The Determination of the Constants of Harmonic Vibrations

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indicated in Table I. This gives the correct number of unpaired electrons to account for the magnetic data.

Although the $4d$ energy levels are considerably higher than the $3d$ levels, the shift from $3d^24s4p^3$ bond orbitals to $4s4p^34d^2$ bond orbitals is favored by the greater overlapping which the latter can give with the atomic orbitals of the surrounding atoms. The $4s4p^34d^2$ bonds should be more polar than $3d^24s4p^3$ bonds and should predominate for bonds connecting a metal atom to very electronegative atoms. The magnetic data show this to be the case.

For the square cupric, ferrous and ferric complexes, the bond orbitals may be of the $3d4s4p^2$ type, as suggested by Pauling and Coryell for the cupric case, or of the $4s4p^24d$ type. The latter seems to the writer the more probable. The similar beryllium phthalocyanine[7]

probably contains $2s2p^23d$ bonds. These would be expected to be very weak, in agreement with the observed reactivity of this compound. Tetrahedral bonds would undoubtedly be much stronger, but they are apparently impossible in view of the rigidity of the plane phthalocyanine structure.

Pauling's original theory also requires modification to account for the existence of CoS_2, NiS_2, $NiAsS$ and other similar compounds containing bivalent cobalt or nickel or trivalent nickel atoms apparently bonded by octahedral bonds to six surrounding electronegative atoms.[8] As in the cupric compounds just discussed, two alternatives are possible (Table I). Magnetic data from NiS_2 might help to decide between them.

[7] R. P. Linstead and J. M. Robertson, J. Chem. Soc. 1736 (1936).

[8] M. L. Huggins, Phys. Rev. 19, 369 (1922); J. Am. Chem. Soc. 44, 1841 (1922); L. Pauling and M. L. Huggins, Zeits. f. Krist. A87, 205 (1934); M. J. Buerger, Zeits. f. Krist. A95, 83 (1936).

The Determination of the Constants of Harmonic Vibrations

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A general method is developed to find the relations between constants of the potential energy and the frequencies of point systems for harmonic vibrations. Useful formulas are derived (Eqs. (16) and (23)); and matrices required frequently for the solution of problems are tabulated. Relations are also found between the force constants of a molecule with a number of equivalent atoms and the vibration frequencies of an isotopic molecule of a lower degree of symmetry. This also gives the relations between the frequencies of isotopic molecules of different degrees of symmetry.

EXCEPT for the simplest molecules laborious calculations are required to obtain the connection between the potential energy constants and the vibration frequencies of a molecule; this is the case even if we restrict ourselves to the study of harmonic vibrations. The amount of calculation required in each individual case is reduced to a minimum if the *general* treatment is carried out *as far as possible*. This is the object of the present study which is connected with previously published remarks on the subject.[1] A special

treatment is necessary for the case where the symmetry of a molecule is lowered when one or more of a number of equivalent atoms are replaced by isotopes.

Complex Coordinates

As shown already by Brester,[2] the use of complex variables greatly simplifies the necessary transformations of coordinates in the case of any molecule with one threefold or higher proper or improper axis. We start with the Cartesian co-

[1] O. Redlich, Zeits. f. physik. Chemie B28, 371 (1935). The product formula derived there was found previously by E. Teller who did not publish it, however.

[2] C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Dissertation (Utrecht, 1923).

ordinates $q_a{}^i$ of the displacements. The index $a = 1, 2 \cdots n-1$, n gives the number of the atom; $i = 1, 2, 3$ corresponds to the directions x, y and z, respectively. The coordinate system is fixed with respect to the molecule; its origin is at the center of gravity and its axes coincide with the principal axes of inertia. We assume that the (principal) symmetry axis coincides with the z axis. We pass now from the Cartesian to complex coordinates r_c $(c = 1, 2, \cdots (3n-1), 3n)$:

$$q_a{}^1 = 2^{-\frac{1}{2}}(r_a + r_a{}^*); \qquad r_a = 2^{-\frac{1}{2}}(q_a{}^1 + iq_a{}^2);$$

$$q_a{}^2 = i \cdot 2^{-\frac{1}{2}}(-r_a + r_a{}^*); \quad r_{a+n} = r_a{}^* = 2^{-\frac{1}{2}}(q_a{}^1 - iq_a{}^2);$$

$$q_a{}^3 = r_{a+2n}; \qquad\qquad r_{a+2n} = q_a{}^3. \qquad (1a)$$

The coordinates r_{n+1} to r_{2n} are thus the complex conjugates of r_1 to r_n, the real coordinates r_{2n+1} to r_{3n} are the z components.

If we consider these coordinates as the components of $3n$ dimensional vectors q and r, the coefficients in Eqs. (1a) form the ath step of a unitary matrix U; i.e., the reciprocal matrix U^{-1} is equal to the adjoint $U^\dagger$ (conjugate transposed $\tilde{U}^*$).[3] Hence the transition from q to r can also be represented by

$$q = Ur; \quad r = U^\dagger q; \quad UU^\dagger = E. \qquad (1b)$$

We combine the atomic masses M_a to a diagonal matrix with $3n$ rows so that the mass of an atom corresponds to its coordinates. The ath $(a+n)$th and $(a+2n)$th component form a scalar step, namely, the three-rowed unit matrix multiplied by M_a; the steps of U and M are similar. The matrix product MU consists thus of the steps of U multiplied by the corresponding masses. It follows that U and M commute

$$MU = UM; \quad UMU^\dagger = M. \qquad (2)$$

We get now for the transformation of the kinetic energy

$$2T = \sum_{a=1, i=1}^{a=n, i=3} M_a \dot{q}_a{}^{i2} = (M\dot{q}, \dot{q})$$

$$= (MU\dot{r}, U\dot{r}) = (U^\dagger MU\dot{r}, \dot{r}) = (M\dot{r}, \dot{r})$$

$$= \sum_{c=1}^{3n} M_c \dot{r}_c{}^* \dot{r}_c. \qquad (3)$$

[3] Cf. for example, M. Born and P. Jordan, *Quantenmechanik* (J. Springer, Berlin, 1930); particularly §§6 and 9.

