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INFLUENCE OF VIBRATIONS ON MOLECULAR STRUCTURE DETERMINATIONS. I. GENERAL FORMULATION OF VIBRATION-ROTATION INTERACTIONS.*

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Abstract

The structure of a polyatomic molecule derived from observed spectroscopic moments of inertia differs appreciably from both the equilibrium structure and the zero-point average structure. A perturbation expansion of the moments of inertia is derived here in a form which allows the vibrational displacements to be referred to any fixed configuration of the atoms as origin. A method for evaluating the expansion coefficients is given which proceeds "atom-by-atom." Linear WXYZ, branched WXYZ, and symmetric WXY_3 molecules are treated in detail.

Empirical data show that the anharmonicity of the vibrations gives rise to the most important of the corrections required to obtain the equilibrium structure. Except for a few molecules, the anharmonicity is not accurately known. It is shown, however, that the anharmonic contributions are completely absorbed (to a practical approximation), in displacing the average configuration from the equilibrium one. Therefore the moments of inertia for the zero-point average configuration of a molecule can be derived from the observed effective moments by applying corrections which depend only upon the harmonic part of the vibrational potential.

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The traditional model of point masses connected by weightless rigid rods gives a remarkably good fit to the rotational spectra of most molecules. However, molecular vibrations make the "effective" moments of inertia obtained from a rigid rotor analysis differ appreciably from the moments for the equilibrium structure of the molecule. Even in the ground state, the contribution of zero-point vibrations to the effective moments is usually of the order of 1%. This is far larger than experimental uncertainties in high resolution spectroscopy, particularly microwave spectroscopy, which commonly yields moments accurate to 0.002% or better.

Except for diatomic molecules and the simplest polyatomic molecules, experimental determination of the vibrational contributions has not been feasible. Theoretical calculations have been forestalled by their complexity as well as lack of sufficient information about vibrational potential functions. Some of the conceptual difficulties are evident in the discussions,[1] enlivened by several wrong conclusions, which led to Eckart's formulation[2] of the conditions necessary to define an internal axis system that would insure the maximum uncoupling of vibration and rotation.[3] Wilson and Howard[4] carried out a perturbation treatment of the vibration-rotation coupling and showed that the rotational spectrum of most molecules (after allowance for centrifugal distortion) should be that of a fictitious rigid rotor. Wilson and Howard emphasized that the effective moments of inertia are not simply related either to the average of the instantaneous moments or to the average of their reciprocals, because of Coriolis forces and

other interactions, but this point has since often been overlooked. Nielsen, Dennison, and others extended the treatment and derived explicit expressions relating the effective moments to the equilibrium moments of inertia.[5] Unfortunately, the terms that are nearly always the most important in these relations involve the anharmonic part of the vibrational potential, which is accurately known for only a few polyatomic molecules.

The problem of deriving equilibrium structures for polyatomic molecules has therefore remained intractable, and the general practice has been to make direct use of the effective moments. The structures obtained are usually referred to as "r_o structures." The inconsistencies in r_o parameters caused by zero-point vibrations are particularly noticeable in microwave data for isotopic molecules,[6] and attempts have been made to estimate their effect in a number of specific cases.[7-11] Also, Costain[12] has proposed a general procedure of analysis, in which Kraitchman's equations[13] are used to determine structures by fitting the differences of the effective moments of isotopic species rather than the absolute values of the moments. Costain has designated the parameters obtained by this "substitution" method as the "r_s structure." He has shown cases where remarkably consistent r_s parameters are obtained even when there is considerable variation in the r_o parameters obtained by fitting different combinations of the absolute values of the moments. Pierce[14] has discussed the use of second differences in cases where multiple isotopic substitutions are made. Although these semi-empirical methods have given promising results, it has not been clear whether they make the optimum use of the data, and several

vexing problems remain, including the difficulty of locating atoms near principal axes, the means of allowing for "inertial defects," and the question of the proper procedure for analyzing data when all atoms have not been isotopically substituted.

Another question which is not yet resolved is the relation of the empirically determined r_o or r_s structures to some well defined physical concept such as the equilibrium structure or the average structure. With the continued refinement of electron diffraction and other methods of structure determination, it is becoming more important to find a common basis for comparison of structural parameters obtained by different techniques. Recent accurate studies of hydrocarbons by electron diffraction[15] and by microwave spectroscopy,[16] for example, have given significantly different values for CH bond lengths; it seems likely that part of the discrepancy arises from the inherent difference in the nature of the experimentally determined quantities.

In the present study the aim has been to examine these practical problems of structure analysis from the viewpoint of the general theory of vibration-rotation interactions. Much of the physical content and the theoretical methods applied here are implicit in work already existing.[5] However, the available discussions have usually been oriented toward the interpretation of spectra rather than any specific understanding of problems of structure determination, and we have found it advantageous to take an approach which differs in many details. In particular, the treatment is modified here so that the perturbation expansions are not restricted to the equilibrium configuration, but may be referred to any arbitrarily

chosen configuration of the atoms. From this it is found that the moments of inertia for the average configuration of a molecule may be derived from the observed effective moments by applying corrections which depend only upon the harmonic part of the vibrational potential.[17] Also, the calculations are simplified by a formulation which takes advantage of Wilson's methods for vibrational analysis.[18] This paper outlines the derivations together with some qualitative considerations. Applications to structure analysis are presented in succeeding papers on the calculation of average structures (Part II), inertial defects (Part III), and isotopic substitution (Part IV).

PRELIMINARY ANALYSIS OF SIMPLE CASES

The basis for approximations to be introduced in the general treatment can be illustrated most simply with diatomic and triatomic molecules.

