heat of dissociation plus the half quantum of vibrational energy, W_0, associated with the lowest vibrational state of the molecule, r_e is the equilibrium separation of the nuclei, and

$$a = 2\pi\nu_e\,(\mu c/2Dh)^{1/2} = 0.006547\;\nu_e(M/D')^{1/2} \qquad (40)$$

ν_e being given in cm.$^{-1}$ and taken from equation 22. M is the reduced mass in atomic weight units, D is in cm.$^{-1}$, and D' is in kg.-cals. This mode of representation is not perfect, basing its validity on the energy level approximation given in equation 22 (two terms only—and not making use of higher powers in the approximation). Birge[6] has recently shown that vibrational energy levels obey a peculiar discontinuous law, for which no theoretical reason has so far been advanced. This means that the Morse curve can never be more than a rough approximation, albeit it is perhaps the best at present available.

The importance of finding a valid potential energy curve arises from the possibility of explaining many kinds of chemical data thereby. By proposing the principle that electronic excitation occurs so rapidly that it is over before the nuclei have a chance to change their position (even though they are vibrating), Franck (1b) was able to derive the conditions for photochemical dissociation. By the further principle that the molecule spends most of its time at the ends of its vibratory swings where the motion is slowest, Condon (22) was able to explain the parabolic form of the v', v'' intensity charts. Many of the facts of predissociation have been explained by an application of this principle (23). Villars (1h) was able, by applying it in conjunction with the principle of energy conservation during allegiance exchange and assuming zero change in translational energy, to calculate the heat of activation of a chemical reaction (hydrogen iodide decomposition); the same considerations were applied by Franck and Rabinowitsch (24), who, in spite of the doubtful assumption that reaction is to be explained on the basis of translational energy alone, were able, by using much more qualitative data (ratio of equilibrium nuclear separation to gas-kinetic collision separations), to explain puzzling differences in behavior of different members of the same chemical family in the same type reaction.

Next in importance to obtaining the potential energy curves of the different electronic levels of a molecule is perhaps the task of suitably naming them. A good name should connote the quantum numbers of the electrons in the molecule as well as their resultant multiplicity and angular momentum. The detailed discussion of this topic is beyond the scope of the present article. Suffice it to say that Greek letters are used throughout to replace Roman ones whenever a molecular designation is implied in place of an atomic designation. Thus, Σ, Π, Δ (corresponding to S, P, D) mean that the component of electronic angular momentum along the line joining the nuclei, Λ, (corresponding to L in atomic spectra) is respectively 0, 1, 2. A superscript to the left of the letter denotes, as in atomic spectra, the multiplicity. A + or − superscript to the right of the symbol denotes a "symmetric" or, respectively, "antisymmetric" eigenfunction with respect to reflection in any *plane* passing through the nuclei. Since each state with $\Lambda > 0$ has both, the superscript is not used, but the state has double *a priori* probability nevertheless. A subscript, g or u (*gerade* even, or *ungerade*, odd), to the right is used for diatomic molecules, both nuclei of which are the same, and denotes a "symmetric" or, respectively, "antisymmetric" eigenfunction with respect to a reflection through the *mid-point* of the line joining the nuclei. (Quotation marks are used since symmetric or antisymmetric refers usually only to an interchange of like particles.) This character may be ascertained (6, 25) by computing the arithemetical sum of all the separate l values of all component electrons of both atoms. If the sum is even, the term is g; if odd, u. The terms $\overset{+}{g}$ and $\bar{u}$ are symmetric in the *nuclei*; the terms $\bar{g}$ and $\overset{+}{u}$ are antisymmetric in the *nuclei*. The above symmetry properties demand certain selection rules. Thus, only transitions between + and +, or − and − states are allowed, and only those between even and odd ones (as in atomic spectra).

2. Polyatomic molecules. Potential energy curves for the polyatomic molecule have not as yet been systematically considered. As data on higher vibrational levels are accumulated, it should be possible eventually to draw one potential energy curve for each normal vibration. These individual potential energy curves will then be as important to the elucidation of transition probabilities between the various vibrational states of electronic levels of polyatomic molecules as are the Franck-Condon curves for diatomic molecules. Urey (16) has recently applied such considerations to SO_2 and ClO_2. A hint of their importance is disclosed by a recent article of Kato (26), who believes that the deformation vibration of acetylene leads to polymerization to benzene whereas excitation of the valence vibrations causes polymerization to cuprene.

The vibrational energy levels of electronically excited polyatomic molecules are to be represented in the same manner as for unexcited molecules, *i.e.*, by a sum of as many equations similar to equation 22 as there are normal coördinates, each quantum number of vibration being capable of independent variation. Equation 22 need not hold continuously for all quantum numbers; indeed it has been found that there is a discontinuity in the case of some molecules (27), the vibrational energy levels of excited SO_2 actually getting wider and wider apart as the molecule vibrates more strongly, with the spacing passing through a maximum before the levels start to converge. Before the maximum, the levels obey equation 22 with one set of parameters; after the maximum (spacing), they obey equation 22 with a different set of constants.

Another characteristic, although not unique, property of polyatomic molecules is the phenomenon of predissociation (28). We shall not go into this subject more than to indicate its bearing on the energy level problem. If a discrete energy level of the molecule happens to be superimposed over a system of continuous levels of a different electronic state, radiationless transitions (resulting in dissociation) may occur from the quantized state to the unquantized state, provided certain rules are obeyed, and the result is that the discrete energy level becomes fuzzy. This is of great importance to certain photochemical processes, as it connotes a mechanism of photochemical dissociation. The rules which govern such radiationless transitions were laid down by Kronig (29), (*1*) Total moment of momentum must be conserved

(*2*) $\Delta\Lambda \ngtr 1$

(*3*) Both states must have same symmetry as regards reflection through origin (one state may not be *g* with the other *u*)

(*4*) Both states must have same symmetry in electrons (same electronic multiplicity)

(*5*) Both states must have same symmetry in nuclei

and by Franck and Sponer (23).

Radiationless transitions are most probable at nuclear separations where the potential energy curves cross.

The only pretentious article so far published which discusses electronic states of polyatomic molecules is that of Dunkel (30), who seeks to systematize the ground states of molecules. He attempts to assign quantum numbers to the individual electrons in the molecule, but touches the more important question of naming and describing the significance of the complete resultant state only in the few instances where the molecule described is chemically saturated, $^1\Sigma$.

In extending the Greek notation of diatomic molecules to polyatomic molecules, it is natural to inquire what is the meaning of resultant molecular angular momentum, such as Λ. In diatomic molecules, only the component of L along the internuclear axis is conserved, the perpendicular component being averaged out to zero due to precession around this axis. Which axis is to be chosen in a polyatomic molecule? Naturally, it must be the symmetry axis, if there is one. This will apply to collinear molecules, or symmetrical tops. In the asymmetrical top, this quantum number will no longer have meaning and the electronic motions will be very complicated.

Hund (6) has recently made some helpful suggestions along these lines. He points out that collinear molecules have exactly the same symmetry classes as the diatomic molecule and that the same electronic state notation is applicable as that outlined above, down even to the designation of the multiplicity ($2S + 1$, superscript to left) and $\Lambda + \Sigma$ (usually Ω, subscript to right). Furthermore, one may designate even and odd terms in symmetrical molecules such as HCCH. Terms with $\Lambda > 0$ have likewise a double statistical weight. This is no longer true for non-linear molecules. If the deviation from linearity be slight, the + and − terms of $\Lambda > 0$ will be resolved and one may designate the components as Π^+, Π^-, Δ^+, Δ^-, etc. These letters may be surrounded by brackets, if one wishes to denote that the angular momentum indicated really has no longer any meaning but has "historical" significance only (for example, refers to an atomic state from which the molecule was derived). Similar notation may be used for individual electrons. Systems in which the nuclei are arranged symmetrically about a plane allow a separation of terms into + and − with respect to reflection in the said plane. Other types of symmetry will allow corresponding division of the terms into symmetry classes but must be worked out for the special case.

* Recent articles closely related to the subject of electronic energy levels of polyatomic molecules which should be called to the attention of the reader are those of Hund (30.1) and Mulliken (30.2). The latter amplifies his earlier discussion (30b) of the bonding power of different electrons and extends it to the polyatomic molecules and ions, H_2O, NH_3, CH_4, CF_4, CI_4, ClO_4^-, SO_4^{--}, ClO_3^-, SO_3^{--}, CO_2 and others. Two significant points in nomenclature are the recognition, by Mulliken, of an extra difference in the three pairs of p electrons of H_2O and NH_2^-, due to the molecular symmetry, by adding an a, b and a c, thus—$2pa^2$, $2pb^2$, $2pc^2$—, in H_3O^+, NH_3 by the inclusion of the small Greek letter in brackets, thus, $2p\,[\pi]^4$, $2p\,[\sigma]^2$ and the introduction of the designation q-valence by Hund to describe those terms which are combinations of $s-p$ ones. Pauling (30.3) and Slater (30.4) were the first to show that the proximity of the $sp^3\ {}^5S$ level in carbon to the ground state $s^2p^2\ {}^3P$ modifies the lowest term in CH_4 so much that it is no longer correct to speak of sp^3 or s^2p^2 electrons. This requantization is the direct cause of the tetrahedral symmetry of the valence bonds of carbon. To quote from Hund (30.1, page 27), "The configuration q^4 (s^2p^2) can saturate four valences. This seems to be the *adapted concept of the C valence.* In common with the Heitler-Herzberg (30.5) concept, it is essential that the

---

* Paragraphs marked with an asterisk are insertions made on September 30, 1932.

energies of the s and p states be not very different. While, however, there, the carbon bond is explained as coming from the sp^3 ^5S term, here the quadrivalence is a property of the whole group of terms, s^2p^2, sp^3, p^4 called q^4 in short. The ground state of the molecule can thereby dissociate into the lowest state of the atoms (C in s^2p^2 ^3P)".

Statistical weights of electronic states

* The *a priori* probability of an electronic state of a molecule is determined from its spin and electronic angular momentum in the same way as that of an atom, with this difference: the quantum number, Λ, of a molecule corresponds to the quantum number, M_L, of an atom in an axially symmetrical electric field. The latter is doubly degenerate, inasmuch as positive and negative values of M_L in an electric field have the same energy associated with them, whereas the energies would be split, one sent up and the other down, if resolved in a magnetic field. Therefore, any molecular state of $\Lambda > 0$ is double, (Λ type doubling), one being positive ($^+$) and the other negative ($^-$). It is to be noted[8] that the *a priori* probability due to angular momentum is not $2\Lambda + 1$, since Λ corresponds to M_L and not to L. The total statistical weight of an electronic state is therefore

$$\begin{aligned} p_e &= (2S + 1)\, e^{-\epsilon_0/kT} \quad \Lambda = 0 \\ &= 2(2S + 1)\, e^{-\epsilon_0/kT} \quad \Lambda > 0 \end{aligned}$$

If the molecule is homonuclear, the states $\overset{+}{g}$ and $\bar{u}$ are S_N, $\bar{g}$ and $\overset{+}{u}$ are A_N as mentioned above, and these symmetries must be accounted for in deriving the term weights for the different nu-

---

[8] Such as hydroxyl (reference 19). The author wishes herewith to correct the statistical weights of the ground electronic states of hydroxyl given in reference 19. These weights were computed on the misapprehension that Λ corresponds to L, not to M_L. The first term on the right of the equation for $S_{\mathrm{ele_0}}$ of OH at the bottom of p. 707 (19) should read (statistical weight in the parenthesis):

$$R \ln(2 + 2\, e^{-h\Delta\nu/kT})$$

This means the entropies given in that paper are too high by about 1.0 at 298.1°K. and 0.8 at 2500°K. and a corresponding error resides in the equilibrium constants. In the paper of Bonhoeffer and Reichardt (Z. physik. Chem. **139A**, 75–97 (1928)) the same error is made.