The transformation of the potential energy V and of the matrix A which characterizes it in the Cartesian coordinate system is given by

$$2V = \sum_{a=1, b=1, i=1, j=1}^{a=n, b=n, i=3, j=3} A_{ab}{}^{ij} q_a{}^i q_b{}^j = (Aq, q)$$

$$= (U^\dagger AUr, r) = (Cr, r) = \sum_{c=1, d=1}^{3n} C_{cd} r_c{}^* r_d; \qquad (4)$$

$$C = U^\dagger AU; \quad C_{cd} = \sum_{abij} U_{ac}{}^{i*} A_{ab}{}^{ij} U_{bd}{}^j; \qquad (4a)$$

$$C_{ab} = \tfrac{1}{2}[A_{ab}{}^{11} + A_{ab}{}^{22} + i(-A_{ab}{}^{12} + A_{ab}{}^{21})]$$

$$= C_{ba}{}^* = C^*{}_{a+n, b+n} \qquad (4b)$$

$$C_{a, b+n} = \tfrac{1}{2}[A_{ab}{}^{11} - A_{ab}{}^{22} + i(A_{ab}{}^{12} + A_{ab}{}^{21})]$$

$$= C^*{}_{b+n, a},$$

$$C_{a, b+2n} = 2^{-\frac{1}{2}}(A_{ab}{}^{13} + iA_{ab}{}^{23}) = C^*{}_{b+2n, a},$$

$$C_{a+n, b+2n} = 2^{-\frac{1}{2}}(A_{ab}{}^{13} - iA_{ab}{}^{23}) = C^*{}_{b+2n, a+n},$$

$$C_{a+2n, b+2n} = A_{ab}{}^{33} = C^*{}_{b+2n, a+2n}.$$

The remaining coefficients and a number of further relations may be obtained by interchanging the indices taking into account that $A_{ab}{}^{ij} = A_{ba}{}^{ji}$ or $A = \tilde{A}$. Eqs. (4a) or (4b) show that $C = C^\dagger$, hence C is a hermitian matrix. This result, by the way, follows already from the fact that V is real or that A is real and symmetrical and U is unitary.

TRANSFORMATION OF COORDINATES

It has been shown previously[1] that there exists at least one transformation matrix H independent of the atomic masses which transforms the Cartesian coordinates q into "symmetry coordinates"[4] p so that the following conditions are satisfied:

(a) the coordinates p behave the same way as the normal coordinates under the symmetry operations of the undistorted molecule.

[4] Cf. J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 630 (1934). These authors have only stressed condition (a) when they introduced the expression "symmetry coordinates"; furthermore, they did not have them independent of the atomic masses. We think that we may restrict their definition in the way indicated here since coordinates which do not satisfy conditions (b) and (c) are not likely to have much practical importance. See also C. Manneback, Ann. Soc. Sci., Bruxelles **55**, 129 (1935). J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936) call these coordinates "geometrical symmetry coordinates."

(b) H is a step matrix; the elements of each step correspond to the coordinates of equivalent points.

(c) H is orthogonal: $H\tilde{H} = E$.

The same is true for the representation in terms of complex coordinates, the only difference being that the orthogonality condition is replaced by the more general requirement of having H unitary:

(c) $$HH^\dagger = E.$$

The following derivations hold formally both if we start with the real variables

$$q = Hp \qquad (5a)$$

and the complex variables

$$r = Hp. \qquad (5b)$$

H and p and the various quantities that will be introduced obviously have a different meaning in the two cases. A confusion is all the more unlikely since the real and complex coordinates are used in entirely different cases. The complex form is convenient only in the presence of an n-fold axis, $n \geq 3$ otherwise the real representation should be used.

We note first that the matrix M defined above consists of steps similar to those of the transformation matrix H. Each step is formed by the unit matrix multiplied by the mass of the atom corresponding to it. (Each one of these steps has three times as many rows as there are equivalent points corresponding to it.) Hence H and M commute

$$HM = MH; \qquad HMH^\dagger = M. \qquad (6)$$

When we pass to symmetry coordinates we obtain similarly to Eq. (3) for the kinetic energy

$$2T = (M\dot{q}, \dot{q}) = (M\dot{r}, \dot{r})$$
$$= (H^\dagger MH\dot{p}, \dot{p}) = (M\dot{p}, \dot{p}); \qquad (7)$$

hence the matrix M remains in the expression for $2T$ also in the case of the new coordinates.

For the potential energy we obtain

$$2V = (Aq, q) = (Cr, r) = (Bp, p), \qquad (8)$$

where either $B = \tilde{H}AH; \quad B = \tilde{B}$ (8a)

or $\qquad B = H^\dagger CH; \quad B = B^\dagger.$ (8b)

Due to the above mentioned symmetry properties of the coordinates p and the invariance of V with respect to the symmetry operations, the components of B with indices referring to coordinates of different types of vibration will vanish. B is hence a step matrix, its steps correspond to the types of vibration. By vibrations of one type we mean vibrations corresponding the same irreducible representation of the group. Different types correspond to different representations.