Diatomic Molecules

The vibrational average of any function of internuclear distance is readily obtained from a series expansion in $\xi = (r-r_e)/r_e$, the relative deviation from the equilibrium distance. Thus the average $\underline{n}^{th}$ power of the bond distance is given by[19]

$$\langle r^n \rangle^{1/n} = \kappa r_e \qquad (1)$$

where the scale factor is

$$\kappa = 1 + \langle \xi \rangle - \tfrac{1}{2}(1-n)\langle \xi^2 \rangle + \cdots \qquad (2)$$

The corresponding correction terms for moments of inertia and rotational constants are given by

$$I = r^2 = \kappa^2 I_e, \tag{3a}$$

$$B = h/8\pi^2 I = \kappa^{-2} B_e. \tag{3b}$$

In these formulas

$$\langle \xi \rangle = -a_1 (3B_e/\omega_e)(v + \tfrac{1}{2}) \tag{4a}$$

$$\langle \xi^2 \rangle = (2B_e/\omega_e)(v + \tfrac{1}{2}) \tag{4b}$$

where ω_e is the harmonic vibrational frequency and a_1 is a (dimensionless) cubic anharmonic constant.[20] In Eqs. (4) and elsewhere only terms linear in the vibrational quantum number are retained; this approximation is well justified empirically.

In Table I various kinds of average bond lengths are compared. For the ground vibrational state the direct average, $\langle r \rangle$, is essentially the same as the parameter $r_g(0)$ obtained from electron diffraction.[21] This is always larger than the effective bond length, r_o (n = -2 average), obtained from rotational spectroscopy, which is in turn larger than Costain's substitution parameter, r_s. The inverse cube average, $\langle r^{-3} \rangle^{-1/3}$, appears in interaction constants measured in magnetic resonance[19] or microwave maser[22] experiments.

As indicated in Table I, the deviation of $\langle r \rangle$ from r_e is due entirely to anharmonicity. Furthermore, Eq. (1) gives the same anharmonic contribution for any $\underline{n}^{th}$ power average. Any of these averages can therefore be derived from $\langle r \rangle$ by means of a correction which involves just the harmonic vibrational amplitude,

$$\langle r^n \rangle^{1/n} = \langle r \rangle - \tfrac{1}{2}(1-n)\langle \xi^2 \rangle r_e \quad . \tag{5}$$

This gives rise to the parallelism displayed in Fig. 1, in which the value of $\kappa - 1$ for each bond length is plotted versus the anharmonic constant. The ordinate scale is marked in multiples of $\langle \xi^2 \rangle$; thus, for a typical ground state value of $\langle \xi^2 \rangle = 10^{-3}$, each division corresponds to an 0.1% deviation from r_e.

The anharmonic constant can be determined from α_e, the spectroscopic vibration-rotation interaction constant. Since

$$B_v = B_e - (v + \tfrac{1}{2})\, \alpha_e, \tag{6}$$

comparison with Eq. (3b) gives

$$\alpha_e = -(6B_e^2/\omega_e)(1 + a_1) \tag{7}$$

In structure analysis it is convenient to use instead a parameter ϵ which gives the correction to the effective moment of inertia,

$$I_v = K/B_v = I_e + (v + \tfrac{1}{2})\epsilon \tag{8}$$

$$\epsilon = I_e(\alpha_e/B_e) = -(6K/\omega_e)(1 + a_1), \tag{9}$$

where $K = h/8\pi^2$. In terms of ϵ, the scale factor for the effective bond length is

$$\kappa = 1 + \tfrac{1}{2}(v + \tfrac{1}{2})(\epsilon/I_e). \tag{10}$$

The ratio of the anharmonic and harmonic vibrational contributions in Eq. (10) is just equal to the anharmonic constant,

$$\epsilon_a/\epsilon_h = a_1 \ , \tag{11}$$

as seen from Eq. (9). Since a_1 is between -2 and -4 for almost all diatomic molecules,[23] the anharmonic term predominates; however, the harmonic term is of opposite sign and compensates for about 25% to 50% of the anharmonic displacement. For the general $\underline{n}^{th}$ power average the ratio in Eq. (11) becomes $3a_1/(1-n)$, so only for $n > 1$ does the harmonic term reinforce the anharmonic one. On the other hand, only for large negative values of n does the cancellation become substantially complete (at $n = -5$ for $a_1 = -2$; at $n = -11$ for $a_1 = -4$).

The effect of vibrations on structures determined by isotopic differences[12] is considered in Part IV, where it is shown that the scale factor for the r_s bond length is

$$\kappa = 1 + \tfrac{1}{2}(v + \tfrac{1}{2})(\epsilon/I_e)f \ , \qquad (12a)$$

with

$$f = (\mu/m_1)[1+(\mu_1/\mu)^{\frac{1}{2}}]^{-1} + (\mu/m_2)[1+(\mu_2/\mu)^{\frac{1}{2}}]^{-1}. \qquad (12b)$$

Here m_1 and m_2 denote the masses of the atoms in the parent molecule and μ_1, μ_2 the reduced masses of the isotopically substituted molecules. The factor f varies only slightly with isotopic substitution. It approaches an upper limit of one-half when both μ_1 and μ_2 differ negligibly from μ, whereas $f = 0.414$ for deuterium substitution in H_2. As seen by comparing Eqs. (10) and (12), the deviations from equilibrium

$$r_s - r_e = f(r_v - r_e)$$

$$I_s - I_e = f(I_v - I_e)$$

are correspondingly less than those for the effective bond length.[12] Similarly, it is found that r_s will show about 50% less variation with isotopic species than does r_v. However, the use of isotopic differences does not alter the ratio of anharmonic and harmonic contributions, which is still given by Eq. (11).