TABLE 6

Constants of triatomic molecules of XY_2 *type**

	NON-LINEAR					COLLINEAR		
	$H_2O^{(a)}$	$H_2S^{(h)}$	O_3	$SO_2^{(r)}$	$ClO_2^{(V)}$	$CO_2^{(31)}$	CS_2	$NNO^{(p)}$
$I_1'' \times 10^{40}$ g.cm.^{2}	$2.985^{(85)}$	1.33		550		$70.2^{(j)}$	$172^{(y)}$	66.0
$I_2'' \times 10^{40}$	$1.907^{(85)}$			500		$70.2^{(j)}$	$172^{(y)}$	66.0
$I_3'' \times 10^{40}$	$1.09^{(85)}$			47		$0^{(j)}$	0	0
Θ (bond-sym. axis)	$51\frac{1}{4}°^{(85)}$			$12°^{(r)}$, $34°^{(s)}$	65°10′	90°	90°	90°
r''_{XY}Å	$0.972^{(85)}$			$4.8^{(r)}$		1.14	1.27	$1.14^{(12b)}$
r''_{YY}	$1.516^{(85)}$			$2.0^{(r)}$		2.30	$2.54^{(y)}$	$1.10^{(12b)}$
$\nu(\pi)$ $(Y \rightarrow X \leftarrow Y)$ cm.$^{-1}$	$3830\text{–}95v_\pi{}^{(b)}$	2615	$435^{(q)}$	1164	727.0	$1285.8^{(41)}$	$655.5^{(y)}$	1285.7
or $\nu(s)$				$-9(v_\pi + \frac{1}{2})^{(s)}$				
$\nu(\sigma)$ $(Y \rightarrow \leftarrow X\ Y \rightarrow)$	$3950\text{–}100\ v_\sigma{}^{(b)}$	2685		1369	857.7	$2326^{(41)}$	$1523^{(y)}$	2224.1
or $\nu(a)$				$-11\ (v_\sigma + \frac{1}{2})^{(s)}$				
$\delta(\pi)$ $(Y\downarrow\ X\uparrow\ Y\downarrow)$	$1600^{(d)}$	1180		610	528.8	$667.5^{(41)}$	$396.8^{(y)}$	589.01
or $\delta(a)$				$-2.3(v_\delta + \frac{1}{2})^{(s)}$				
Raman shift cm.$^{-1}$	$211.8^{(c)}$	$2615^{(i)}$		5243 (liq.)$^{(t)}$		$1264.5^{(k)}$	$655.5^{(x)}$	$1281.8^{(k)}$
	$699^{(f)}$			$1154^{(u)}$ (liq.)		$1285.1^{(k)}$	$795.0^{(x)}$	$2226^{(z)}$
	$3655^{(w)}$			1145.9 (liq.)$^{(t)}$		$1387.7^{(k)}$		
	$\approx 2.75\mu^{(g)}$			1340 (liq.)$^{(t)}$		$1408.4^{(k)}$		
	$\approx 3.13\mu^{(g)}$							

* Vibrational frequencies changing with v given here are defined (for convenience only) as the energy divided by hcv or $hc\,(v + \frac{1}{2})$ respectively according as v or $(v + \frac{1}{2})$ is used in expressing the energy level formula.

(a) For a different assignment of fundamental vibrational frequencies cf. Ellis (35) and Plyler: Phys. Rev. **39, 77** (1932). The latter gives $\Theta = 57.5°$, $\nu(\pi) = 3742$, $\nu(\sigma) = 5309$, and $\delta = 1597$.

(b) Lueg and Hedfeld (38).

(c) Rideal (32).

(d) Mecke (15a).

(e) Gerlach: Physik. Z. **31,** 695 (1930).

(f) Meyer and Port: Physik. Z. **31,** 509 (1930).

(g) Mahanti: Physik. Z. **32,** 108 (1931).

(h) Mecke (12b) from Nielsen and Barker: Phys. Rev. **37,** 727 (1931).

(i) Bhagavantam: Nature **126,** 502 (1930).

(j) Houston and Lewis (39).

(k) Dickinson, Dillon, and Rasetti (49).

(l) Bailey and Cassie: Proc. Roy. Soc. London **132A,** 236 (1931).

(m) Watson and Parker: Phys. Rev. **37,** 1013, A7(1931). Also data on excited (28880 cm.$^{-1}$) state; $\nu(\pi)' = 215$, $\nu(\sigma)' = 270$ cm.$^{-1}$

(n) Gavesan and Venkateswaran: Nature **124,** 57 (1929); Ghosh and Mahanti: Nature **124,** 92 (1929).

(p) Plyler and Barker (45). For Raman spectra discussion, see Langseth and Nielsen: Nature **130,** 92 (1932).

(q) Wulf: Proc. Nat. Acad. Sci. **16,** 507 (1930).

(r) Bailey, Cassie, and Angus: Proc. Roy. Soc. London **130A,** 142–56 (1930).

(s) Watson and Parker: Phys. Rev. **37,** 1484 (1931). Also data on excited state ($\nu_e = 31468$ cm.$^{-1}$). $\nu(\pi) = 387 + 12\,(v'_\pi + \frac{1}{2})$ with $v'_\pi \leq 3$; $\nu(\pi) = 524\text{–}6(v'_\pi + \frac{1}{2})$ with $v'_\pi > 3$. $\nu(\sigma) = 341 + 14\,(v'_\sigma + \frac{1}{2})$ with $v'_\sigma \leq 4$; $\nu(\sigma) = 556\text{–}7(v'_\sigma + \frac{1}{2})$ with $v'_\sigma > 4$. $\delta' = 290 + 3(v'_\delta + \frac{1}{2})$ with $v'_\delta \leq 3$; $\delta' = 350\text{–}7(v'_\delta + \frac{1}{2})$ with $v'_\delta > 3$.

(t) Dickinson and West: Phys. Rev. **35,** 1126 (1930).

(u) Bhagavantam: Nature **126,** 995 (1930).

(v) Urey (16). Also similar data for electronically excited (19795.38 cm.$^{-1}$) ClO_2; $\Theta = 18°47'$ or $38°28'$, $\nu(\pi)' = 382.1$, $\nu(\sigma)' = 304.82\text{–}2.488\,(v'_\sigma + \frac{1}{2})$ and $\delta = 719.34\text{–}2.817\,(v'_\delta + \frac{1}{2})$ partly from Urey and Johnston: Phys. Rev. **38,** 581, A2, 2131 (1931).

(w) Daure and Kastler: Compt. rend. **192,** 1721–3 (1931).

(x) Krishnamurti: Indian J. Physics **5,** 109 (1930); cf. also note n.

(y) Dennison and Wright: Phys. Rev. **38,** 2077L (1931); cf. also note m for another fundamental frequency assignment and (l) for another moment of inertia. Cf. Bhagavantam (Phys. Rev. **39,** 1020L (1932)) who discusses a ν'_1 at 795.0 which is closely related to ν_1 at 655.5.

(z) Bhagavantam: Nature **127,** 817 (1931).

clear symmetry varieties. An excellent summary of the rules which these sublevels obey is to be found in Mulliken's treatise on band spectra (30.6).

Part II. Illustrative Examples

TRIATOMIC MOLECULES

H_2O.—The simplest triatomic molecule containing hydrogen atoms is water. Unfortunately it has resisted complete analysis, belonging as it does to the asymmetrical rotator class. Such a molecule, all atoms of which are in the same plane, obeys a fundamental relation between the moments of inertia

$$I_1 = I_2 + I_3 \tag{41}$$

where I_1 is the moment perpendicular to the plane.

The pure rotational spectrum of H_2O has been classified into three series (31) of lines having the wave numbers:

$$\bar{\nu}_1 = 24.5\,m = (h/4\pi^2 I_1)\,m \quad p = \text{const.};\ m \longrightarrow m - 1 \tag{41}$$

$$\bar{\nu}_2 = 16.8(p + 1/2) = (h/4\pi^2)\,(1/I_2 - 1/I_1)\,(p + 1/2) \quad m = \text{const.};\ p \longrightarrow p - 1 \tag{42}$$

$$\bar{\nu}_3 = 55.5(r + 1/2) = (h/4\pi^2 I_3)\,(r + 1/2) \quad \begin{array}{l} p = \text{const.}; \\ m = \text{const.}; \\ r \longrightarrow r - 1 \end{array} \tag{43}$$

These equations give the moments of inertia and internuclear distances appearing in table 6. The angle of inclination of the bond to the symmetry axis is given by Rideal (32) as

$$\tan^2 \theta = 8I_2/9I_3$$

or

$$\theta = 42 \text{ or } 47° \tag{44}$$

in agreement with the recent theories of directed valence (33), which predict a bond angle close to 90°.

The vibrational-rotational spectrum of H_2O is given in figure 5, taken from Mischke (34), Hettner (34), and Lueg and Hedfeld (38). The three types of normal vibrations are designated in figure 4. As the angle θ (between bond and symmetry axis)

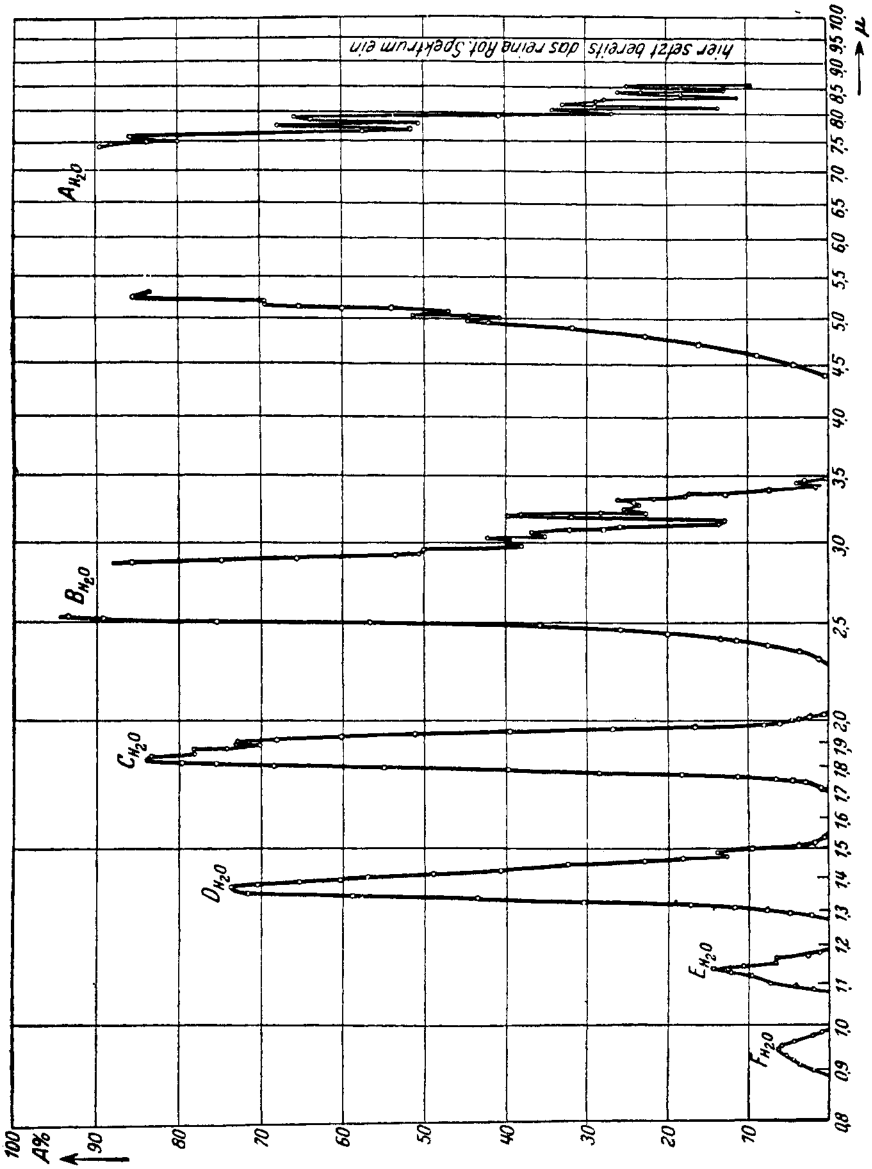


Fig. 5a The Water Vapor Spectrum
(From Mischke-Hettner (34))

approaches 90°, $\nu(\pi)$ goes into $\nu(s)$ (ν_1, Dennison (10, figure 4)) and becomes inactive, $\delta(\pi)$ becomes $\delta(a)$, (ν_2), and $\nu(\sigma)$ becomes $\nu(a)$, (ν_3), the latter two being active. Mecke (15) assigns the following values to these fundamental oscillations

$\nu(\pi)$ (Hund's ξ) = 3740 cm.$^{-1}$ (2.67μ)
$\nu(\sigma)$ (Hund's ζ) = 3850 (2.59μ)
$\delta(\pi)$ (Hund's η) = 1600 (6.25μ)

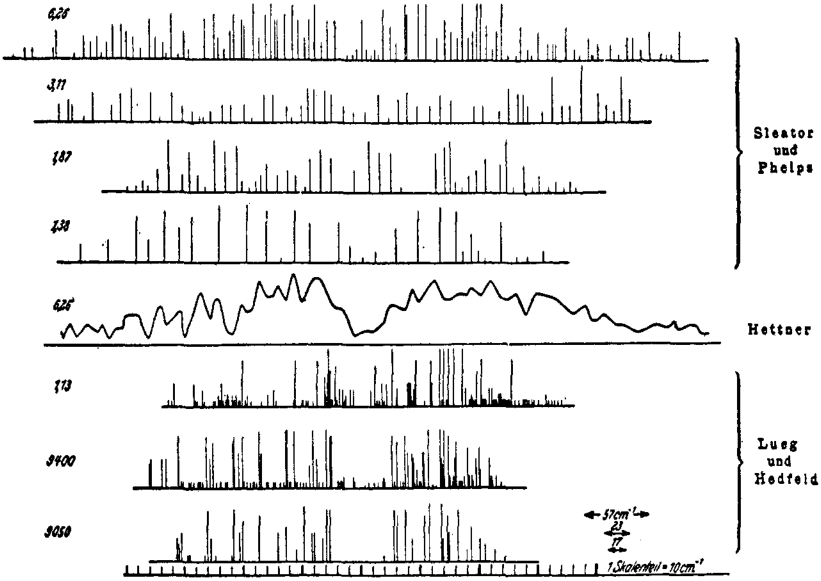


FIG. 5b. WATER VAPOR SPECTRA
(From Lueg and Hedfeld (38))

These are, however, not certain, Ellis (35) choosing for fundamentals the frequencies[9] corresponding to the bands at 6.1 and 2.9μ (1450 and 3450 cm.$^{-1}$ respectively) and Hund (4) those at 6 and 2.6μ. Plyler (36) gives for the fundamental frequencies 1.8835μ ($\sim$ 5310 cm.$^{-1}$), 2.67μ ($\sim$ 3745 cm.$^{-1}$), and 6.26μ ($\sim$ 1598 cm.$^{-1}$), and θ = 57.5°. Johnston and Walker (37) observe

[9] See also Phys. Rev. **38**, 582, A3 (1931) for new bands at 1.74μ (5750 cm.$^{-1}$) and 1.79μ (5590 cm.$^{-1}$) which are supposed to be combinations of 2.79μ (3580 cm.$^{-1}$), 6.1 (1640), and 19.5 (510); and of 290 (3450), 6.1 and 1.95μ.

the following Raman frequencies, which they believe to represent the fundamental vibrations: $\nu(\sigma) = 984$; $\nu(\pi) = 3654$; and $\delta = 1648$ cm.$^{-1}$. Mecke (12b) believes this assignment of the 984 frequency should go to a dihydrol vibration. In table 2 the values given are those of Lueg and Hedfeld (38).