It is known from Lagrange's equations that

$$(B - \omega^2 M)p = 0 \qquad (9)$$

or $|B - \omega^2 M| = 0$ if the circular frequency is denoted by ω. As a consequence of the diagonal form of M, ω^2 appears only in the diagonal of the secular determinant.

Useful Formulas

The solution $\omega^2 = 0$ is contained six times in the $3n$ solutions of the secular determinant, corresponding to the six improper vibrations (the rotations and translations). It is possible to eliminate them quite generally by a method the essentials of which were indicated before.[1] The conservation of angular and linear momenta may be represented by means of the rectangular matrices G and F (6 rows, $3n$ columns) as

$$GMq = GMHp = GHMp = FMp = 0;$$
$$G = F\tilde{H}; \qquad (10a)$$

or

$$GMr = GMHp = GHMp = FMp = 0;$$
$$G = FH.^\dagger \qquad (10b)$$

In the subsequent discussion we shall let the index 1 indicate that the corresponding vector or the corresponding submatrix refers to the first $3n - 6$ coordinates; the index 2 will denote the last 6 coordinates. Accordingly since the rectangular matrices F and G have 6 rows they can only have 2 as first index. Let the original coordinates be so arranged that the determinant of the submatrix G_{22} does not vanish; this is also the case then for F_{22}. This arrangement is always possible (with the exception of trivial cases).

Eqs. (9) and (10) cause the problem to be six times over-determined, i.e., the potential field referred to a coordinate system fixed with respect

to the molecule is already determined by the submatrix B_{11}. The relations between the components of B and F which are necessary for further calculations are found in the following way. If we multiply Eq. (9) with F from the left and take Eqs. (10) into account, then

$$FBp = (F_{21}B_{11} + F_{22}B_{21})p_1 \\ + (F_{21}B_{12} + F_{22}B_{22})p_2 = 0. \quad (11)$$

Since this equation must be satisfied identically:

$$F_{21}B_{11} + F_{22}B_{21} = F_{21}B_{12} + F_{22}B_{22} = 0. \quad (12)$$

It is possible with the help of Eq. (12) to eliminate $B_{12}p_2$ from the system of equations

$$(B_{11} - \omega^2 M_{11})p_1 + B_{12}p_2 = 0, \quad (13)$$

$$F_{21}M_{11}p_1 + F_{22}M_{22}p_2 = 0, \quad (14)$$

which we use instead of Eq. (9). We have to take into account for this the fact that $B_{12} = B_{21}{}^\dagger$, a result which follows directly from Eq. (8). Then:

$$\{B_{11}[E + F_{21}{}^\dagger (F_{22}{}^{-1})^\dagger (M_{22})^{-1} F_{22}{}^{-1} F_{21}M_{11}] \\ - \omega^2 M_{11}\}p_1 = 0 \quad (15)$$

or finally we obtain as the first formula suitable for actual calculation

$$\left| B_{fg} + \sum_{huvw} \frac{M_g}{M_v} B_{fh} F_{uh}{}^* F_{wg} (F^{-1})_{vu}{}^* (F^{-1})_{vw} \\ - \omega^2 M_g \delta_{fg} \right| = 0, \quad (16)$$

where f, g, h refer as before to indices from 1 to $3n-6$ and u, v, w to indices from $3n-5$ to $3n$. It is to be noted that we may assume $F_{22} = E$ or

$$(F^{-1})_{vu}{}^* = \delta_{vu}; \quad (F^{-1})_{vw} = \delta_{vw}.$$

For we can replace the six equations represented by $FMp = 0$ by six others which may be obtained from them by multiplying the rows with constant factors and adding them together. This operation, however, corresponds to a multiplication from the left with any square six-rowed matrix. If we choose for this $(F_{22})^{-1}$, we obtain a matrix which is reduced with reference to the last six columns.

We obtain a second useful formula in the following way. By means of the transformation

$$p_1 = s_1 + F_{21}{}^\dagger s_2; \quad p_2 = F_{22}{}^\dagger s_{20} \quad (17)$$

with the help of Eq. (12) we obtain from Eqs. (13) and (14)

$$(B_{11} - \omega^2 M_{11})s_1 - \omega^2 M_{11}F_{21}{}^\dagger s_2 = 0, \quad (18)$$

$$F_{21}M_{11}s_1 + FMF^\dagger s_2 = 0. \quad (19)$$

We introduce now the six-rowed square matrix:

$$S = GMG^\dagger = FH^\dagger MHF^\dagger = FMF^\dagger; \quad (20)$$

its invariance follows from Eqs. (6) and (10). The elements denoted by S_{uv} were calculated previously for real coordinates: in the diagonal are the three moments of inertia referred to the three coordinate axes and three times the total mass of the molecule, the other elements are zero. In the complex representation we have for the components S_{uv}

$$S_{11} = S_{22} = \tfrac{1}{2}(I_1 + I_2); \quad S_{12} = S_{21} = \tfrac{1}{2}(I_2 - I_1) \quad (21)$$

(I_1 and I_2 are moments of inertia with respect to the x and y axes). The other elements have the same value as in the real representation. If the z axis coincides with a threefold or higher order axis, then due to $I_1 = I_2$ S is a diagonal matrix in the complex representation as well.