Triatomic Molecules

The effective moment of inertia for a linear triatomic molecule,

$$I_v = I_e + \Sigma_s (v_s + \tfrac{1}{2} d_s)\epsilon_s ,$$

contains contributions from the symmetric (s = 1) and antisymmetric (s = 3) stretching vibrational modes and from the doubly degenerate bending (s = 2, d_2 = 2) mode. These corrections may be written in a form

$$d_s \epsilon_s = -(6K/\omega_s)(H_s + A_s) \qquad (13)$$

analogous to Eq. (9). The harmonic terms H_s are readily evaluated from formulas given in Part II. However, except for a few cases,[24] the anharmonic potential constants are not known sufficiently well to allow reliable values of the A_s to be calculated. Experimental values of some of the ϵ_s coefficients are available for several molecules and by subtracting calculated values of the harmonic contributions we have evaluated the A_s terms. Table II lists the ratios

$$\epsilon(\text{anharmonic})/\epsilon(\text{harmonic}) = A_s/H_s$$

which were obtained. It is seen that for all the linear molecules the anharmonic contribution is dominant and opposite in sign to the harmonic contribution, just as for diatomic molecules. For the

symmetric stretching mode, the ratio is roughly the same as that given by Eq. (11) for related diatomics. In most cases, however, the anharmonic contribution is enhanced considerably in the other modes and in the total correction.

This pattern does not hold for H_2O, especially in the bending mode. As yet there is virtually no information available for other nonlinear triatomic molecules.

Unlike the diatomic case, in isotopic differences the ratio of contributions from A_s and H_s does not remain constant. Often it is widely different for different modes. Again the anharmonicity nearly always gives the dominant contribution, as shown in Part IV.

Figure 2 indicates the relative contribution of the stretching and bending modes. Data is included for all polyatomic molecules for which the equilibrium moment of inertia is known. It is found that the contributions from bending are usually opposite in sign to those from stretching, but somewhat smaller in magnitude. Consequently, the total correction,

$$\epsilon = \Sigma_s d_s \epsilon_s,$$

(shown by the solid points) in most cases falls substantially below the dashed line, which gives the corrections due to stretching alone. Another comparison (shown by open points) with the sum of stretching terms is obtained by assigning to each bond the observed ϵ_s value for the corresponding diatomic molecule. Except for C_2H_2, HCN, and H_2O, this proves to be a considerable underestimate. An example in which the contribution from bending outweighs that from stretching is the a-axis principal moment of inertia of H_2O.

For a linear, symmetric XY_2 molecule, it is feasible to express the n^{th} power average of the bond distance, $\langle r^n \rangle^{1/n}$, and the vibration-rotation parameters of Eq. (13) as explicit functions of the force constants, atomic masses, and geometry. The results are collected in Table III. As indicated, the quadratic and cubic force constants refer to internal displacement coordinates, and symmetry allows only certain terms to appear in the potential energy.[18] For the symmetric stretching mode, the form of the vibrational parameter λ_1 and the coefficients H_1 and A_1 is the same as in the diatomic case; however, this is not so for the other modes. The calculation of $\langle r^n \rangle^{1/n}$ starts from the relation

$$2r = 2r_e + S_1 + S_3.$$

Up to terms linear in $v + \frac{1}{2}$, the only normal coordinate which enters is the symmetric stretch, proportional to $S_1 + S_3$, and the vibrational averages may be evaluated as indicated in Eqs. (34) and (35) and Appendix C. It is found that Eqs. (1)-(3) and (5) still hold, but ξ is replaced by $\frac{1}{2}(S_1 + S_3)$ and the averages in Eq. (4) take the values given in Table III.

From these results, it is readily shown that the effective rotational constant B_v is not simply the vibrational average, $\langle B \rangle$. The latter is given by

$$\langle B \rangle = K\langle I^{-1} \rangle = (K/2m)\langle r^{-2} \rangle,$$

where m is the mass of the Y atom. From Tables I and III, we find

$$\langle r^n \rangle^{1/n} = \langle r \rangle - (1-n)(B_e/\omega_1)(v_1 + \tfrac{1}{2}) \qquad (14)$$

The effective bond length, however, is given by

$$r_v = \kappa r_e = (I_v/2m)^{1/2},$$

with

$$\kappa = 1 + \tfrac{1}{2}\Sigma_s(v_s + \tfrac{1}{2}d_s)(\epsilon_s/I_e),$$

as in Eq. (10). Thus we find

$$r_v = \langle r\rangle - \Sigma_s(3B_e/\omega_s)H_s(v_s + \tfrac{1}{2}) \qquad (15)$$

so that r_v has terms involving H_2 and H_3 not present in $\langle r^{-2}\rangle^{-1/2}$. As shown for the general case in Eq. (26) and Appendix B, these "extra" terms arise from Coriolis interactions. Only for diatomic molecules is the effective rotational constant simply proportional to $\langle I^{-1}\rangle$.

In Eqs. (14) and (15) it is again found, however, that any of the n^{th} power average bond lengths may be computed from the effective bond length without knowledge of the anharmonic force constants, just as in Eq. (5) for the diatomic case.

Table IV gives a detailed analysis of the contributions to $I_o - I_e$ for CO_2. It is seen that the Coriolis terms H_2 and H_3 are comparable to H_1. Another typical feature, found for all the linear triatomic molecules of Fig. 2, is the substantial cancellation which occurs between bending and stretching and between harmonic and anharmonic terms.