The proper analysis of these vibrational frequencies can be made only in conjunction with the symmetry properties of the eigenfunctions. Such an analysis has so far not been made but is promised by Dennison (10). Hund (4) has shown that, of the rotational levels when $\tau = 0$, the even numbered j levels are symmetric ($S(2)$) in the nuclei, and the odd ones are antisymmetric ($S(1 + 1)$). The levels for which $\tau > 0$ are double, one being $S(2)$ and the other $S(1 + 1)$. These properties are represented in figure 6, taken from Hund. As to the vibrational

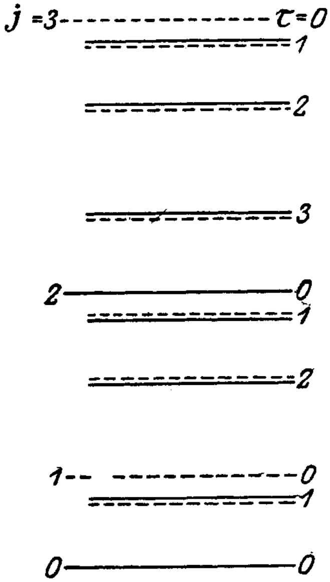
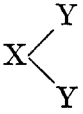


FIG. 6. ROTATIONAL LEVELS OF XY_2 TYPE SYMMETRICAL TOP MOLECULE (From Hund (4, p. 822)). In H_2O, an asymmetrical top, each level where $\tau > 0$, splits into two.

——— = symmetric term, $S(2)$.

………… = antisymmetric term, $S(1 + 1)$.

symmetry properties, the $\nu(\pi)$ and $\delta(\pi)$ vibrations are both symmetric in the nuclei. The $\nu(\sigma)$ vibrations are, beginning with the quantum number zero, alternately $S(2)$ and $S(1 + 1)$.

* Mecke (12b) has worked out approximations for the fundamental frequencies of an  $\mathrm{X}\!\left\langle{}^{\mathrm{Y}}_{\mathrm{Y}}\right.$ type molecule.

$$\nu_\pi^2 + \delta_\pi^2 = \omega_\mathrm{Y}^2 [\sin^2 \varphi(1 + p\beta) + \cos^2 \varphi(p + \beta) + \gamma_s^2 p] \qquad (44.1)$$

$$\nu_\pi^2 \, \delta_\pi^2 = \omega_\mathrm{Y}^4 \, p \, [\beta + \gamma_s \sin^2 \varphi] \qquad (44.2)$$

$$\nu_\sigma^2 = \omega_\mathrm{Y}^2 \, [1 + \gamma_a \cos^2 \varphi] \, [\cos^2 \varphi + p \sin^2 \varphi] \qquad (44.3)$$

where

$$p = 1 + 2\mathrm{Y}/\mathrm{X}$$

$$4\pi^2 \, \omega_\mathrm{Y}^2 = 2k/\mathrm{Y}r^2$$

the γ's are coupling constants between dipoles, and β that of a bending bond. The frequency ω_Y may be estimated from

$$\omega_\mathrm{Y}^2 \, (p + 1) \sim \nu_\pi^2 + \nu_\sigma^2 \sim 2 \, \nu_\mathrm{XY}^2 \, (b \sim \eta \sim \epsilon \sim 0) \qquad (44.4)$$

or

$$\omega_\mathrm{Y}^2 \, (p + 1) \sim \nu_\pi^2 + \nu_\sigma^2 + \delta_\pi^2 - (\nu_\pi \cdot \nu_\sigma \cdot \delta_\pi/\omega_\mathrm{Y}^2)^2/p \, (\epsilon \sim \eta \sim 0) \qquad (44.5)$$

"In non-linear molecules the relative bond interaction is much greater, around 30 per cent, than in collinear molecules, since it is through this interaction that a stable bond angle is achieved. In hydrides, it can be explained as a dipole stability ($\epsilon = \eta =$ 6 volts, $b \sim 0$), in the halogens as angle stability ($b \sim 10$ volts, $\epsilon = 0$) and polarizability perpendicular to the molecular axis ($\eta < 0$). Here the valence vibrations are characteristic vibrations, i.e., $\nu(\pi) \sim \nu_\mathrm{XY} \sim \nu(\sigma)$."

** Mecke, still more recently (85), has published the results of an analysis of the 9400, 9050, 8230, 7900 and 7230 Å. bands of water. The molecular constants given in table 6 have accord-

---

** Paragraphs added in proof, November 18, 1932.

ingly been revised to give his latest values. Approximate 1:3 intensity alternations were observed to occur. These alternations show that, in the non-vibrating molecule, when j is even, the lowest term (S) is weak, the next being strong; where j is odd, the order is reversed. From this he concludes that the obtuse-angled form is the correct one and that the ground term is $^1\Sigma_g$ as in H_2 and C_2H_2.

CO_2.—Carbon dioxide is an illustration of the collinear triatomic molecule. The moment of inertia indicated by Raman data (39) is 70.2×10^{-40} g.cm.². As this is probably more correct than that obtained from infra-red analyses as they now stand, Mecke's values for the inter-nuclear distances have been recalculated and the revisions are given in the table. Since the molecule is linear, it has one more normal vibration than the non-linear triatomic molecule. This extra vibration shows up in the doubling of the deformation frequency. The structure (40) of the unsymmetrical vibration $\nu(a)$, indicates that we probably have here alternating intensities. The deformation oscillation, δ, appears as a classical doublet (40). Martin and Barker (41) have investigated the absorption bands[10] at 4.3μ ($\sim$ 2326 cm.$^{-1}$) and 14.9μ ($\sim$ 673 cm.$^{-1}$) "with a grating spectrometer of resolving power sufficient to separate the rotation lines. The 4.3μ band consists of positive and negative branches only, with rotation lines about 1.5 cm.$^{-1}$ apart, and shows considerable convergence. The spacing is the same as in the long wave band, and is about twice the value obtained when estimated in the usual way from the doublet separation. This indicates that the molecule is linear, with the carbon atom midway between the two oxygen atoms. In the low frequency band, a strong zero branch appears at 14.9, with twenty or more rotation lines on either side, about equally spaced. . . . . A second harmonic band appears at 4.8μ, but there is no first harmonic. Superposed on the fundamental are three other bands, considerably less intense, of which two correspond to absorption by molecules already excited to the first vibration state by thermal impacts, while the third is a

---

[10] CO_2 bands at 4.3μ. $\Delta\tilde{\nu} = 1.5$ cm.$^{-1}$

difference band involving the inactive symmetrical vibration." The quadruple character of the Raman line of CO_2 (only one, $\nu(s)$, should be expected) is explained by Fermi (42) as due to a coupling effect between the $\nu(s)$ energy level and the 2δ level which is close by and likewise between the $\nu(s)$, δ level and the 3δ level.

* Mecke's (12b) approximate formulas for the fundamental frequencies of a Y—X—Y collinear molecule are

$$\nu(a)/\nu(s) \sim p^{1/2} \tag{44.6}$$

$$\nu_{XY}/\nu(s) \sim [(p+1)/2]^{1/2} \tag{44.7}$$

$$\nu^2(s)p - \nu^2(a) \sim 2\delta^2 \tag{44.8}$$

$$\nu^2(s) + \nu^2(a) \sim 2\nu^2_{XY} \tag{44.9}$$

where ν_{XY} is the vibration of the diatomic molecule XY. According to him, triatomic molecules arranged in a straight line are only found when a triple bond is present (CO_2, CS_2, N_2O, and HCN), which can be expressed in the ordinary notation as :Y: :X: : :Z:. The interaction between bonds, caused by Coulomb repulsion and attraction terms of induced polarizations is small and amounts only to 3 to 6 per cent of the bond firmness. A consequence of this is that the deformation vibration comes out quite small ($\delta:\nu(a) \sim \frac{1}{4}$) and the relation (equation 44.6) holds well.

The fundamental vibrational frequencies in table 6 lead to the following formula for the heat capacity of carbon dioxide

$$C_v/R = 5/2 + 2\,\varphi(956/T) + \varphi(1841)/T) + \varphi(3331/T) \tag{45}$$

where

$$\varphi(\Theta/T) \equiv e^{\Theta/T}(\Theta/T)^2/(e^{\Theta/T} - 1)^2 \tag{46}$$

Smyth (43) has analyzed an emission system of CO_2 from 2700 to 5000 reported by Fox, Duffendach, and Barker (44). Of two hundred bands, one hundred were partially separated into fifteen progressions of heads, of frequencies $\tilde{\nu} = 26271 - \nu_x + 1136.85\,v - 1.85v^2$ where ν_x takes on a particular value for each progression and $v = 0, 1 \ldots 10$. Both levels are electronically excited.

** Schmid (86) has photographed in the third order of a twenty-one foot grating the red degraded CO_2 bands at λ 3247, 3254, 3370, 3377, 3503, 3511, 3534, 3545, 3674 and 3839 Å. He finds these bands to be composed of *P* and *R* branches (no *Q* branches), which surprisingly contain no missing lines (cf. below) but some of which (2nd, 4th, 6th, 7th, and last named above) do show a staggering, which is interpreted as a missing level effect, caused by something akin to Λ type doubling. From the absence of a *Q* branch it is concluded that the transition may be a $^1\Pi \rightarrow {}^1\Pi$ or a $^1\Sigma \rightarrow {}^1\Sigma$, and it would seem that the former is indicated by the staggering effect, although the author does not state it definitely. The single structure of the bands indicates that the molecule is linear in both the initial and final states.

It is of interest to examine the effect of nuclear symmetry of the CO_2 eigenfunctions on the *a priori* probabilities. In the ground state of O_2, only the odd rotational levels are present and this is accounted for by the fact that the zero nuclear spin is incapable of taking on any but a symmetric configuration. This is still true for CO_2. One-half of its levels must therefore be missing, either those represented in figure 6 by the solid line (symmetric), or those represented by the dotted lines (antisymmetric), depending on whether $\sum_{\tau=1}^{2\times 8} l_\tau$ is respectively odd or even. This is concluded from the rules presented in Part I; oxygen, having an even number of protons in its nucleus, must contribute to carbon dioxide a total eigenfunction completely symmetric in the nuclei. This is for the ground vibrational state, and, in fact, for any vibrational state except those of the active valence (unsymmetrical) oscillation, $\nu(a)$, where the quantum number is odd, in which case the above statements are to be reversed. The Raman data of Houston and Lewis (37) show that only the even rotational levels are present in the ground state. Σl_τ is therefore even and the antisymmetric dotted levels of figure 6 are the missing ones.

The same considerations as the above apply to SO_2 and ClO_2, and similar ones may be developed for NON, with the difference that in the latter case both types of levels shown in figure 8 should appear, with a ratio of 2:1 (owing to the nuclear spin of unity), instead of 3:1 (H_2O) or 1:0 (CO_2) as before. Plyler and Barker (45) deduce from the absence of such intensity alternation in the lines of nitrous oxide that it has the unsymmetrical, though linear structure[11] $N \equiv N = O$.