Eliminating s_2 from Eqs. (18) to (20), we obtain

$$(B_{11} - \omega^2 M_{11} + \omega^2 M_{11}F_{21}{}^\dagger S^{-1} F_{21}M_{11})s_1 = 0 \quad (22)$$

or as the second useful formula (valid for the complex variable calculation only if the symmetry elements include a threefold or higher order proper or improper axis).

$$\left| B_{fg} - \omega^2 M_f \delta_{fg} + \omega^2 M_f M_g \sum_v \frac{F_{vf}{}^* F_{vg}}{S_{vv}} \right| = 0. \quad (23)$$

The first formula (16) is better adapted to the determination of the ω's from the B_{fg}'s, the second one for the inverse procedure. It need not be mentioned specially that both determinants factor out and that each factor corresponds to a special type of vibration.

ISOTOPIC MOLECULES OF DIFFERENT DEGREES OF SYMMETRY

If in a molecule with several equivalent atoms we replace one or more of these by its isotope we obtain a molecule of a lower degree of symmetry (we shall later discuss as an example p-$C_6H_4D_2$).

We shall denote henceforth by original molecule the molecule with a higher degree of symmetry and by substituted molecule the isotopic molecule with a lower degree of symmetry. If we may assume that the potential field is not changed when an atom is replaced by its isotope, we can obtain the frequencies of the substituted molecule in terms of the constants of the potential energy of the original one. The number of constants is thus smaller than in the case of a non-isotopic molecule with the same configuration (for example, $p\text{-}C_6H_4Cl_2$). General formulas may be set up for the connection between the frequencies of the substituted molecule with the constants of the potential energy of the original molecule.

In the subsequent discussion we shall use the same notation as before for the substituted molecule; matrices referring to the original one will be written in Gothic script, e.g., $\mathfrak{H}$, $\mathfrak{F}$, $\mathfrak{B}$. Let $\mathfrak{p}$ denote the coordinates of the displacements obtained by performing on the Cartesian or complex coordinates of both molecules a transformation $\mathfrak{H}$, which satisfies the rules given above for the original molecule. The $\mathfrak{p}$'s are thus symmetry coordinates for the original but not for the substituted molecule. The connection between the p's and the $\mathfrak{p}$'s is given by

$$q = Hp = \mathfrak{H}\mathfrak{p}; \quad \text{or} \quad r = Hp = \mathfrak{H}\mathfrak{p}; \quad p = H^\dagger \mathfrak{H}\mathfrak{p}. \quad (24)$$

The product $H^\dagger \mathfrak{H}$ is unitary but its steps obviously do not correspond to points equivalent with respect to the symmetry elements of the substituted molecule; they are larger and correspond to points equivalent with respect to the symmetry elements of the original molecule. For the kinetic energy we obtain

$$2T = (M\dot{p}, \dot{p}) = (\mathfrak{H}^\dagger H M H^\dagger \mathfrak{H}\dot{\mathfrak{p}}, \dot{\mathfrak{p}})$$
$$= (\mathfrak{H}^\dagger M \mathfrak{H}\dot{\mathfrak{p}}, \dot{\mathfrak{p}}) = (N\dot{\mathfrak{p}}, \dot{\mathfrak{p}}); \quad N = \mathfrak{H}^\dagger M \mathfrak{H}. \quad (25)$$

The Hermitian matrix N or to be more accurate its deviation from M, represents a measure of the difference in symmetry between the two molecules. The potential energy is given by

$$2V = (Bp, p) = (\mathfrak{H}^\dagger H B H^\dagger \mathfrak{H}\mathfrak{p}, \mathfrak{p})$$
$$= (\mathfrak{B}\mathfrak{p}, \mathfrak{p}); \quad \mathfrak{B} = \mathfrak{H}^\dagger H B H^\dagger \mathfrak{H}. \quad (26)$$

By analogy to Eq. (9) we obtain from Eqs. (25) and (26)

$$(\mathfrak{B} - \omega^2 N)\mathfrak{p} = 0. \quad (27)$$

To eliminate the improper vibrations we obtain first the connection between the matrices F and $\mathfrak{F}$ of the angular and linear momenta expressed in terms of the symmetry coordinates of both molecules. We make use of the fact that the matrix G (Eq. (10)) which depends only on the atomic distances is the same for both molecules. Hence

$$G = FH^\dagger = \mathfrak{F}\mathfrak{H}^\dagger; \quad F = \mathfrak{F}\mathfrak{H}^\dagger H; \quad (28)$$

the expressions for the momenta take on the form

$$FMp = FMH^\dagger \mathfrak{H}\mathfrak{p} = FH^\dagger M\mathfrak{H}\mathfrak{p}$$
$$= \mathfrak{F}\mathfrak{H}^\dagger M\mathfrak{H}\mathfrak{p} = \mathfrak{F}N\mathfrak{p} = Q\mathfrak{p} = 0; \quad Q = \mathfrak{F}N. \quad (29)$$

The six-rowed matrix S defined by Eq. (20) is

$$S = FMF^\dagger = \mathfrak{F}\mathfrak{H}^\dagger H M H^\dagger \mathfrak{H}\mathfrak{F}^\dagger$$
$$= \mathfrak{F}\mathfrak{H}^\dagger M\mathfrak{H}\mathfrak{F}^\dagger = \mathfrak{F}N\mathfrak{F}^\dagger. \quad (30)$$