GENERAL FORMULATION

The results found for the diatomic and linear XY_2 molecules suggest that even in a polyatomic molecule the main effect of vibrational anharmonicity is to displace the average configuration of the atoms from the equilibrium one. We shall confirm this by deriving relations between the effective moments of inertia obtained from spectroscopy and the moments that correspond to various configurations of the atoms. Although a perturbation treatment parallel to the usual one[5] gives the same results, another approach, patterned after the treatment of diatomics, is used here to simplify the formulation.

Coordinates and Hamiltonian

The positions of the atoms are specified by vectors $\underset{\sim}{r}_i$ whose Cartesian components $(\alpha_i, \beta_i, \gamma_i)$ are referred to a set of axes moving with the molecule (the so-called "molecule-fixed" axes). A standard configuration of the atoms, which need not be the equilibrium configuration but should not differ greatly from it,[26] is defined by a set of coordinates $(\alpha_i^*, \beta_i^*, \gamma_i^*)$. Vibrational displacements from the standard configuration are described by normal coordinates Q_s, which are defined in terms of the increments

$$\delta\alpha_i = \alpha_i - \alpha_i^* ,$$

etc. The increments are not all independent, but must satisfy the Eckart conditions,

$$\Sigma_i m_i \delta\alpha_i = 0 \tag{16}$$

$$\Sigma_i m_i (\alpha_i^* \delta\beta_i - \beta_i^* \delta\alpha_i) = 0, \tag{17}$$

etc. These six conditions serve both to define the molecule-fixed axis system and to complete the transformation equations which relate the 3N atomic displacements to the 3N-6 normal coordinates.[2,18]

$$\delta\alpha_i = m_i^{-1/2} \Sigma_s \ell_{is}^{(\alpha)} Q_s \tag{18a}$$

and

$$Q_s = \Sigma_\alpha \Sigma_i m_i^{1/2} \ell_{si}^{(\alpha)} \delta\alpha_i \tag{18b}$$

The mass adjustment makes the transformation orthonormal, so that

$$\Sigma_i \Sigma_\alpha \ell_{is}^{(\alpha)} \ell_{it}^{(\alpha)} = \delta_{st}. \tag{19}$$

We shall consider later a method of evaluating the transformation coefficients, as our final results will be expressed in terms of them.

The potential energy associated with the vibrational displacements is expanded as

$$2V = \Sigma_s V_s Q_s + \Sigma_s \lambda_s Q_s^2 + \Sigma_s k_{sss} Q_s^3 + 3\Sigma_s \Sigma_t k_{sst} Q_s^2 Q_t + \cdots \tag{20}$$

Unless the standard configuration is the equilibrium one, the coefficients of the linear terms will not vanish. In any case, however, the normal coordinates can be chosen to eliminate cross terms in the quadratic part of the potential energy. Furthermore, we can relate the coefficients in (20) to the usual parameters, which refer to an expansion about the equilibrium configuration. As shown in Eq. (42), for practical purposes the vibration frequencies and cubic constants are unchanged and the coefficient of the linear term takes the form

$$V_s = -3[\sigma_{ss}\langle Q_s^2\rangle + \Sigma_t \sigma_{ts}\langle Q_t^2\rangle] \ , \tag{21}$$

where the constants σ_{ss} and σ_{ts} are a linear combination of λ_s, k_{sss}, and k_{tts}.

The Hamiltonian for vibration and rotation may be written as

$$2H = \underset{\sim}{\pi}^{\dagger}\underset{\sim}{I}^{-1}\underset{\sim}{\pi} + (\underset{\sim}{P} - \underset{\sim}{\rho})^{\dagger}(\underset{\sim}{P} - \underset{\sim}{\rho}) + 2V \ , \tag{22}$$

as shown in Appendix A. (See Table V for notation.) If the molecule were vibrating but not rotating, only the terms[18]

$$2H_{vib} = \underset{\sim}{P}^{\dagger}\underset{\sim}{P} + 2V \tag{23}$$

would remain, whereas if the molecule were "frozen" in the standard configuration, only the kinetic energy of rigid rotation would appear,

$$2H_{rigid} = \underset{\sim}{\pi}^{\dagger}(\underset{\sim}{I}^{-1})^{*}\underset{\sim}{\pi} \ . \tag{24}$$

This involves just the inverse of the moment of inertia tensor for the standard configuration and since principal axes are used

$$I_{\alpha}^{*} = \Sigma_i m_i(\beta_i^{*2} + \gamma_i^{*2}) \tag{25a}$$

$$I_{\alpha\beta}^{*} = -\Sigma_i m_i \alpha_i^{*}\beta_i^{*} = 0 \ . \tag{25b}$$

In the vibrating molecule additional contributions to the rotational energy arise in two ways. One is the dependence of the moments of inertia of the distorted molecule on the normal coordinates. This can be evaluated by a straightforward vibrational average, using the eigenfunctions ψ_{vib} associated with (23). The other contributions come from the terms involving ρ in (22). As shown in Appendix A, the operator ρ is proportional to $\underset{\sim}{\pi}$ and represents the part of

the vibrational momentum that arises from Coriolis forces in the rotating molecule. A second order perturbation treatment of these Coriolis interactions therefore yields terms quadratic in $\underset{\sim}{\mathcal{M}}$ which contribute to the effective moments of inertia. Hence the effective moments are given by

$$\underset{\sim}{I}_v = \langle \underset{\sim}{I}^{-1} \rangle^{-1} + \text{Coriolis terms.} \tag{26}$$

The vibrational average of $\underset{\sim}{I}^{-1}$ is evaluated in the next section and the Coriolis terms are treated in Appendix B.