QUADRATOMIC MOLECULES

NH_3.—Symmetry considerations indicate that the equilibrium shape of ammonia should be that of an equilateral triangular pyramid, with the nitrogen atom at the apex. If h is the height of this pyramid, the relations between the moments of inertia are as follows:

$$I_1 = I_2 = I_3/2 + \mu h^2 \tag{47}$$

where

$$1/\mu \equiv 1/3\mathrm{H} + 1/\mathrm{N} \tag{48}$$

and

$$\mu r^2_{\mathrm{N-H}} = I_1 + (\mathrm{N} - 3\mathrm{H})I_3/2(\mathrm{N} + 3\mathrm{H}) \tag{49}$$

$$= I_1 + 11I_3/34 \tag{50}$$

The infra-red spectra of ammonia are given in figure 7, taken from Lueg and Hedfeld (56). Sleator (48) notes the discovery of a new band at 16.1μ. The pure rotational spectrum satisfies the relation (42)

$$\tilde{\nu}_{\mathrm{rot}} = 19.957\, m - 0.0050826\, m^3 \tag{51}$$

Dickinson, Dillon, and Rasetti (49) find by Raman effect the levels

$$E_{\mathrm{rot}}/hc = 9.921\,(m + 1/2)^2 - 0.00063\,(m + 1/2)^4 \tag{52}$$

---

[11] Bailey and Cassie (Phys. Rev. **39**, 534L (1932)) reason that this structure should be further modified to be $N^- = N^+ = O$.

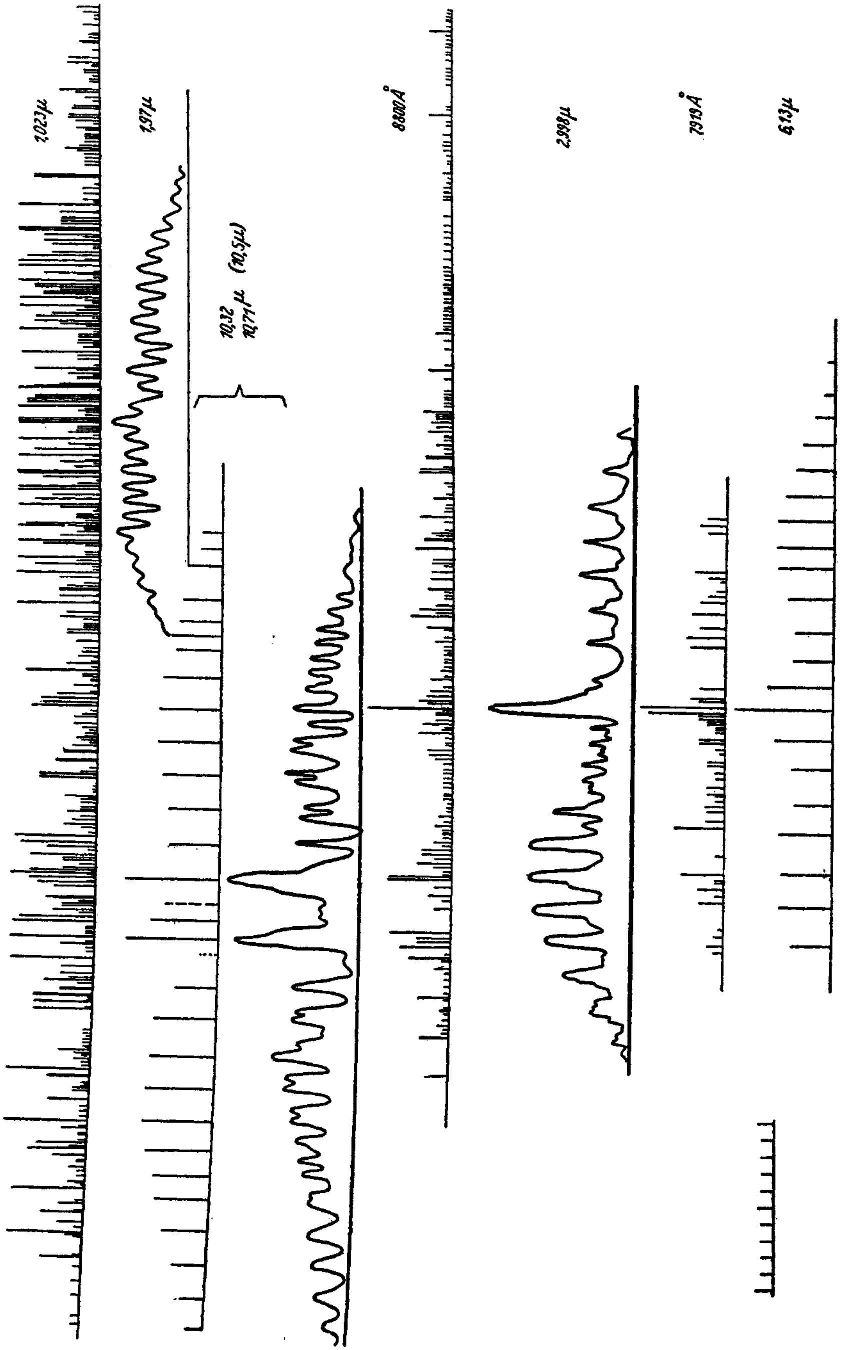


FIG. 7. NH_3 BANDS
(From Lueg and Hedfeld (56))
1 scale division = 10 cm.$^{-1}$

and a vibration frequency of 3333.6 cm.$^{-1}$. The latter is characteristic of the N—H bond. Langseth (50) obtains a resolution of the Raman lines of the first vibrational band

$$\bar{\nu} = 3317.4 \pm 19.87J \tag{53}$$

A rotational energy level diagram for ammonia has already been given in Part I, figure 2, and the statistical weights are enumerated in table 2. There are four distinct normal vibrations, two being double, making six in all (figure 4). Dennison (51) picks for the fundamentals, the bands at 10.7, 6.14, 2.97, and 2.22μ. The corresponding frequencies are those given in table 7. Higher harmonics of 2.97, $\nu(\sigma)$ are reported by Mecke and Badger (52), the third at 7920 Å., the fourth at 6474 Å. At 8810 Å., they find two series of lines having the same spacing as the band at 2μ, $\nu(\pi)$, but displaced. Another weak band at 5490 Å. is reported by Badger (53).

TABLE 7

Constants of quadratomic molecules, XY_3 type

	NH_3(a)	PH_3	AsH_3	PCl_3	PBr_3
$I_1'' \times 10^{40}$ g.cm.^{2}..	2.82				
$I_2'' \times 10^{40}$.........	2.82				
$I_3'' \times 10^{40}$.........	4.91				
Θ (XY bond-sym. axis)............	73°15′				
h (in Å.)..........	0.3				
r_{XY}..............	1.04				
r_{YY}..............	1.72				
$\nu(\pi)$cm.$^{-1}$.........	4450			510	397
$\nu(\sigma)$..............	$3396–60v_{\nu\,(\sigma)}$	$2374–47v_{\nu\,(\sigma)}^{(c)}$	$2162–47v_{\nu\,(\sigma)}^{(c)}$	485(d)	379(d)
$\delta(\pi)$..............	966	993(c)	906(c)	256	161
$\delta(\sigma)$..............	1630.9(b)	1125.0(b)	1005.4(b)	190	115
Raman...........	3333.6				

(*a*) Lueg and Hedfeld (56). They interpret the spectrum in terms of only three fundamental frequencies, 933–936, 1630, and 5054 cm.$^{-1}$.

(b) Robertson: Trans. Faraday Soc. **25**, 899 (1929).

(c) Badger and Mecke: Z. physik. Chem. **5B**, 333 (1929).

(d) Trumpy: Z. Physik **68**, 675 (1931).

The symmetry character of the rotational levels of the ground vibrational state, given in figure 2, is double, two series of energy levels of reciprocal character being superposed, each originating from a separate level of the doubly degenerate ground vibrational state. The latter ($\delta(\pi) = 0$) is double, because of the possibility of the existence of mirror image positions of the nitrogen atom with respect to the plane defined by the three hydrogen atoms (4); one level is symmetric, $S(3)$, and the other antisymmetric, $S(1 + 1 + 1)$. The purely rotational energy level diagram might perhaps be better represented by the left-hand series alone, were it not for the fact that the two superposed ground vibrational levels were indistinguishable, except for a slight resolution which Barker (47, 54) believes[12] to be manifested as a duplicity in the 10.7μ band ($\delta(\pi)$). The symmetry character of the different vibrational levels and their *a priori* probabilities are summarized in table 8. The resultant character and *a priori* probability of the final vibrational state is the product of the corresponding quantities for all the different types of vibration. The number of $S(3)$ states obtained on multiplying two $S(2 + 1)$ types is one-fourth of the product; likewise, the number of $S(1 + 1 + 1)$.

TABLE 8

Symmetry character and a priori probabilities of normal vibrations of NH_3 *type molecule*

NORMAL VIBRATION	v	p		
		S (3)	S (2 + 1)	S (1 + 1 + 1)
$\nu(\pi)$	$2m$	1	0	0
	$2m + 1$	0	0	1
$\delta(\pi)$	any	1	0	1
$\nu(\sigma)$	0	1	0	0
	1	0	2	0
	2	1	2	0
	3	1	2	1
	$2m$	1	$2m$	0
	$2m + 1$	1	$2m$	1
$\delta(\sigma)$	Same as for $\nu(\sigma)$			

---

[12] Confirmation of this is given by Dennison and Hardy (55).

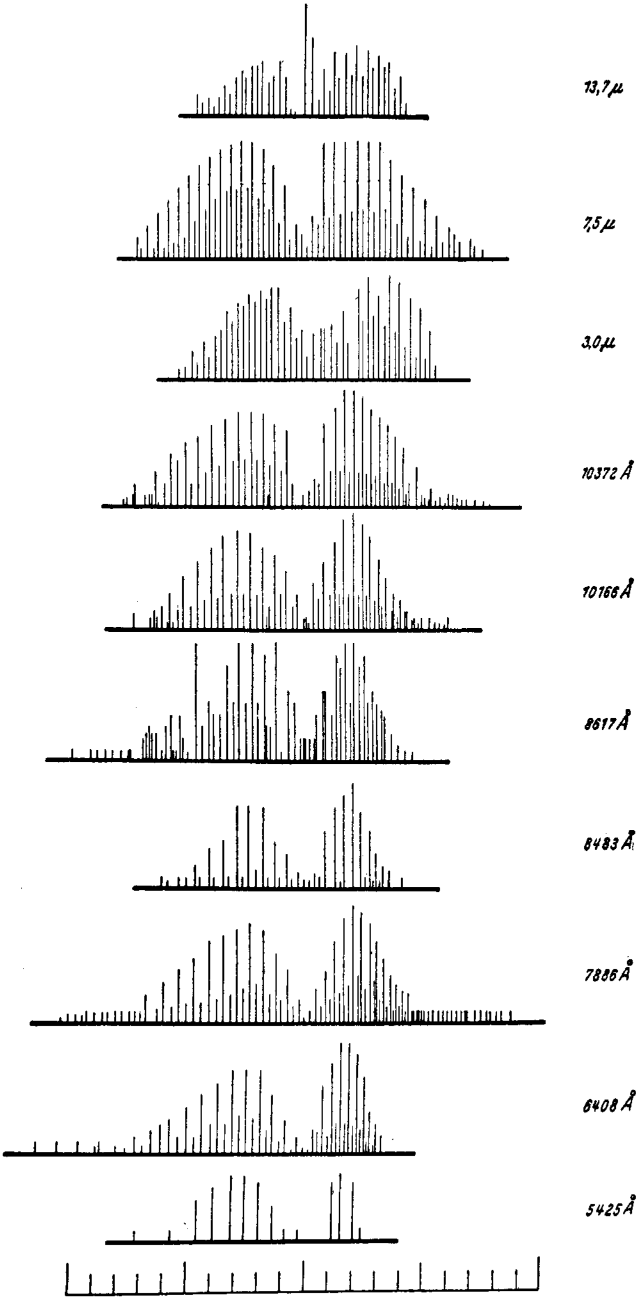


FIG. 8. C_2H_2 BANDS
(From Hedfeld and Lueg (64))
1 scale division = 10 cm.$^{-1}$

The remaining half are $S(2 + 1)$. These rules have been already enumerated in Part I.

* Two important articles on NH_3, contributed during the present year, have been by Dennison and Hardy (55) and by Lueg and Hedfeld (56).