By a calculation analogous to the transition from Eqs. (9) and (10) to Eqs. (15) and (22) we find

$$\mathfrak{B}_{11}[E + \mathfrak{F}_{21}{}^\dagger(\mathfrak{F}_{22}{}^{-1})^\dagger Q_{22}{}^{-1}Q_{21}]$$
$$- \omega^2(N_{11} - N_{12}Q_{22}{}^{-1}Q_{21})\mathfrak{p}_1 = 0; \quad (31)$$

$$(\mathfrak{B}_{11} - \omega^2 N_{11} + \omega^2 Q_{21}{}^\dagger S^{-1}Q_{21})\mathfrak{s}_1 = 0; \quad (32)$$

where $\mathfrak{s}_1$, is defined analogously to s, in Eq. (17). These equations give us the connection between the frequencies ω of the substituted molecule and the constants $\mathfrak{B}$ of the potential energy of the original molecule in a form suitable for further calculation.

We can also eliminate the submatrices $\mathfrak{B}_{12}$, $\mathfrak{B}_{21}$, and $\mathfrak{B}_{22}$ from $B = H^\dagger \mathfrak{H}\mathfrak{B}\mathfrak{H}^\dagger H$ with the help of the equation analogous to Eq. (12); the value obtained for B_{11} can be substituted directly in Eqs. (15) or (22).

The corresponding determinants break up into factors which correspond to the types of vibration of the substituted molecule.

If a symmetry type contains no improper vibrations, Eqs. (31) and (32) become identical with Eq. (27). We shall derive as an example for this simple case the totally symmetrical vibrations A_1 of p-dideuterobenzene, a result we used before without deriving it then.[5] The indices 1 to

[5] O. Redlich, W. Stricks, Mh. Chem. **68**, 374 (1936); also Sitz. Ber. Akad. Wiss. Wien (IIb) **145**, 594 (1936). We should like to point out that the zero determinant given there differs only formally and not actually from Wilson's result for the type of symmetry $E_g{}^+$. The determinants may be transformed into one another if $d = H/2$ and $D = k - H\eta^2/4$. We are grateful to Dr. Wilson for pointing it out to us. The numerical results remain unchanged.

6 of the Cartesian coordinates refer to C (mass M_1); 7 and 10 to D (mass M_2''); 8, 9, 11, and 12 to H (mass M_2'). The indices of p and $\mathfrak{p}$ are chosen with regard to Wilson's numbering of the vibrations. No further explanation should be necessary for the following scheme of coefficients which contain the necessary parts of H, $\mathfrak{H}$ and N.

COMPONENTS OF H AND $\mathfrak{H}$

	q	$p_1(p_2)$	$p_6(p_7)$	$p_8(p_9)$	$\mathfrak{p}_1(\mathfrak{p}_2)$	$\mathfrak{p}_6(\mathfrak{p}_7)$	$\mathfrak{p}_8(\mathfrak{p}_9)$
$M_1(M_2'')$	$x_1(x_7)$	$1/\sqrt{2}$	0	0	$1/\sqrt{6}$	$1/\sqrt{3}$	0
	$x_4(x_{10})$	$-1/\sqrt{2}$	0	0	$-1/\sqrt{6}$	$-1/\sqrt{3}$	0
$M_1(M_2')$	$x_2(x_8)$	0	$1/4$	$\sqrt{3}/4$	$1/2\sqrt{6}$	$-1/4\sqrt{3}$	$\sqrt{3}/4$
	$x_3(x_9)$	0	$-1/4$	$-\sqrt{3}/4$	$-1/2\sqrt{6}$	$1/4\sqrt{3}$	$-\sqrt{3}/4$
	$x_5(x_{11})$	0	$-1/4$	$-\sqrt{3}/4$	$-1/2\sqrt{6}$	$1/4\sqrt{3}$	$-\sqrt{3}/4$
	$x_6(x_{12})$	0	$1/4$	$\sqrt{3}/4$	$1/2\sqrt{6}$	$-1/4\sqrt{3}$	$\sqrt{3}/4$
	$y_2(y_8)$	0	$\sqrt{3}/4$	$-1/4$	$1/2\sqrt{2}$	$-1/4$	$-1/4$
	$y_3(y_9)$	0	$\sqrt{3}/4$	$-1/4$	$1/2\sqrt{2}$	$-1/4$	$-1/4$
	$y_5(y_{11})$	0	$-\sqrt{3}/4$	$1/4$	$-1/2\sqrt{2}$	$1/4$	$1/4$
	$y_6(y_{12})$	0	$-\sqrt{3}/4$	$1/4$	$-1/2\sqrt{2}$	$1/4$	$1/4$

COMPONENTS OF N

$$N_{11} = N_{66} = N_{88} = M_1; \qquad N_{99} = M_2'; \qquad N_{22} = r = (M_2'' + 2M_2')/3;$$
$$N_{27} = N_{72} = s = (M_2'' - M_2') \cdot \sqrt{2/3}; \qquad N_{77} = t = (2M_2'' + M_2')/3;$$

the other components are zero.

With these coefficients of N we obtain the zero determinant corresponding to Eq. (27) given in the previous reference.