The result of this perturbation treatment is to replace (22) with an effective rotational Hamiltonian,

$$H_{rot} = \underset{\sim}{\mathcal{M}}^{\dagger} \underset{\sim}{B} \underset{\sim}{\mathcal{M}} = \Sigma_\alpha \Sigma_\beta B_{\alpha\beta} \mathcal{M}_\alpha \mathcal{M}_\beta \tag{27}$$

in which the rotational constants take the form

$$B_{\alpha\beta} = (K/I^*_\alpha)\delta_{\alpha\beta} - \Sigma_s (v_s + \tfrac{1}{2} d_s) \alpha_s^{\alpha\beta} \tag{28}$$

The vibration-rotation interactions[27] thus contribute both diagonal and nondiagonal terms to the effective moment of inertia tensor, whose elements may be written as

$$I^v_{\alpha\beta} = I^*_\alpha \delta_{\alpha\beta} + \Sigma_s (v_s + \tfrac{1}{2} d_s) \epsilon_s^{\alpha\beta} \tag{29}$$

where

$$\epsilon_s^{\alpha\beta} = (I_\alpha I_\beta / K) \alpha_s^{\alpha\beta},$$

as found by inverting (27). The calculation indicated in (26) will provide expressions for the coefficients $\epsilon_s^{\alpha\beta}$ as functions of the molecular geometry, atomic masses, and potential energy parameters.

Vibrational Averages

The components of the instantaneous moment of inertia tensor may be expanded as

$$I_{\alpha\beta} = I^*_\alpha \delta_{\alpha\beta} + \Sigma_s a_s^{\alpha\beta} Q_s + \Sigma_s \Sigma_t A_{st}^{\alpha\beta} Q_s Q_t + \cdots , \qquad (30)$$

where the coefficients

$$a_s^{\alpha\beta} = (\partial I_{\alpha\beta}/\partial Q_s)_*$$

$$A_{st}^{\alpha\beta} = (\partial^2 I_{\alpha\beta}/\partial Q_s \partial Q_t)_*$$

are evaluated in terms of the transformation relations (18) as indicated in Eq. (48). The corresponding expansion of the inverse moment of inertia tensor is given by

$$(I^{-1})_{\alpha\beta} = \delta_{\alpha\beta}/I^*_\alpha - \Sigma_s a_s^{\alpha\beta} Q_s$$

$$- \Sigma_s \Sigma_t [A_{st}^{\alpha\beta} - \Sigma_\gamma a_s^{\alpha\gamma} a_s^{\beta\gamma}/I_\gamma] Q_s Q_t + \cdots \qquad (31)$$

In the vibrational average there is no mixing of the contributions from the various parts of (31) and the Coriolis terms of Appendix B, as long as only terms linear in $v_s + \frac{1}{2}$ are retained. The cross terms $\langle Q_s Q_t \rangle$ also do not contribute in this order of approximation. Thus, after averaging and re-inverting (31) we have

$$\langle (I^{-1})_{\alpha\beta} \rangle^{-1} = I^*_\alpha \delta_{\alpha\beta} + \Sigma_s a_s^{\alpha\beta} \langle Q_s \rangle$$

$$+ \Sigma_s [A_{ss}^{\alpha\beta} - \Sigma_\gamma a_s^{\alpha\gamma} a_s^{\beta\gamma}/I_\gamma] \langle Q_s^2 \rangle + \cdots \qquad (32)$$

To this we must add the Coriolis contributions from Eq. (B6),

$$- 4\Sigma_s\Sigma_t[\zeta^{\alpha}_{st}\zeta^{\beta}_{st}\lambda_s/(\lambda_s-\lambda_t)]\langle Q_s^2\rangle \ , \qquad (33)$$

in order to obtain the effective moment of inertia. The requisite vibrational averages are given by

$$\langle Q_s\rangle = -\frac{3}{2}[(k_{sss}-\sigma_{ss})\langle Q_s^2\rangle + \Sigma_t(k_{tts}-\sigma_{ts})\langle Q_t^2\rangle]/\lambda_s \qquad (34)$$

and

$$\langle Q_s^2\rangle = (2K/\omega_s)(v_s + \tfrac{1}{2}d_s) \ , \qquad (35)$$

as shown in Appendix C. When (34) is substituted into (32), there results a double sum over the nondiagonal cubic constants. However, this may be rearranged to make a common factor of $\langle Q_s^2\rangle$ appear in all the terms. Thus we obtain

$$\epsilon_s^{\alpha\beta}(\text{har}) = (2K/\omega_s)[A_{ss}^{\alpha\beta} - \Sigma_\gamma a^{\alpha\gamma}a^{\beta\gamma}/I_\gamma - 4\Sigma_t\zeta^{\alpha}_{st}\zeta^{\beta}_{st}\lambda_s/(\lambda_s-\lambda_t)] \qquad (36)$$

$$\epsilon_s^{\alpha\beta}(\text{anhar}) = (-3K/\omega_s)[a_s^{\alpha\beta}(k_{sss}-\sigma_{ss})/\lambda_s + \Sigma_t a_t^{\alpha\beta}(k_{sst}-\sigma_{st})/\lambda_t] \qquad (37)$$

as the general formulas for the "harmonic" and "anharmonic" parts of the coefficients in Eq. (2$\dot{9}$). By comparison with (30) and (31) it is seen that the first term in $\epsilon_s(\text{har})$ represents a direct average over the instantaneous moment of inertia, $\langle I\rangle$; the second term arises because it is the reciprocal moment which is actually averaged; and the third term accounts for the Coriolis contributions.[28] The two latter effects do not enter $\epsilon_s(\text{anhar})$, however. These formulas enable us to relate the moments of inertia for any choice of the standard configuration to the observed effective moments.