C_2H_2.—Acetylene has a linear structure (57, 15a). Figure 8 illustrates the structure of its infra-red bands. Three bands at λ 7887, 7956, and 8622 have been reported by Hedfeld and Mecke (58). The band at λ 7887 Å. was analyzed by them and by Childs and Mecke (59). It is a $^1\Sigma \longleftrightarrow {^1\Sigma}$ transition and gives a ground state moment of inertia

$$I'' = 23.509 \times 10^{-40} \text{ g.cm.}^2$$

If one assumes the C—H distances to be the same as in CH_4, the internuclear distances may be calculated and are

$$r_{\text{C—H}} = (1.08) \text{ Å.}$$

$$r_{\text{C—C}} = 1.19 \text{ Å.}$$

(The C—C distances in diamond and in the Swan (C_2) bands are respectively 1.54 and 1.31 Å.) The band lines show an alternating intensity of ratio odd J: even $J = 3$, which is to be explained as due to the nuclear moments, $i_H = \frac{1}{2}$ and $i_C = 0$. An ultraviolet band at 2400 Å. has been partially analyzed by Kistiakowsky (60). It gives a moment of inertia, for the excited state of

$$I' = 25.6 \times 10^{-40} \text{ g.cm.}^2$$

Herzberg (61) has found two band systems of $\lambda < 2070$ Å. System A is equivalent to the $^3\Sigma$ 8.18 v. $\rightarrow$ $^1\Sigma$ 0.0 v. bands of nitrogen. The excited state manifests the vibrational frequencies 1365 and 865 cm.$^{-1}$. The second system (at λ 1540) is analogous to the Lyman, Birge, Hopfield bands of nitrogen at 1450 Å. ($^1\Pi$ 8.5 v. $\rightarrow$ $^1\Sigma$ 0.0 v.). It exhibits a vibrational frequency of 1710 cm.$^{-1}$.

The normal vibrations have been given in Part I, figure 4. Their values, as derived by Mecke (12c), are given in table 9.

Olson and Kramers (62) took exception to Mecke's original assignment (15a) of the deformation oscillations, calculating them to have a ratio of $\delta(a):\delta(s) = 0.816$ instead of Mecke's original, 1.88. The ratio now agrees, its value being 0.825, with the newer assignment. The deformation vibrations are double. Raman lines at $\Delta\bar{\nu} = 1974$ and 3372 have been found by Bhagavantam (63). These agree with Mecke's inactive frequencies, $\nu_2(s) = 1975$ and $\nu_1(s) = 3365$.

TABLE 9

Spectrum analysis of acetylene and ethylene

Mecke (12c)

C_2H_2			C_2H_4		
13.71μ	729.27	$\delta(a)$	10.5 μ	949.7	$\delta(\sigma, a), \delta'(\sigma, a)$
7.53	1328.5	$\delta(a) + \delta(s)$	6.95	1443.9	$\delta(\pi, a)$
3.78	2643.2	$\nu_1(s) - \delta(a)$	5.29	1889.7	$\delta'(\sigma, a) + \delta'(\sigma, s)$
3.75	2669.7	$\nu(a) - \delta(s)$	4.88	2047.0	$\delta(\sigma, a) + \delta(\sigma, s)$
3.72	2683.0	?	3.35	2988.2	$\nu(\pi, a)$
3.70	2702.2	$\delta(a) + \nu_2(s)$	3.22	3107.4	$\nu(\sigma, a)$
3.05	3276.85	$\nu(a)$	2.38	4207.9	$2\,\delta(\pi, a) + \delta(\pi, s)$
2.56	3897.9	$\nu(a) + \delta(s)$	2.31	4324.3	$\nu(\pi, a) + \delta(\pi, s)$
2.44	4092.0	$\nu_1(s) + \delta(a)$	2.22	4515.5	$2\,\delta(\pi, a) + \nu_2(\pi, s)$
2.14	4690	$\nu_1(s) + \delta(a) + \delta(s)$	2.10	4729.0	$\nu(\sigma, a) + \nu_2(\pi, s)$
1.9	5250	$\nu(a) + \nu_2(s)$	0.872	11465.0	$4\,\nu$
1.54	6500	$\nu(a) + \nu_1(s)$			
1.04	9610	$3\,\nu(a)$	*Ra*	1342 (20)	$\delta(\pi, s)$
1.18	8450 (?)	$\nu(a) + \nu_1(s) + \nu_2(s)$	*Ra*	1623 (15)	$\nu_2(\pi, s)$
0.862	11593	$3\,\nu(a) + \nu_2(s)$	*Ra*	2880 (3)	$2\,\delta(\pi, a)$
0.789	12675.59	$4\,\nu(a)$	*Ra*	3019 (20)	$\nu_1(\pi, s)$
			Ra	3240 (2)	$\nu(\sigma, s)$
Ra	1975	$\nu_2(s)$	*Ra*	3272 (1)	?
Ra	3370	$\nu_1(s)$			

Molecular constants of acetylene

$\nu_2(s)$	1975	$\delta(s)$	600
$\nu_1(s)$	3370	$\delta(a)$	729
$\nu(a)$	3277		—
ν_{CH}	(3200)	ν_{CC}	2100
r_{CH}	1.08	r_{CC}	$1.19 \cdot 10^{-8}$
k_{CH}	20 Volt	k_{CC}	69 Volt

For a discussion of the symmetry relations, the reader is referred to Dennison (10).

* A recent article of interest in addition to that of Mecke (12c) is one by Hedfeld and Lueg (64) who investigated the spectrum with high dispersion (2.6 Å. per mm.) in the region from 11000 to 5000 Å. by means of the new sensitized photographic technique in the near infra-red. They determine the moment of inertia to be

$$I'' = 23.51 \times 10^{-40} \text{ g.cm.}^2$$

$$I' = 23.82$$

* Lochte-Holtgreven and Eastwood (65) report the discovery of two more bands at 10164.8 and 10369.8 Å. The latter band is interpreted as the third harmonic, $3\nu(a)$. It possesses strongly developed P and R branches and a weak line near the origin. The former band is assigned as $\nu(a) + 2\nu_2(s)$. Other bands assigned are

$$\nu_1(s) + 3\nu(a) \quad 8622 \text{ Å.}$$

$$\nu_2(s) + 3\nu(a) \quad 7887 \text{ Å.}$$

This assignment agrees with Dennison's (10) theory that only odd integral multiples of the optically active frequencies can be seen in the spectrum and that the combinations must involve at least one of these frequencies.

H_2CO (Cf. table 10 and figure 4).—A third type of quadratomic molecule is represented by formaldehyde. This absorbs infra-red radiation at the regions 4.7, 3.38, 1.8, 1.4, 2.3 and 1.25μ (given in order of decreasing intensities) (66). The second of these bands has been further resolved into three (67), 3.61, 3.52, and 3.37μ, the first and third of which show P, Q, and R branches with a spacing of 3.5 cm.$^{-1}$. The second gives one branch only, with groups of closely spaced lines, the groups being 14.0 cm.$^{-1}$ apart. The band at 4.7μ is similar to those at 3.61 and 3.37μ. From the above spacings, these authors have derived the following moments of inertia.

$$A = 2.7 \times 10^{-40} \text{ g.cm.}^2$$
$$B = 18.0 \times 10^{-40}$$
$$C = 21.0 \times 10^{-40}$$

Formaldehyde absorbs ultra-violet light at about λ 3570 Å. (corresponding to the Schumann-Runge $^3\Sigma$ 6.09 v. → $^3\Sigma$ 0.0 v. oxygen bands) and shows the phenomenon of predissociation (68) at λ 2750. Herzberg (61) has shown that the important vibrational frequencies of the excited state are 1187 and 830 cm.$^{-1}$ (the latter instead of 360 cm.$^{-1}$ of Henri and Schou). The frequency shown in the ground state[13] is 1300 cm.$^{-1}$, and corresponds to a transverse vibration. Herzberg believes the 1187 cm.$^{-1}$ frequency in the excited state to be a valency vibration of $H_2C \leftrightarrow O$ analogous to the oxygen vibration (708 cm.$^{-1}$) in

TABLE 10

Constants of quadratomic molecules of Y_2XZ *type*

	H_2CO	$COCl_2$	$SOCl_2$^(d)^
$A \times 10^{40}$ g.cm.^{2}	2.951 (61.2)		
B	21.63 (61.2)		
C	24.58 (61.2)		
$\nu(\pi, s)$	2945^(d)^	571^(d)^	488
$\nu(\sigma)$		444	451
$\nu(\pi, a)$	1770	1810	1229?
$\delta(\pi)$	1460	301 ?	343?
$\delta(\sigma)$	1040		282?
$\delta(\sigma)$	920		192?
Raman cm.$^{-1}$	920 1040 1460 1770 2945 (b) 1285^(c)^	567 cm.$^{-1}$ 444 290 (a)	

(a) Henri and Howell: Proc. Roy. Soc. London **128A,** 190, 192 (1930).
(b) Mecke (69).
(c) Hibben: J. Am. Chem. Soc. **53,** 2418 (1931).
(d) Mecke (12d).

---

[13] Doubt is cast on the correctness of this assignment by Herzberg and Franz (72).

the upper $^3\Sigma$ Schumann-Runge band state of O_2. The lower frequency, 830 cm.$^{-1}$, is probably that of the transverse oscillation of the hydrogen atoms.

At λ 1650, a very strong discontinuous absorption is found (55), three bands of which are separated by the distance 1180 cm.$^{-1}$.

As pointed out by Mecke (69) in the discussion of the work of Herzberg, there are six oscillations for a non-linear quadratomic molecule such as HCHO. He takes for five frequencies of the ground level, the Raman frequencies 920, 1040, 1460, 1770, and 2945 cm.$^{-1}$. The sixth missing one is supposed to be 3000 cm.$^{-1}$ (which is a general characteristic of a C—H bond vibration).

The symmetry characteristics of the eigenfunctions of H_2CO have not been worked out, to the author's knowledge. The states should fall, however, into two classes, H nuclear singlet and triplet, since the hydrogen nucleus has a spin of $\frac{1}{2}$, and the carbon and oxygen each have zero spin. It should be possible to observe alternating intensities in the ratio of 1:3 in certain of the band lines. Two other types of symmetry should also exist, namely, those with respect to reflection about the line joining the carbon and oxygen nuclei and those with respect to reflection by the plane perpendicular to the line joining the hydrogen nuclei and passing through the carbon and oxygen nuclei.

* Four papers on formaldehyde have appeared during the present year since the original submission of this review. Patty and Nielsen (70) give the detailed work which was summarized in their Physical Society Abstracts (66 and 67). The average spacing of the lines in the P and R branches in the 4.8μ region is now given as 3.1 cm.$^{-1}$ (instead of 3.5).

* Dieke and Kistiakowsky (71) have studied the ultra-violet absorption bands, 3520, 3430, 3390, of formaldehyde in the third order of a forty foot grating. The molecule proves to be almost a symmetrical top, deviations occurring only for $\tau < 4$ and resulting in a shift and doubling of the lines which increases with increasing J. Intensity alternations occur, verifying the prediction made above. The three moments of inertia for the ground level are

	Ground State	Excited State $v = 0$	Excited State $v = 1$
$A =$	24.58	27.98	28.13×10^{-40} g.cm.^{2}
$B =$	21.63	24.81	24.94
$C =$	2.951	3.176	3.190

This gives

$$r_{\text{H—H}} = 1.88\ \text{Å}.$$

$$\left.\begin{array}{l} r_{\text{C—O}} = 1.19 \\ r_{\text{C—H}} = 1.15 \end{array}\right\} \text{Assuming } \angle \text{ HCH is tetrahedral}$$

The type and intensities of bands occurring are as follows:

pP and *rR* both strong; they are the only branches for high τ.

pQ and *rQ* strong for small values of τ.

pR and *rP* weak and present only for small values of τ.

In the above, the small letters refer to changes in τ in the symmetrical top formula for energy levels, equation 7 of Part I, while the large letters refer to changes in J.

$$\Delta J = J' - J'' = -1,\ 0,\ +1 \quad \text{for}$$

$$P \quad Q \quad R \text{ branches respectively}$$

* Herzberg and Franz (72) have investigated the ultra-violet spectrum of formaldehyde by exciting it to fluorescence by a carbon arc. They obtain a frequency formula

$$\begin{aligned} \bar{\nu} = 26967 &- (1723\, v_1'' - 10 v_1''^2) \\ &- 1023\, v_2'' - 37 v_1''\, v_2'' \end{aligned} \tag{52.5}$$

The frequency 1713 corresponds to the Raman (liquid state) 1768, while 1023 corresponds to Raman 1039, which Mecke explains as being the $\delta(\sigma)$ vibration. But Teller has derived a rule for electron transitions in polyatomic molecules according to which practically only the parallel (π) vibrations may change their quantum numbers, when the symmetry of the molecule in the upper and lower states is the same. These authors therefore conclude that both frequencies appearing in fluorescence must be π vibrations. The 1023 oscillation must be $\delta(\pi)$ and involves the vibration of the hydrogen atoms against one another. This frequency is remarkably small. The decrease in the C—O vibration, $\nu(\pi, a)$, from 1725 cm.$^{-1}$ to 1180 on excitation indicates an extensive bond loosening and this is used to explain, by application of the Franck-Condon principle, the large number of bands which arise in this progression. This is in harmony with the hypothesis that the excitation occurs in the C—O bond, for all compounds which contain this bond have a discrete absorption in this same region (λ 3500). On the other hand, excitation affects the C—H bond little. The transversal vibration of the hydrogen atoms decreases from 1040 in the ground state to only 830 in excited state and accordingly only one band of this series occurs with appreciable intensity.