EVALUATION OF THE DETERMINANTS

With the abbreviations

$$K_{11} = M_{11}^{-1} + F_{21}^{\dagger}(F_{22}^{-1})^{\dagger}M_{22}^{-1}F_{22}^{-1}F_{21}; \quad (33)$$

$$L_{11} = M_{11} - M_{11}F_{21}^{\dagger}S^{-1}F_{21}M_{11}, \quad (34)$$

Eqs. (15) and (22) take the form[6]

$$(B_{11}K_{11} - \omega^2 E)M_{11}p_1 = 0;$$
$$(B_{11} - \omega^2 L_{11})s_1 = 0. \quad (35)$$

The secular determinants can be written:

$$\sum_{j=0}^{3n-6} \psi_j(-\omega^2)^{3n-6-j} = 0. \quad (36)$$

Ψ_j/Ψ_0 represents on one hand the sum of the products of the jth order of the squares of the frequencies obtained by writing the $\binom{3n-6}{j}$ combinations of the jth class without repeating any factors. On the other hand Ψ_j may also be represented:

(a) as the sum of the $\binom{3n-6}{j}$ principal minors of the jth order of the determinant

$$|B_{11}K_{11}| = \left|\sum_h B_{fh}K_{hg}\right|.$$

[6] It should be noted that $K_{11}L_{11} = E$.

(b) or as the sum of the $\binom{3n-6}{j}^2$ products of the minors of the jth order which belong to corresponding elements of the determinants $|B_{11}|$ and $|K_{11}|$.

(c) or as the sum of the $\binom{3n-6}{j}^2$ products of the minors of the $(3n-6-j)$th order of $|L_{11}|$ with the corresponding minors of the jth order of $|B_{11}|$.

The same results hold also for the treatment of Eqs. (31) and (32), the meaning of K_{11} and L_{11} being changed, however. Naturally the reasoning can also be applied separately to each type of vibration.

If we have the frequencies ω_f' and ω_f'' of two isotopic molecules we can make use of simpler relations between force constants and frequencies, which might sometimes be valuable for the determination of the force constants. We start from Eq. (9) from which the improper vibrations have not yet been eliminated. The coefficients ϕ_k of the secular equation

$$\sum_{k=0}^{3n} \phi_k(\omega^2)^{3n-k} = 0$$

are again on one hand equal to the sum of the products of the kth order of the squares of the frequencies, and on the other hand equal to the sum of the principal minors of kth order of the determinant $|BM^{-1}| = |B_{ab}/M_b|$. In particular,

we obtain[7]

$$\sum_{f=1}^{3n-6} \omega_f'^2 = \sum_{a=1}^{3n} \frac{B_{aa}}{M_a'}; \quad \sum_{f=1}^{3n-6} \omega_f''^2 = \sum_{a=1}^{3n} \frac{B_{aa}}{M_a''};$$

$$\sum_{f=1}^{3n-6} \Delta\omega_f^2 = \sum_{a=1}^{3n} B_{aa}\Delta\frac{1}{M_a}. \quad (37)$$

The second coefficient of the secular equation gives

$$\sum_{f \neq g}^{3n-6} \omega_f^2 \omega_g^2 = \sum_{ab}^{3n} \frac{B_{aa}B_{bb} - B_{ab}^2}{M_a M_b}; \quad (38)$$

in both summations each pair of indices is to appear only once. The last two relations give

$$\sum \omega_f^4 = \left(\sum \omega_f^2\right)^2 - 2\sum_{f \neq g} \omega_f^2 \omega_g^2 = \left(\sum_a \frac{B_{aa}}{M_a}\right)^2$$

$$-2\sum_{ab} \frac{B_{aa}B_{bb} - B_{ab}^2}{M_a M_b} = \sum_a \frac{B_{aa}^2}{M_a^2} + 2\sum_{a \neq b} \frac{B_{ab}^2}{M_a M_b} \quad (39)$$

or if $a = b$ is also permitted and each combination of indices may appear twice (for a, b and b, a):

$$\sum_f \omega_f^4 = \sum_{ab} \frac{B_{ab}^2}{M_a M_b}; \quad \sum_f \Delta\omega_f^4 = \sum_{ab} B_{ab}^2\Delta\frac{1}{M_a M_b}. \quad (40)$$

If only one kind of atom c is replaced by its isotope these relations are further simplified to

$$\sum_{f=1}^{3n-6} \Delta\omega_f^2 = \Delta\frac{1}{M_c}\sum_c B_{cc};$$

$$\sum_{f=1}^{3n-6} \Delta\omega_f^4 = 2\Delta\frac{1}{M_c}\sum_{ac} \frac{B_{ac}^2}{M_a} + \left(\Delta\frac{1}{M_c}\right)^2 \sum_c B_{cc}^2. \quad (41)$$

In these equations the index c refers to coordinates of atoms replaced by their isotopes; the index a takes on all values from 1 to $3n$.

We can obviously proceed to higher powers in similar fashion. These relations are of particular advantage for treating types of vibration which do not include improper vibrations.

TABLES FOR SOME OF THE TRANSFORMATION MATRICES

As mentioned before, the quantities H given in Eqs. (5) are step matrices; each step corre-

sponds to a set of equivalent points. In the appendix the elements of these submatrices are tabulated for some of the more important point groups.