Comparison of Equilibrium and Average Configurations

When the equilibrium configuration is the standard, $\sigma_{ss} = \sigma_{st} = 0$ and the formulas (36) and (37) become equivalent to the results derived by Nielsen.[5] When the average configuration is taken as the standard, we shall find that

$$\epsilon_s^{\alpha\beta}(\text{anhar}) = 0 \ . \tag{38}$$

In the following comparisons, we indicate by an overhead bar quantities which refer to the equilibrium configuration as the standard. Thus from (18) we have

$$\alpha_i - \bar{\alpha}_i = m_i^{-1/2} \Sigma_s \bar{\ell}_{is}^{\alpha} \bar{Q}_s ,$$

and these normal coordinates of course differ somewhat from those used when the average configuration is the standard. The displacement of the average configuration from the equilibrium one is therefore given by

$$\begin{aligned} \alpha_i^* - \bar{\alpha}_i &= \langle \alpha_i - \bar{\alpha}_i \rangle \\ &= m_i^{-1/2} \Sigma_s \bar{\ell}_{is}^{(\alpha)} \langle \bar{Q}_s \rangle \ . \end{aligned} \tag{39}$$

Here the wavefunction $\bar{\psi}_{vib}$ to be used in the vibrational average also refers to the equilibrium configuration as the standard. From (39) we see that a displacement from the average configuration may be expressed as

$$\alpha_i - \alpha_i^* = m_i^{-1/2} \Sigma_s \bar{\ell}_{is}^{\alpha} [\bar{Q}_s - \langle \bar{Q}_s \rangle]$$

so that a comparison with (18) establishes the relations

$$Q_s = \Sigma_t T_{st}[\bar{Q}_t - \langle \bar{Q}_t \rangle] \tag{40a}$$

and

$$\bar{Q}_s = \langle \bar{Q}_s \rangle + \Sigma_t T_{st} Q_t, \tag{40b}$$

where

$$T_{st} = \Sigma_i \Sigma_\alpha (\ell_{is}^\alpha \bar{\ell}_{it}^\alpha). \tag{41a}$$

From Eqs. (40) we can derive corresponding relations between the coefficients that appear in the expansion of the potential energy. For example, the linear term in Eq. (20) involves

$$\frac{1}{2} V_s = (\partial V/\partial Q_s)_* = \Sigma_t (\partial V/\partial \bar{Q}_t)_* \, T_{ts}$$

and

$$(\partial V/\partial \bar{Q}_t)_* = \bar{\lambda}_t \langle \bar{Q}_t \rangle + \tfrac{3}{2} \bar{k}_{ttt} \langle \bar{Q}_t \rangle^2 + \cdots$$

Only the first term in this derivative need be retained, as the others will be at least quadratic functions of $(v + \frac{1}{2})$. Furthermore, the difference between the two sets of transformation coefficients is so slight that (41) may be approximated by

$$T_{st} = T_{ts} = \delta_{st} \, . \tag{41b}$$

The result then reduces to

$$V_s = -3[\bar{k}_{sss} \langle \bar{Q}_s^2 \rangle + \Sigma_t \bar{k}_{tts} \langle \bar{Q}_t^2 \rangle], \tag{42a}$$

after introducing (34) with $\bar{\sigma}_{ss} = \bar{\sigma}_{ts} = 0$. In the same way we find

$$\lambda_s = (\partial^2 V/\partial Q_s^2)_* = \bar{\lambda}_s + \cdots \tag{42b}$$

$$k_{sss} = \bar{k}_{sss} + \cdots \, , \tag{42c}$$

etc. The vibration frequencies and cubic constants can be taken to be the same for both configurations, since in the effective Hamiltonian of Eq. (27) the corrections thereby omitted would not show up in the terms proportional to $(v + \frac{1}{2})$. For the same reason we can omit the bars from the quantities in (42). Thus we obtain the form given in Eq. (21) and find that

$$\sigma_{ss} = k_{sss}, \quad \sigma_{ts} = k_{tts} \tag{43}$$

when the standard is the average configuration. Substitution of these results in the general Eqs. (34) and (37) then leads to (38). This demonstrates that (up to terms linear in $v + \frac{1}{2}$) only the harmonic part of the vibrational potential is required in order to calculate the moments of inertia for the average structure from the observed effective moments. Such calculations are given for several molecules in Part II of this series.

A similar derivation shows that other choices for the standard configuration would again lead to Eq. (21) with Eqs. (43) replaced by expressions analogous to those found in Table I for the diatomic case.

CALCULATION OF PARAMETERS

The numerical evaluation of the vibration-rotation parameters in Eqs. (36) and (37) requires, in addition to the potential constants, a calculation of the coefficients, $a_s^{\alpha\beta}$ and $A_{ss}^{\alpha\beta}$, in the expansion of the moment of inertia and the Coriolis constants, ζ_{st}^{α}. These quantities may be expressed in terms of the transformation coefficients $\ell_{is}^{(\alpha)}$ which define the normal coordinates.[5] As seen from Eq. (18), the

coefficients can be written as derivatives,

$$m_i^{-1/2}\, \ell_{is}^{(\alpha)} = (\partial \alpha_i / \partial Q_s)_* \,, \tag{44a}$$

but proper account must be taken of the Eckart conditions (since there are 3N displacement coordinates $\delta\alpha_i$ and only 3N-6 normal coordinates Q_s). This gives rise to a number of useful relations involving the parameters $a_s^{\alpha\beta}$, $A_{ss}^{\alpha\beta}$, and ζ_{st}^{α}, which have been fully developed by Meal and Polo[29] and by Oka and Morino.[30] Particularly convenient is the general relation,[30]

$$[A_{ss}^{\alpha\beta} - \Sigma_\gamma a_s^{\alpha\gamma}\, a^{\beta\gamma}/I_\gamma] = 4\Sigma_t \zeta_{st}^{\alpha} \zeta_{st}^{\beta} - 3A_{ss}^{\alpha\beta} \,,$$

which enables us to rewrite Eq. (36) as

$$\epsilon_s^{\alpha\beta}(\mathrm{har}) = (-6K/\omega_s)[A_{ss}^{\alpha\beta} - \tfrac{4}{3}\Sigma_t \zeta_{st}^{\alpha} \zeta_{st}^{\beta} \lambda_t/(\lambda_t - \lambda_s)]. \tag{45}$$