PENTATOMIC MOLECULES

CH_4 (Cf. table 13).—The infra-red bands of methane have been measured by Cooley (73) and are given in figure 9. The third overtone of the 3.3μ band has been found at 8900 Å. by Dennison and Ingram (74). The lines of the 7.7 and 3.31μ bands may be represented by the formulas

$$\bar{\nu}_{7.7\mu} = 1320.4 + 5.409\, m - 0.0377\, m^2 \tag{54}$$

$$\bar{\nu}_{3.31\mu} = 3019.3 + 9.771\, m - 0.0351\, m^2 \tag{55}$$

These spacings together with that of the 3.5μ band (9.77, 5.41, and 15.3 cm.$^{-1}$) give three values for the moment of inertia ($I = 5.66$, 10.2, and 3.61×10^{-40}), and for a long time it was in doubt which was correct. The Raman investigations of Dickinson, Dillon, and Rasetti (45) have given us the rotational energy levels

$$E_0/hc = 5.363\, (m + 1/2)^2 \tag{56}$$

$$E_1/hc = 3022.1 + 5.313\, (m + 1/2)^2 \tag{57}$$

and the corresponding moment of inertia is

$$I_0 = 5.17 \times 10^{-40} \text{ g.cm.}^2$$

This value is the best one obtainable up to the present. It is exactly confirmed by the measurements of Moorhead (75) on the 2.20μ band. He got a different spacing of 10.4 cm.$^{-1}$ in a 1.66μ band corresponding to 5.32 × 10^{-40} g.cm.^{2}. The different infra-red values deviate from the true one on account of an interaction of vibration and rotational energies[14], and not because of a pyramidal form of the CH_4 molecule.

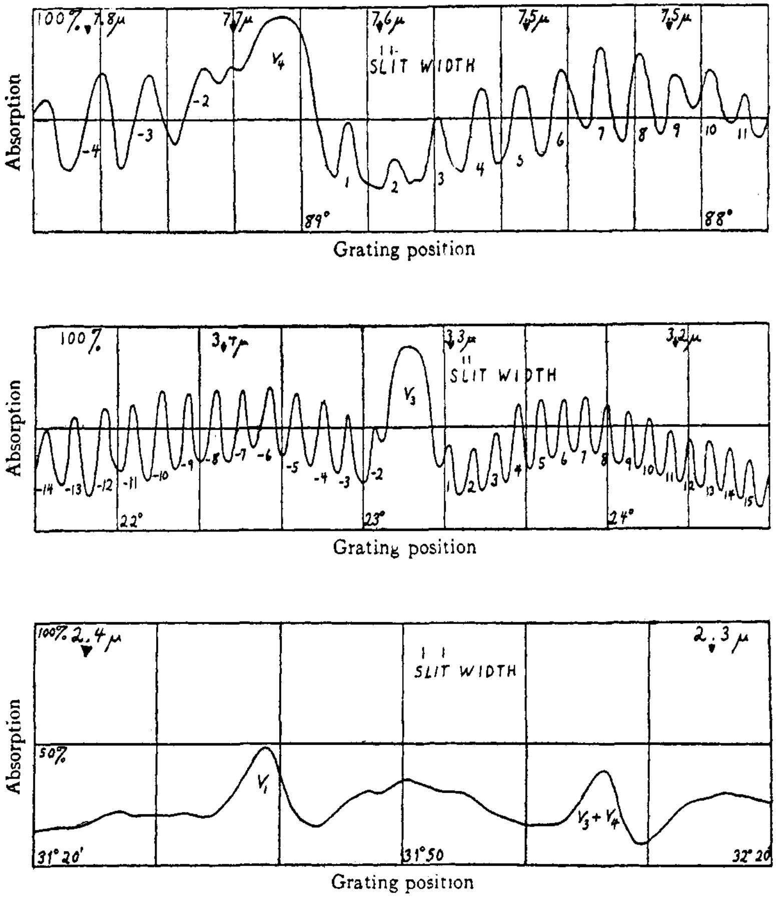


FIG. 9. INFRA-RED SPECTRA OF METHANE
(From Cooley (73))

---

[14] In a private communication, Professor Hund informs me that this has been demonstrated by Teller and Tisza (76).

The vibrational bands are given in table 11, together with an assignment of fundamentals, altered from Dennison's (77) in order to agree with the Raman data (45). In methane there are nine normal vibrations. The first, $\nu(s)$, is a valence oscillation of the hydrogen atoms moving with their center of gravity fixed and coinciding with the carbon center. This vibration is therefore inactive and cannot show up as an infra-red band, except in combination. It is the only single frequency. The second vibration, $\delta(a)$, is double, and is a deformation vibration in which the center of gravity of the hydrogen atoms still remains fixed. It is therefore also inactive. The remaining six vibrations are distributed in two fundamental levels ($\nu(a)$ and $\delta(s)$) of triple degeneracy and are active. They are the ones to be found with greatest intensity in the infra-red spectrum. The theoretical equations for these frequencies, as given by Dennison (77), are as follows:

TABLE 11

Vibrational frequencies of CH_4

$\bar{\nu}$ OBSERVED	INTENSITY	COMBINATION	$\bar{\nu}$ CALCULATED	Θ†
1304	50	$\delta(s)$		1867
(1520)		$\delta(a)$	1520	2177
2600	0.07	$2\delta(s)$	2608	
2824	0.5	$\delta(a) + \delta(s)$	(2824)	
2914.8	20 Ra*	$\nu(s)$		4174
3014	20	$\nu(a)$		4316
3022.1	5d Ra			
3071.5	2 Ra			
4122	0.1	$\delta(a) + 2\delta(s)$	4128	
4217	1	$\nu(s) + \delta(s)$	4218.8	
4315	0.7	$\nu(a) + \delta(s)$	4318	
4543	0.2	$\delta(a) + \nu(a)$	4534	

* Ra = Raman frequency.

† Θ = "characteristic" temperature = $hc\nu/k$.

$$\nu(s) = (1/2\pi)\,(k_2/m)^{1/2}\,(4\alpha + 1)^{1/2} \tag{58}$$

$$\delta(a) = (1/2\pi)\,(k_2/m)^{1/2}\,(\alpha - \beta/4)^{1/2} \tag{59}$$

$$\left.\begin{matrix}\nu(a)\\ \delta(s)\end{matrix}\right\} = (1/2\pi)\,(k_2/m)^{1/2}\Big[\alpha + 5/9 - 13\beta/36 \pm \{(\alpha + 5/9 - 13\beta/36)^2 - 8\,\alpha/9 + 16\alpha\beta/9 + 10\beta/9 + 4\beta^2/9\}^{1/2}\Big]^{1/2} \qquad (60)\ (61)$$

where

$$\alpha \equiv k_1/k_2 \qquad (62)$$

$$\beta \equiv k'/k_2 \qquad (63)$$

$$k_1 \equiv (\partial^2 W_1/\partial q^2)_0 \qquad (64)$$

$$k_2 \equiv (\partial^2 W_2/\partial r^2)_0 \qquad (65)$$

$$k' \equiv -\,(8/3a^2)^{1/2}\,(\partial W_2/\partial r)_0 \qquad (66)$$

$$W = \sum_1^6 W_1(q_i) + \sum_1^4 W_2(r_i) = \text{potential energy} \qquad (67)$$

the q's are the mutual displacements of the hydrogen particles relative to one another, and the r's the displacements of each of the hydrogens relative to the carbon. The forces, k_2, between the carbon and hydrogen are presumably much greater than those between the hydrogens, k_1, and α is therefore less than unity. The constant β should be close to zero and with these simplifications, one may derive the order of decreasing frequencies as $\nu(s)$, $\nu(a)$, $\delta(a)$, and $\delta(s)$ if $\alpha \doteq 1$ or $\nu(a)$, $\nu(s)$, $\delta(a)$, and $\delta(s)$ if $\alpha \doteq 0$. In this respect, our modified assignment of fundamental frequencies is therefore concordant with theory, as well as Dennison's, and is in better agreement with the Raman data. The three frequencies associated with $\nu(a)$ by the bracket in table 11 may be due to a slight resolution of the triple degeneracy or to an interaction between a fundamental (2914.8) and an overtone (2 × 1520) as in CO_2 (42).

If these frequencies are the correct fundamentals, the specific heat of methane at higher temperatures is to be represented by the equation:

$$C_v/R = 3 + \varphi(4174/T) + 2\,\varphi(2177/T) + 3\,\varphi(4316/T) + 3\,\varphi(1867/T) \qquad (68)$$

where φ is defined by equation 46.

The symmetry characteristics of the rotations and vibrations of methane have been worked out by Elert (8). The *a priori* probabilities of the rotational states are given in table 3 of Part I. The *a priori* probabilities of the vibrational states are given in table 12. The $\nu(s)$ state is double, one being symmetric $S(4)$ and the other antisymmetric, $S(1 + 1 + 1 + 1)$, (in the nuclei). The statistical weight of any $\delta(a)$ state is $v_{\delta(a)} + 1$, just as it is for the doubly degenerate vibrations of ammonia (and in fact, because it is doubly degenerate). Higher order perturbations may resolve these into $v_{\delta(a)}/2 + 1$ separate levels, the $S(2 + 2)$ ones ($v_{\delta(a)}$ in number) existing still as $v_{\delta(a)}/2$ unresolved pairs. The triple $\nu(a)$ and $\delta(s)$ levels have a total *a priori* probability of $2v_{\nu(a)} + 1$ and are distributed as given in the table. The nomenclature $\equiv 1$ (mod 6) indicates numbers which are divisible by six with 1 left over. The symmetry character distribution of the *rotational* states is the same as that of the $\nu(a)$, $\delta(s)$ vibrational states. This latter distribution, combined with the nuclear variety weights allowed by the Fermi statistics, is given in table 3. Constants for various tetrahedral pentatomic molecules are given in table 13.

TABLE 12

Symmetry character and a priori probabilities of normal vibrations of CH_4 *type molecule*

NORMAL VIBRATION	v	p			
		S (4)	S (3 + 1)	S (2 + 2)	S (1 + 1 + 1+ 1)
$\nu_1 = \nu(s)$	any	1	0	0	1
$\nu_2 = \delta(a)$	0	1	0	0	0
	1	0	0	2	0
	$2m$	1	0	$2m$	0
	$2m + 1$	1	0	$2m$	1
$\nu_3 = \nu(a)$	$\equiv 0$ (mod 6)	$v/6 + 1$	$3v/2$	$v/3$	
	$\equiv 1$	$(v - 1)/6$	$(3v + 3)/2$	$(v - 1)/3$	
	$\equiv 2$	$(v/2 - 1)/3$	$3v/2$	$(v - 2)/3 + 2$	
	$\equiv 3$	$(v - 3)/6 + 1$	$(3v + 3)/2$	$(v - 3)/3$	
	$\equiv 4$	$v/6 + 1/3$	$3v/2$	$v/3 + 2/3$	
	$\equiv 5$	$(v - 5)/6$	$(3v + 3)/2$	$(v - 5)/3 + 2$	
$\nu_4 = \delta(s)$	Same character as for ν_3				

* In an article of which the author was unaware at the time of submission of this review, Bhagavantam (78) had already made the alteration in fundamental frequency assignment of $\nu(s)$ proposed independently above. Polarization evidence in support of this has been cited in the present year (79). The Raman shift, 2918, is nearly completely polarized, whereas 3019 is nearly unpolarized. This is in complete analogy with the third and fourth fundamentals of tetrachloride spectra. In the Raman spectra, 3019 appears accompanied by rotational vibrational components, while the more intense 2918 does not. Further evidence for the correctness of this assignment is contributed by the Kettering, Andrews, and Shutts model (13). This indicates (80) a much lower vibrational frequency $\nu(s)$ for methane than was given by Dennison's assignment (77).

TABLE 13

Constants of pentatomic molecules of XY_4 *type*

	CH_4	CBr_4(d)	$SiBr_4$(a)	$SnBr_4$(b)	CCl_4(b)	$SiCl_4$(b)	$TiCl_4$(b)	$SnCl_4$(b)
$I'' \times 10^{40}$ g. cm.^{2}	5.17							
r_{XY} Å	1.08							
r_{YY}	1.77				3.1(c)			
$\nu(s)$ cm.$^{-1}$ (Dennison, ν_1)	2914.8	265	249	220	454	422	386	367
$\delta(a)$ (ν_2)	1520	125	90	64	214	148	119	104
$\nu(a)$ (ν_3)	3014	667	487	279	790,760	608	491	401
$\delta(s)$ (ν_4)	1304	183	137	88	311	220	139	136
Raman cm.$^{-1}$	2914.8 3022.1 3071.5		89.6 136.9 247.3 488.2 others					

(a) Trumpy: Z. Physik **68,** 675 (1931).
(b) Trumpy: Z. Physik **66,** 790 (1930).
(c) Debye, Bewilogua, and Ehrhardt: Physik. Z. **30,** 84 (1929).
(d) Dadieu and Kohlrausch: Monatsh. **57,** 488 (1931).