The tables are headed by the symbol of the point group and (in parentheses) the coordinates of the equilibrium configuration. The left (upper) part of each table contains the elements of the submatrix of $m^{\frac{1}{2}}H$ where m gives the number of equivalent points in question. On the left are given the indices of the Cartesian coordinates q (real), or r (complex). The indices of the first column refer to the $x-$ or (in the complex case) to the $2^{-\frac{1}{2}}(x+iy)$ coordinates of the m atoms, the indices of the second column to the $y-$ or the $2^{-\frac{1}{2}}(x-iy)$-coordinates; the third column corresponds to the z coordinates. The sequence of the m atoms may be seen from the heading of the table. The upper three rows contain the indices of the symmetry coordinates p. The scheme of elements of $m^{\frac{1}{2}}H$ belongs to the first column of the indices of q (or r) and to the first row of the indices of p as well as to the second column and second row and the third column and third row. For the sake of clarity we give in detail the submatrix H for C_2 which may be compared with the corresponding table

$1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0	0
$-1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0	0
0	$1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0
0	$-1/\sqrt{2}$	0	0	$1/\sqrt{2}$	0
0	0	$1/\sqrt{2}$	0	0	$1/\sqrt{2}$
0	0	$1/\sqrt{2}$	0	0	$-1/\sqrt{2}$

The right (lower) part of each table contains the elements of the submatrices of $m^{-\frac{1}{2}}F$; the columns correspond in order to the symmetry coordinates p in the same numbering as given in the upper three rows of the tables for $m^{\frac{1}{2}}H$. The upper row gives the symmetry types in Placzek's notation;[8] then come the components of the angular momentum and finally the components of the linear momentum. The vacancies correspond to zeros.

For points situated on a symmetry element we use only those operations valid for the general type of points which do not refer to this particular element.

The matrices H may be developed from Brester's[2] results. In some special cases they have also been given by other authors (Wilson, Manneback, and others). Their explicit tabulation seemed to us to be of interest, since reference to such tables would save a great deal of work and also because Brester's paper is rather inaccessible.

The calculation of a molecular model proceeds

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[7] H. Tompa, Nature **137**, 951 (1936). The quantity in the second equation there should be A_{ab}^2 instead of A_{ab}.

[8] G. Placzek, *Handbuch der Radiologie*, second edition, Vol. 6.

hence in the following way. We select a system of coordinates with its origin at the center of gravity and its axes along the principal axes of inertia. The z axis is taken to be along the principal axis of symmetry (if it exists). The x components of the Cartesian coordinates have the indices 1 to n, the y components the indices $n+1$ to $2n$ and the z components the indices $2n+1$ to $3n$. The sequence of the atoms at equivalent points is to be seen from the headings of the table. With the help of the tables for $m^{-\frac{1}{2}}F$ we set up the expressions for the conservation of momenta. We select six of the symmetry coordinates p so that the determinant of the corresponding submatrix $|F_{22}| \neq 0$. In

general there is still some arbitrariness left, however, only within a particular type of symmetry. The connection between the constants B_{ab} of the potential energy and the frequencies of vibration is given for each symmetry type by Eqs. (15) or (22). The meaning of particular symmetry coordinates and hence of particular force constants follows from a discussion of the transformation H. The determination from Eqs. (8) of the force constants referred to the Cartesian coordinates will be in general superfluous.

We believe that with this method of calculation the amount of labor necessary for the solution of each particular problem will be reduced to a minimum.

Appendix. Tables for the Matrices $m^{\frac{1}{2}}H$ and $m^{-\frac{1}{2}}F$

$C_1\ (a, b, c)$

q \ p	1	2	3		c	−b
1	1			−c		a
2		1		b	−a	
3			1	1		
					1	
						1

$C_2\ (a, b, c;\ -a, -b, c)$

	p	4 5 3	1 2 6	A		B	
						c	−b
q						−c	a
1	3 5	1	1	b	−a	1	
2	4 6	1	−1				1

$C_i\ (a, b, c;\ -a, -b, -c)$

	p	4 5 6	1 2 3	g		u
					c	−b
q				−c		a
1 3 5		1	1	b	−a	
2 4 6		1	−1		1	
						1
						1

$C_s\ (a, b, c;\ a, b, -c)$

	p	1 2 6	4 5 3	A'		A''	
						c	−b
q						−c	a
1 3 5		1	1	b	−a		
2 4 6		1	−1	1			
					1		
							1

$C_{2h}\ (a, b, c;\ -a, -b, c;\ a, b, -c;\ -a, -b, -c)$

q \ p					A_g		B_g		A_u		B_u	
		10	4	1	7							
		11	5	2	8			c	−b			
q		9	3	6	12			−c	a			
1	5	9	1	1	1	1	b	−a				
2	6	10	1	1	−1	−1					1	
3	7	11	1	−1	1	−1						1
4	8	12	1	−1	−1	1				1		

$C_{2v}\ (a, b, c;\ -a, b, c;\ a, -b, c;\ -a, -b, c)$

q \ p					A_1		A_2		B_1		B_2	
		7	4	1	10							
		11	2	5	8					c	−b	
q		3	12	9	6					−c	a	
1	5	9	1	1	1	1			b	−a		
2	6	10	1	1	−1	−1					1	
3	7	11	1	−1	1	−1						1
4	8	12	1	−1	−1	1	1					

V $(a, b, c; a, -b, -c; -a, b, -c; -a, -b, c)$

q \ p	10 8 6	1 5 9	4 2 12	7 11 3	A	B_1	B_2	B_3
								$c\ -b$
							$-c\quad a$	
						$b\ -a$		
1 5 9	1	1	1	1				1
2 6 10	1	1	-1	-1			1	
3 7 11	1	-1	1	-1		1		
4 8 12	1	-1	-1	1	1			