The parameters $A_{ss}^{\alpha\beta}$ are unity or zero for several simple types of molecules (including the linear XY_2, XYZ, and X_2Y_2 molecules, out-of-plane axis of bent XY_2, and tetrahedral XY_4). Furthermore, the methods derived by Meal and Polo often circumvent much or all of the normal coordinate analysis in calculating the Coriolis constants.[29] Thus, as illustrated in Part II, there are several cases of interest in which $\epsilon_s^{\alpha\beta}(\mathrm{har})$ can be evaluated without a normal coordinate analysis.

We shall outline a convenient method of obtaining the $\ell_{is}^{(\alpha)}$ coefficients for more general cases.[31] This will be used to derive formulas for some examples (linear WXYZ, branched WXYZ, and symmetric XYZ_3 molecules) and to treat a model in which several of the vibrations are regarded as "frozen stiff."

Derivatives Subject to Eckart Conditions

The derivatives in (44a) are to be evaluated at the standard configuration and are referred to the principal axes system of (25). An arbitrary set of increments in the coordinates,

$$\delta \underset{\sim}{r}_i' = (\delta\alpha_i', \delta\beta_i', \delta\gamma_i'),$$

would not in general satisfy the Eckart conditions (16) and (17), since the distorted configuration (when viewed from the original molecule-fixed system) would have its center of mass displaced along the α-axis by an amount

$$\delta\tau_\alpha = \Sigma_i m_i \delta\alpha_i'/M \tag{46a}$$

and would be rotated through an angle

$$\delta\vartheta_\gamma = \Sigma_i m_i (\alpha_i^* \delta\beta_i' - \beta_i^* \delta\alpha_i')/I_\gamma^* \tag{46b}$$

about the γ-axis.[32] However, any such set of displacements can be converted into a set

$$\delta \underset{\sim}{r}_i = (\delta\alpha_i, \delta\beta_i, \delta\gamma_i)$$

which does satisfy the Eckart conditions by subtracting the appropriate rigid translations and rigid rotations of the whole molecule.[33] From Eqs. (46) we find

$$\delta\alpha_i = \delta\alpha_i' - \delta\tau_\alpha - (\gamma_i^* \delta\vartheta_\beta - \beta_i^* \delta\vartheta_\gamma) . \tag{47}$$

The freedom which this formulation allows in the choice of the primed displacements is an important advantage. Thus, a comparison with (18) now shows that the derivatives in (44a) are given by

$$\delta\alpha_{is} = (\partial\alpha_i/\partial Q_s)_* , \tag{44b}$$

where $\delta\alpha_{is}$ denotes the increment computed from (47) by choosing a set of primed displacements such that $Q_s = 1$ and all other normal coordinates ($t \neq s$) vanish. We shall refer to such a set of displacements $\delta\underset{\sim}{r}'_{is}$ as an "expansion of normal mode Q_s."

Before presenting a scheme for constructing the special set of increments, let us note that this leads to a very simple formulation of the vibration-rotation coefficients. Substitution of (44b) into Nielsen's definitions[5] gives

$$a_s^{\alpha\alpha} = 2\Sigma_i m_i(\beta_i^* \delta\beta_{is} + \gamma_i^* \delta\gamma_{is}) \tag{48a}$$

$$a_s^{\alpha\beta} = -\Sigma_i m_i(\alpha_i^* \delta\beta_{is} + \beta_i^* \delta\alpha_{is}) \tag{48b}$$

$$A_{ss}^{\alpha\alpha} = \Sigma_i m_i[(\delta\beta_{is})^2 + (\delta\gamma_{is})^2] \tag{48c}$$

$$A_{ss}^{\alpha\beta} = -\Sigma_i m_i \delta\alpha_{is}\delta\beta_{is} \tag{48d}$$

$$\zeta_{st}^{\alpha} = \Sigma_i m_i(\delta\beta_{is}\delta\gamma_{it} - \delta\gamma_{is}\delta\beta_{it}) \tag{49}$$

These expressions may also be obtained directly from Eq. (18) and (A11) of Appendix A. From Eq. (30) we find that the moment of inertia components corresponding to the expanded configuration specified by (44) are given by[34]

$$I_{\alpha\beta}(\underset{\sim}{r}_i^* + \delta\underset{\sim}{r}_{is}) = I_{\alpha\beta}(\underset{\sim}{r}_i^*) + a_s^{\alpha\beta} + A_{ss}^{\alpha\beta} ,$$

where $I_{\alpha\beta}(\underset{\sim}{r}_i^*) = I_\alpha^* \delta_{\alpha\beta}$, as given by (25). This may be confirmed by inspection of (48). Also we see that

$$A_{ss}^{\alpha\beta} = I_{\alpha\beta}(\delta\underset{\sim}{r}_{is}) \tag{50}$$

and therefore

$$a_s^{\alpha\beta} = I_{\alpha\beta}(\underset{\sim}{r}_i^* + \delta\underset{\sim}{r}_{is}) - I_{\alpha\beta}(\delta\underset{\sim}{r}_{is}) - I_{\alpha\beta}(\underset{\sim}{r}_i^*) \ . \qquad (51)$$