* Although the empirical explanation of the infra-red spectrum of methane is as satisfactory with the new fundamental frequency assignment as with the Dennison assignment, a quantitative calculation of Dennison's three constants from three of the

fundamentals does not lead to a satisfactory check with the fourth. Thus, by suitable elimination of the constants in equations 58 to 61, one gets for the second frequency (rough slide rule estimate)

$$\nu_2^2 = 0.314\ \nu_1^2 - 0.0642(\nu_3^2 + \nu_4^2) \pm [-\ 0.044\ \nu_1^4 + 0.0879\ \nu_1^2(\nu_3^2 + \nu_4^2) + 0.00412(\nu_3^4 + \nu_4^4) - 0.11\ \nu_3^2\ \nu_4^2]^{1/2} \tag{68.1}$$

By making the following postulates of the values of ν_1, ν_3, and ν_4 in the first three rows, the author calculated the value of ν_2. This is given in the fourth row and is compared with the empirical frequency.

$\nu_1 = \nu(s)$	2915	2915	2915	3071	Postulated
$\nu_3 = \nu(a)$	3014	3071.5	3071	3014	
$\nu_4 = \delta(s)$	1304	1304	3022.1	1304	
$\nu_2 = \delta(a)$	1960	1970	1686	2045	Calculated
	1520	1520	1304 1520	1520	Observed

It is seen that the agreement is impossible.

**Biswas (87), citing the evidence by Tronstad (88) and others for two different geometrical forms of NH_3, argues for a similar state of affairs in methane. The fundamental vibration of the unsymmetrical tetrahedron, he places at 2914 (instead of Dennison's 4217); that of the symmetrical tetrahedron, at 3071 cm.$^{-1}$ The difference between the two, 157 cm.$^{-1}$, represents the activation energy for changes from one form to the other. Such a dynamic isomerism has already been worked out by Morse (89). Such an assignment presents no advantages, as may be seen from the last three columns of the preceding unnumbered table. (The use of the frequency 3071 was inspired by his suggestion). Owing to the extreme stability of the methane molecule, it is exceedingly doubtful that an unsymmetrical isomeric form of it exists at an energy within only 157 cm.$^{-1}$ of its symmetrical form.

* For this reason, the author spent considerable time this spring in an unsuccessful attempt to modify Dennison's theory

of the methane vibrations. It was recognized that it would be desirable to include bending forces in the derivation of frequencies. But from symmetry considerations, the conclusion was reached that Dennison's method of accounting by central forces between the hydrogen atoms was fundamentally equivalent to accounting for C—H bond bending forces since any displacement, $d\theta_{\mathrm{H}}$ could be expressed as proportional to $dr_{\mathrm{H-H}}$ with a different force constant. The discrepancy is therefore not to be explained away as a failure to use bending forces. A possible, although not very probable explanation, is that, owing to an especially rapid convergence of vibration levels, the first observed frequency differs so greatly from the frequency of infinitesimal vibration, ν_e, as to throw the calculations all off. This might be true of one of the δ vibrations.

* Urey and Bradley (81) have calculated the fundamental vibrations of tetrahedral pentatomic molecules on the basis of harmonic restoring forces along the directions of the chemical bonds and perpendicular to them. They obtained unsatisfactory agreement between calculated and observed values. They then introduced a repulsive potential energy term proportional to r_j^{-n} where r_j is the distance between corner atoms, in the fundamental frequency equations and were thereby enabled to get very good agreement between calculated and observed values in the case of CCl_4, $SiCl_4$, $SnCl_4$, CBr_4, and $SnBr_4$ but not so good in that of $TiCl_4$. The value of n may range from 5 to 9 without much effect on the calculated frequencies. Their frequencies are

$$\nu_1 = (1/2\pi)\ \{[k_1 + (n+1)\ \gamma_3]/m\}^{1/2} \qquad (68.2)$$

$$\nu_2 = (1/2\pi)\ \{[k_2 + (n+2)\ \gamma_3/4]/m\}^{1/2} \qquad (68.3)$$

$$\nu_{3,4} = (1/2\pi)\ \Bigg\{[(3n+2)\ \gamma_3/2 + 2k_1 + k_2]/6m + (2\gamma_3 + k_1 + 2k_2)/6\mu \pm$$

$$\sqrt{\left[(\frac{3n+2}{2}\gamma_3 + 2k_1 + k_2)/6m - (2\gamma_3 + k_1 + 2k_2)/6\mu\right]^2 + (2m/9\mu)\ [(\gamma_3 + k_2 - k_1)/m]^2}\Bigg\}^{1/2} \qquad (68.4)$$

where

$$k_1 = (\partial^2 V/\partial r_1^2)_0,\ \gamma_3 = 4nk_3/a^{n+2},\ \mu = mM/(4m + M)$$

and

$$V = V_0 + \sum_1^4 \frac{\partial V}{\partial r_i} \Delta r_i + \tfrac{1}{2} \sum_1^4 \frac{\partial^2 V}{\partial r_i^2} \Delta r_i^2 + \tfrac{1}{2} \sum_1^4 k_2 r_0^2 \Delta\theta_i^2$$

$$+ \sum_1^6 \frac{\partial V}{\partial r_j} \Delta r_j + \tfrac{1}{2} \sum_1^6 \frac{\partial^2 V}{\partial r_j^2} \Delta r_j^2 \qquad (68.5)$$

In a private communication, Professor Urey has informed the writer that they applied their results to methane, but without success. He suggests that the difficulty may be due to the fact that in methane the protons are deeply embedded in the electron shell of carbon, and that this causes the anomalous behavior.

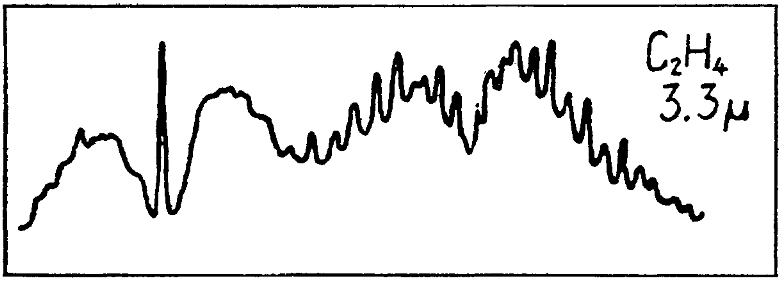


FIG. 10a. 3.3μ BAND OF C_2H_4
(From Barker and Meyer (47))

* Mecke (12c) avoids these difficulties by including in his potential energy equations four constants

$$P = \sum_1^4 k_i(\Delta r/r)_i^2 + \tfrac{1}{2} \sum_1^6 b_{ik}(\Delta\varphi)_{ik}^2 + \tfrac{1}{2} \sum_1^6 \epsilon_{ik}(\Delta l/l)_{ik}^2 + \tfrac{1}{2} \sum_1^6 \eta_{ik} \Delta\chi_2 \qquad (68.6)$$

From four empirical fundamental frequencies, it is thus possible to determine the four constants and have no equations left over to worry one about the possibility of a check. In this equation, k_i represents the harmonic restoring force constant of a C—H vibration, $\Delta\varphi$ the change in a H—C—H angle, with b_{ik} the corresponding restoring force constant; Δl the change in the length of a dipole caused by two neighboring valences, and $\Delta\chi$ the change in the dipole orientation. In other words, the stability of methane is expressed in terms of attractive forces parallel and perpendicular to the C—H valence bonds, and of forces which tend to stretch and turn dipoles set up by the bonds themselves. After all, this is perhaps the most satisfactory solution of a bad problem.

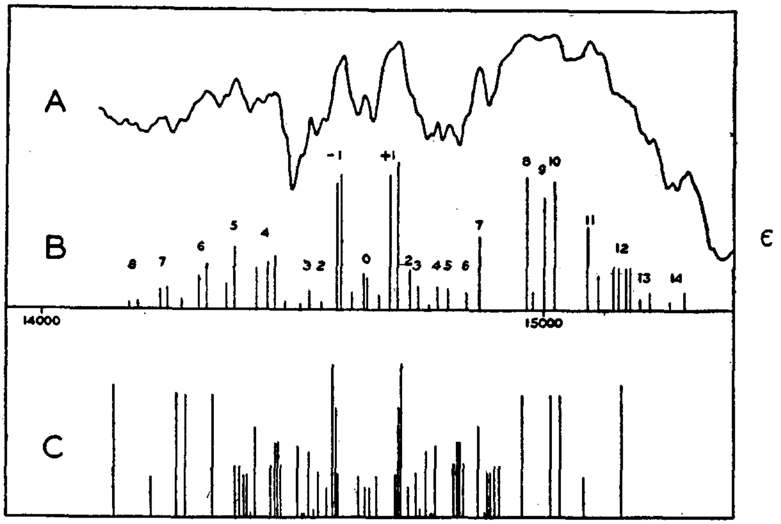


FIG. 10b. 0.872μ BAND OF C_2H_4

A. Photometer curve of a composite picture made from four negatives. B. The principal maxima plotted on a frequency scale. C. Predicted spectrum for a molecule with constant moments of inertia in the ratio 1.14:1:0.14, when the change of electric moment due to vibration is along the intermediate axis. (Calculated by H. H. Nielsen). (From Badger and Binder (82)).

HEXATOMIC MOLECULES

C_2H_4.—As illustration of the hexatomic molecule we pick ethylene, principally because its simplicity has made it vulnerable to analysis. Figure 10 reproduces its infra-red bands at 3.3 and 0.87μ. The rotational analysis of the latter has given as tentative values for the moments of inertia (82):

$$A = 3.8 \times 10^{-40} \text{ g.cm.}^2$$

$$B = 27 \times 10^{-40}$$

$$C = 31 \times 10^{-40}$$

Assuming the same bond angles ∠ HCH as in methane (109°28′) the internuclear distances are

$$r_{C-C} = 1.32 \text{ Å}.$$

$$r_{C-H} = 0.92 \text{ Å}.$$

The Raman shifts produced by ethylene have been measured by Dickinson, Dillon, and Rasetti (49) and are as follows (intensities given in parentheses): 1342.4 (20), 1623.3 (15), 2880.1 (3), 3019.3 (20), 3240.3 (2), and 3272.3 (1) cm.$^{-1}$.

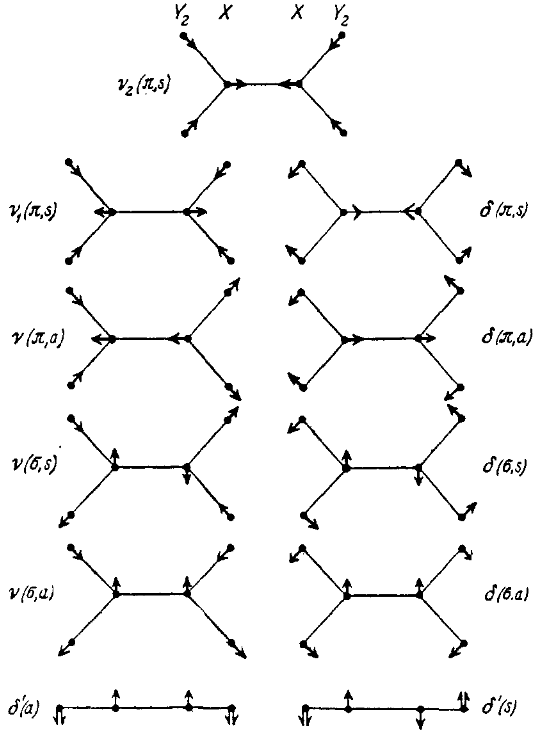


FIG. 11. FUNDAMENTAL NORMAL VIBRATIONS OF C_2H_4
Twelfth vibration is not indicated but is a torsion. (From Mecke (12c)).

As the number of atoms in a molecule increases, its types of oscillations become more and more complicated. The normal vibrations of the ethylene molecule have been analyzed by

Mecke (12c) on the assumption that the restoring force constant for a deformation oscillation is negligible, compared with that for a valence oscillation. He gets the following results. There are twelve normal vibrations,—five valence frequencies and four deformation (two single and two double). They are depicted in figure 11 (Mecke's figure 4). The twelfth vibration, $\delta(d)$ (not pictured), is a deformation torsion around the double bond (*d* stands for "*Dreh*"). Some of the approximate formulas for the deformation oscillations are as follows (15a):

TABLE 14

π *Vibrations of the hydrocarbons* C_2H_n

Mecke (12c)

	C_2H_2	C_2H_4	C_2H_6	C_2Cl_4	C_2Cl_6
$\nu(s)$	1975	1623	990	1570	860
$\nu(s)$	3370	3020	2950	446	432
$\nu(a)$	3277	2988	2900	(780)	?
$\delta(s)$	—	1342	1460	235	216
$\delta(a)$	—	1444	~ 1450	(385)	?
ν_{CC}	2100	1620	990	1420	(850)
ν_{CY}	3200	3000	—	~ 870	?
k_{CC}	69 Volt	52 Volt	26 Volt	~ 40 Volt	(20 Volt)

$$\delta(\sigma,s) = (1/2\pi)\ [2d/(C + 2H)]^{1/2}$$

$$\delta(\sigma,a) = (1/2\pi)\ [d(1/2H + 1/C)/2]^{1/2}$$

$$\delta(\pi,a) = (1/2\pi)\ (d/2H)^{1/2}$$

$$\delta(\pi,s) = (1/2\pi)\ [(k_{C=C} + d/2)\ 2/C]^{1/2}$$

The latter vibration is that of the C═C bond and the absence of the mass and binding constants of the outer atoms is very striking theoretical justification of the frequently observed fact that definite frequencies reappear with unchanged values in all the derivatives of a definite molecule. Table 9 gives Mecke's (12c) analysis of the spectrum of C_2H_4, making use of the fundamental frequencies which are given, together with those of other C_2Y_n molecules, in table 14.