V$_h$ $(a, b, c; a, -b, -c; -a, b, -c; -a, -b, c; -a, -b, -c; -a, b, c; a, -b, c; a, b, -c)$

q \ p	22 20 18	10 8 6	13 17 21	1 5 9	16 14 24	4 2 12	19 23 15	7 11 3
1 9 17	1	1	1	1	1	1	1	1
2 10 18	1	1	1	1	-1	-1	-1	-1
3 11 19	1	1	-1	-1	1	1	-1	-1
4 12 20	1	1	-1	-1	-1	-1	1	1
5 13 21	1	-1	1	-1	1	-1	1	-1
6 14 22	1	-1	1	-1	-1	1	-1	1
7 15 23	1	-1	-1	1	1	-1	-1	1
8 16 24	1	-1	-1	1	-1	1	1	-1

A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
			$c\ -b$				
		$-c\quad a$					
	$b\ -a$						
							1
						1	
					1		

C$_3$ $(a, a^*, c; a\epsilon, a^*\epsilon^2, c; a\epsilon^2, a^*\epsilon, c)$ $\epsilon = e^{2\pi i/3}$

r \ p	4 8 3	1 5 9	7 2 6	A	E	E
						$c\ -a^*$
				$-c\quad a$	
1 4 7	1	1	1	$a^*\ -a$		
2 5 8	1	ϵ	ϵ^2		1	
3 6 9	1	ϵ^2	ϵ			1
				1		

C$_4$ $(a, a^*, c; ia, -ia^*, c; -a, -a^*, c; -ia, ia^*, c)$

r \ p	7 11 3	1 5 12	10 8 6	4 2 9	A	B	E	E
								$c\ -a^*$
							$-c\quad a$	
1 5 9	1	1	1	1	$a^*\ -a$			
2 6 10	1	i	-1	$-i$			1	
3 7 11	1	-1	1	-1				1
4 8 12	1	$-i$	-1	i	1			

S$_4$ $(a, a^*, c; ia, -ia^*, -c; -a, -a^*, c; -ia, ia^*, -c)$

r \ p	7 11 6	1 5 9	10 8 3	4 2 12	A	B	E	E
							$c\ -a^*$	
								$-c\quad a$
1 5 9	1	1	1	1	$a^*\ -a$			
2 6 10	1	i	-1	$-i$			1	
3 7 11	1	-1	1	-1				1
4 8 12	1	$-i$	-1	i		1		

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C_{3h} $(a, a^*, c; a\epsilon, a^*\epsilon^2, c; a\epsilon^2, a^*\epsilon, c; a, a^*, -c; a\epsilon, a^*, \epsilon^2 -c; a\epsilon^2, a^*\epsilon, -c)$ $\epsilon = e^{2\pi i/3}$

r \ p	7 11 6	1 8 18	10 2 15	13 17 3	4 14 12	16 5 9	A'	A''	E'	E'	E''	E''
												c $-a^*$
											$-c$ a	
1 7 13	1	1	1	1	1	1	a^* $-a$					
2 8 14	1	ϵ	ϵ^2	1	ϵ	ϵ^2			1			
3 9 15	1	ϵ^2	ϵ	1	ϵ^2	ϵ				1		
4 10 16	1	1	1	-1	-1	-1		1				
5 11 17	1	ϵ	ϵ^2	-1	$-\epsilon$	$-\epsilon^2$						
6 12 18	1	ϵ^2	ϵ	-1	$-\epsilon^2$	$-\epsilon$						

C_6 $(a, a^*, c; a\epsilon, a^*\epsilon^5, c; a\epsilon^2, a^*\epsilon^4, c; -a, -a^*, c; a\epsilon^4, a^*\epsilon^2, c; a\epsilon^5, a^*\epsilon, c)$ $\epsilon = e^{2\pi i/6}$

r \ p	13 17 3	1 8 18	16 5 9	7 11 6	4 14 12	10 2 15	A	B	E^+	E^+	E^-	E^-
												c $-a^*$
											$-c$ a	
1 7 13	1	1	1	1	1	1	a^* $-a$					
2 8 14	1	ϵ	ϵ^2	ϵ^3	ϵ^4	ϵ^5					1	
3 9 15	1	ϵ^2	ϵ^4	1	ϵ^2	ϵ^4						1
4 10 16	1	ϵ^3	1	ϵ^2	1	ϵ^3		1				
5 11 17	1	ϵ^4	ϵ^2	1	ϵ^4	ϵ^2						
6 12 18	1	ϵ^5	ϵ^4	ϵ^3	ϵ^2	ϵ						

S_6 $(a, a^*, c; a\epsilon, a^*\epsilon^5, -c; a\epsilon^2, a^*\epsilon^4, c; -a, -a^*, -c; a\epsilon^4, a^*\epsilon^2, c; a\epsilon^5, a^*\epsilon, -c)$ $\epsilon = e^{2\pi i/6}$

r \ p	13 17 6	1 8 12	16 5 15	7 11 3	4 14 18	10 2 9	A_g	A_u	E_g	E_g	E_u	E_u
												c $-a^*$
									$-c$ a			
1 7 13	1	1	1	1	1	1	a^* $-a$					
2 8 14	1	ϵ	ϵ^2	ϵ^3	ϵ^4	ϵ^5					1	
3 9 15	1	ϵ^2	ϵ^4	1	ϵ^2	ϵ^4						1
4 10 16	1	ϵ^3	1	ϵ^3	1	ϵ^3		1				
5 11 17	1	ϵ^4	ϵ^2	1	ϵ^4	ϵ^2						
6 12 18	1	ϵ^5	ϵ^4	ϵ^3	ϵ^2	ϵ						