**Mulliken (90) discusses the electronic structure of ethylene and concludes that its energy is considerably lower if the two CH_2 radicals composing it are arranged symmetrically in one plane than if their planes make an angle of 90°. For certain predicted excited states of C_2H_4 (his designations, $^3\Gamma_{4u}$, $^1\Gamma_{4u}$—ground state, $^1\Gamma_{1g}$) and its derivatives, which are probably the upper states of ultra-violet absorption bands of these compounds, he shows that the energy should be higher for the plane form than for the perpendicular form. Suitable absorption of ultraviolet light therefore should enable the plane form to rotate spontaneously into the perpendicular form (90°) and on to the other plane form (180°). In this way we have given us a mechanism for the photochemical *cis-trans* transformation.

CONCLUSION

In conclusion, it is well to reiterate that work in this field is constantly being ground out at such a rapid rate that it is practically impossible to take cognizance of all of it. In particular, we might refer the reader to excellent theoretical developments which are being made in the field of the aromatic and of the higher aliphatic organic compounds and which we have entirely neglected to discuss (83, 84). Finally, the most important future advances in chemistry will come through the application of the knowledge which is to be derived from the analysis of polyatomic molecular spectra.

REFERENCES

(1) (a) Witmer: Proc. Nat. Acad. Sci. **12**, 238 (1926). Heats of dissociation.
(b) Franck: Trans. Faraday Soc. **21**, 536 (1926). Heats of dissociation.
(c) Mecke: Z. physik. Chem. **7B**, 108–29 (1930). Bond strengths.
(d) Giauque: J. Am. Chem. Soc. **52**, 4816 (1930). Heat content.
(e) Villars: Phys. Rev. **38**, 1552–64 (1931). Entropy.
(f) Villars and Scultze: Phys. Rev. **38**, 998–1010 (1931). Specific heats.
(g) Rodebush: Chem. Rev. **9**, 319–46 (1931). Free energy and equilibrium constants.
(h) Villars: J. Am. Chem. Soc. **52**, 1733–41 (1930). Activation heats.
(i) Eyring: J. Am. Chem. Soc. **53**, 2537 (1931). Activation heats.
(2) Bartlett: Phys. Rev. **37**, 327L (1931).
Heitler and Herzberg: Naturwissenschaften **17**, 673 (1929).
(3) Mulliken: Trans. Faraday Soc. **25**, 634 (1929).

(4) Hund: Z. Physik **43**, 805 (1927).
(5) Pauli: Z. Physik **43**, 601 (1927).
(6) Hund: Z. Astrophys. **2**, 217 (1931).
(7) Hund: Z. Physik **43**, 788 (1927).
(8) Elert: Z. Physik **51**, 6–33 (1928).
(9) (a) Kramers and Ittmann; I—Z. Physik **53**, 553 (1929); II—Z. Physik **58**, 217 (1929); III—Z. Physik **60**, 663 (1930).
  (b) Witmer: Proc. Nat. Acad. Sci. **13**, 60 (1927).
  (c) Wang: Phys. Rev. **34**, 243 (1929).
  (d) Klein: Z. Physik **58**, 730 (1929).
(10) Dennison: Rev. Modern Phys. **3**, 280 (1931).
(11) Nielsen: Phys. Rev. **38**, 1432 (1931).
(12) (a) Mecke: Z. physik. Chem. **16B**, 409–20 (1932).
  (b) Mecke: Z. physik. Chem. **16B**, 421–37 (1932).
  (c) Mecke: Z. physik. Chem. **17B**, 1–20 (1932).
  (d) Mecke: Molekülstruktur, p. 23. Leipziger Vorträge, S. Hirzel, Leipzig (1931).
(13) Kettering, Shutts, and Andrews: Phys. Rev. **36**, 531 (1930).
(14) Van Vleck: Proc. Nat. Acad. Sci. **15**, 754–64 (1929).
(15) (a) Mecke: Z. Physik **64**, 173 (1930).
  (b) Mecke: Z. Elektrochem. **36**, 589 (1930).
(16) Urey: Ind. Eng. Chem. **23**, 1241 (1931).
(17) Ludloff: Z. Physik **57**, 227 (1929).
(18) (a) Mulliken: Phys. Rev. **32**, 186–222 (1928).
  (b) Mulliken: Phys. Rev. **32**, 761–72 (1928).
  (c) Mulliken: Phys. Rev. **33**, 730–47 (1929).
  (d) Herzberg: Z. Physik **57**, 601–30 (1929).
  (e) Weizel: Z. Physik **59**, 320–32 (1930).
(19) Villars: Proc. Nat. Acad. Sci. **15**, 705–9 (1929); **16**, 396–7 (1930). For an additional correction, cf. footnote 8.
(20) Kemble and Zener: Phys. Rev. **33**, 532 (1929).
(21) Morse: Phys. Rev. **34**, 57 (1929).
(22) Condon: Phys. Rev. **28**, 1182–1201 (1926).
(23) Franck and Sponer: Nachr. Ges. Wiss. Göttingen, p. 241 (1928).
(24) Franck and Rabinowitsch: Z. Elektrochem. **36**, 794 (1930).
(25) Mulliken: Z. Elektrochem. **36**, 603 (1930), footnote 1.
(26) Kato: Bull. Inst. Phys. Chem. Research **10**, 343 (1931); Sci. Papers Inst. Phys. Chem. Research **15**, 294 (1931).
(27) (a) Watson and Parker: Phys. Rev. **37**, 1485 (1931). SO_2.
  (b) Urey: Ind. Eng. Chem. **23**, 1241 (1931). ClO_2.
(28) Henri: Trans. Faraday Soc. **25**, 765 (1929).
(29) Kronig: Z. Physik **62**, 300 (1930).
(30) (a) Dunkel: Z. physik. Chem. **7B**, 81–107 (1930).
  (b) Mulliken: Chem. Rev. **9**, 347–88 (1931). The preceding paper of this Symposium.
(30.1) (a) Hund: Z. Physik **73**, 1–30 (1931). Chemical binding.
  (b) Hund: Z. Physik **73**, 565–77 (1932).
  (c) Hund: Z. Physik **74**, 1 (1932).

(30.2) Mulliken: Electron Structures of Polyatomic Molecules and Valence. Phys. Rev. **40**, 55–62 (1932).
(30.3) (a) Pauling: Proc. Nat. Acad. Sci. **14**, 359 (1928).
 (b) Pauling: J. Am. Chem. Soc. **53**, 1367 (1931).
 (c) Pauling: J. Am. Chem. Soc. **53**, 3225 (1931).
 (d) Pauling: J. Am. Chem. Soc. **54**, 988 (1932).
 (e) Pauling: J. Am. Chem. Soc. **54**, 3570 (1932).
(30.4) (a) Slater: Phys. Rev. **37**, 481 (1931).
 (b) Slater: Phys. Rev. **38**, 1109 (1931).
 (c) Slater: Phys. Rev. **41**, 255 (1932).
(30.5) Heitler and Herzberg: Z. Physik **53**, 52 (1929).
(30.6) Mulliken: Rev. Modern Phys. **3**, 91, 146 (1931).
(31) Mecke: Bandenspektren und Ihre Bedeutung für die Chemie, p. 14. Gebrüder Bornträger, Berlin (1929).
(32) Rideal: Trans. Faraday Soc. **25**, 922 (1929).
(33) (a) Slater: Phys. Rev. **37**, 481 (1931).
 (b) Pauling: J. Am. Chem. Soc. **53**, 1367 (1931).
(34) Mischke: Z. Physik **67**, 106 (1931).
 Hettner: Ann. Physik **55**, 476 (1918).
(35) (a) Ellis: Phil. Mag. [7] **3**, 618 (1927).
(36) Plyler: Phys. Rev. **38**, 1784L (1931).
(37) Johnston and Walker: Phys. Rev. **39**, 535L (1932).
(38) Lueg and Hedfeld: Z. Physik **75**, 512 (1932).
(39) Houston and Lewis: Phys. Rev. **37**, 227A (1931); Proc. Nat. Acad. Sci. **17**, 229 (1931).
(40) Snow: Proc. Roy. Soc. London **128A**, 294–316 (1930).
(41) Martin and Barker: Phys. Rev. **37**, 1708, A124 (1931); **41**, 291 (1932).
(42) Fermi: Z. Physik **71**, 250 (1931).
(43) Smyth: Phys. Rev. **38**, 2000–15 (1931); **39**, 381L (1932).
(44) Fox, Duffendach, and Barker: Proc. Nat. Acad. Sci. **13**, 302 (1927).
(45) Plyler and Barker: Phys. Rev. **38**, 1827 (1931); **41**, 369 (1932).
(46) Badger and Cartwright: Phys. Rev. **33**, 698 (1929).
(47) Barker and Meyer: Trans. Faraday Soc. **25**, 912 (1929).
(48) Sleator: Phys. Rev. **38**, 147 (1931).
(49) Dickinson, Dillon, and Rasetti: Phys. Rev. **34**, 582 (1929).
(50) Langseth: Nature **128**, 225 (1931).
(51) Dennison: Phil. Mag. [7] **1**, 213 (1926).
(52) Mecke and Badger: Trans. Faraday Soc. **25**, 936 (1929).
(53) Badger: Phys. Rev. **35**, 1038 (1930).
(54) Barker: Phys. Rev. **33**, 684 (1929).
(55) Dennison and Hardy: Phys. Rev. **39**, 938 (1932).
(56) Lueg and Hedfeld: Z. Physik **75**, 599 (1932).
(57) Levin and Meyer: J. Optical Soc. Am. **16**, 137 (1928).
(58) Hedfeld and Mecke: Z. Physik **64**, 151 (1930).
(59) Childs and Mecke: Z. Physik **64**, 162 (1930).
(60) Kistiakowsky: Phys. Rev. **37**, 276 (1931).
(61) Herzberg: Trans. Faraday Soc. **27**, 378–84 (1931).
(62) Olson and Kramers: J. Am. Chem. Soc. **54**, 136–8 (1932).

(63) Bhagavantam: Nature **127,** 817 (1931)

(64) Hedfeld and Lueg: Z. Physik **77,** 446 (1932).

(65) Lochte-Holtgreven and Eastwood: Nature **130,** 403 (1932).

(66) Patty and Nielsen: Phys. Rev. **37,** 472, A69 (1931).

(67) Nielsen and Patty: Nature **37,** 1708, A122 (1931).

(68) Henri and Schou: Z. Physik **49,** 774 (1928).

(69) Mecke: Trans. Faraday Soc. **27,** 385 (1931).

(70) Patty and Nielsen: Phys. Rev. **39,** 957 (1932). Cf. references 58 and 59.

(71) Dieke and Kistiakowsky: Proc. Nat. Acad. Sci. **18,** 367 (1932); Phys. Rev. **40,** 1039, A 50 (1932).

(72) Herzberg and Franz: Z. Physik **76,** 720 (1932).

(73) Cooley: Astrophys. J. **62,** 73 (1925).

(74) Dennison and Ingram: Phys. Rev. **36,** 1451 (1930).

(75) Moorhead: Phys. Rev. **39,** 83–88 (1932).

(76) Teller and Tisza: Z. Physik **73,** 791–812 (1932).

(77) Dennison: Astrophys. J. **62,** 84 (1925).

(78) Bhagavantam: Indian J. Physics **6,** 595 (1931).

(79) Bhagavantam: Nature **129,** 830 (1932).

(80) Teets: Abstract No. 30, Physical and Inorganic Section of the New Orleans meeting of the American Chemical Society, March, 1932.

(81) Urey and Bradley: Phys. Rev. **38,** 1969 (1931).

(82) Badger and Binder: Phys. Rev. **38,** 1442 (1931).

(83) (a) Andrews: Phys. Rev. **36,** 544 (1930).
(b) Andrews: Ind. Eng. Chem. **23,** 1232 (1931).

(84) Yates: Phys. Rev. **36,** 555, 563 (1930).

(85) Mecke: Naturwissenschaften **20,** 657 (1932).

(86) Schmid: Phys. Rev. **41,** 732 (1932).

(87) Biswas: Phil. Mag. **13,** Supplement 455–8 (1932).

(88) Tronstad: Z. physik. Chem. **135,** 333 (1929).

(89) Morse: Proc. Nat. Acad. Sci. **14,** 166 (1928).

(90) Mulliken: Phys. Rev. **41,** 751–8 (1932).