Although the Coriolis constants are not conviently expressed in terms of moments of inertia, there are already available several formulations well suited to numerical calculation.[29] The vector form,

$$\underset{\sim}{\zeta}_{st} = \Sigma_i m_i(\delta\underset{\sim}{r}_{is} \times \delta\underset{\sim}{r}_{it}) \ , \qquad (52)$$

is often useful in identifying which of the components of $\underset{\sim}{\zeta}_{st}$ will be near unity or zero. Also we note that the relation

$$\Sigma_i m_i \delta\underset{\sim}{r}_{is} \cdot \delta\underset{\sim}{r}_{it} = \delta_{st} \qquad (53)$$

implied by the orthogonality condition (19) is frequently useful.

Construction of Normal Mode Expansions

The expansion of a mode can be readily evaluated in terms of the customary internal coordinates S_k, which measure deviations of the bond lengths and angles from their values for the standard configuration. A normal coordinate analysis[18] provides the transformation equations,

$$S_k = \Sigma_t L_{kt} Q_t \ . \qquad (54)$$

The molecular configuration corresponding to $Q_s = 1$, with other $Q_t = 0$, is therefore given by

$$S_k = L_{ks}, \ k = 1, 2, \ldots, 3N-6 \ . \qquad (55)$$

By means of a method borrowed from statistical mechanics,[35,36] we may derive from (55) the 3N Cartesian displacements that comprise the expansion of the mode. This method, which will be described

with the aid of Fig. 3, generates the displacements atom-by-atom. In Fig. 3(a), we start with the atoms in the standard configuration, with coordinates $(\alpha_1^*, \beta_1^*, \gamma_1^*)$. Any atom may be chosen as the first one ($i = 1$) and the others numbered in succession. The internal coordinates are also specified; S_1 is taken as the 1-2 bond stretch, S_2 as the 2-3 bond stretch, S_3 as the 1-2-3 angle bend, etc. Since the six extra degrees of freedom that appear in the Cartesian transcription of (55) are later to be eliminated by use of Eq. (47), we can begin with atom 1 as a fixed origin and also fix the orientation of the 1-2 bond and 1-2-3 plane. Next, in Fig. 3(b), the displacement of atom 2 is obtained by shifting it (and all those "beyond") a distance L_{1s} along the 1-2 bond direction. For atom 3 the displacement is determined by two internal coordinates. Therefore, in Fig. 3(c), we first pull atom 3 and those beyond it outwards a distance L_{2s} parallel to the 2-3 bond (or, if L_{2s} is negative, we push them inwards), and then change the 1-2-3 bond angle by shifting atom 3 a distance $r_{23}^* L_{3s}$ perpendicular to the 2-3 bond. In the same way we find the displacements of atom 4 (given by L_{4s}, L_{5s}, L_{6s}) and the later atoms, which will each involve three internal coordinates.[37] The array of displacements thus obtained does not, of course, give a unique expansion of the mode (as a different order of numbering will lead to different results). After the translations and rotations are removed by use of Eq. (47), however, the description of the distorted configuration becomes unique; this final set of displacements $(\delta\alpha_{is}, \delta\beta_{is}, \delta\gamma_{is})$ might be called the "Eckart expansion of mode Q_s."

It should be emphasized that the customary[18] internal coordinates S_k adopted here are defined so that they transform linearly to Cartesian and to normal coordinates. Consequently, only for infinitesmal amplitudes of vibration does the stretching coordinate S_2, for example, measure the increment in the instantaneous distance between atoms 2 and 3. The S_2 coordinate actually represents the projection of the true instantaneous displacement of the atoms onto the original direction of the undisplaced 2-3 bond.[38] This is why bending displacements take the form illustrated in Fig. 3(c). To maintain the projection constant, we have to make the "bending" motion perpendicular to the bond; whereas, if instead the actual 2-3 distance had to be preserved, we would need to swing atom 3 along an arc of length $(r^*_{23} + L_{2s})L_{3s}$ about atom 2. Since the displacements L_{ks} are generally quite large, these two operations give appreciably different results and it is important to use the first procedure. In this we do not presume the linear relations of Eqs. (18) and (54) to be valid beyond small amplitude vibrations. Rather, in deriving relationships between the transformation coefficients, we use the linear relations merely as definitions of the coefficients, which must remain the same regardless of the size of the displacements.[39]

An analytic form for the expansion of a mode is readily obtained. The linearity of the transformations allows us to write

$$\delta \underset{\sim}{r}'_{is} = \Sigma_k \, \underset{\sim}{\rho}_{ik} L_{ks} \, , \tag{56}$$

where the $\underset{\sim}{\rho}_{ik}$ are displacement vectors, each chosen so that the increment in a particular coordinate S_k is unity while all other internal coordinates remain fixed at their values for the standard

configuration. Such vectors have already been introduced into vibrational analysis by Polo.[40] He points out that these vectors form a set reciprocal to Wilson's[18] well-known $\underset{\sim}{s}$-vectors,

$$\Sigma_i \underset{\sim}{s}_{ik} \cdot \underset{\sim}{\rho}_{i\ell} = \delta_{k\ell} ,$$

and the $\underset{\sim}{\rho}$-vectors are often simply proportional to the $\underset{\sim}{s}$-vectors. For all common types of internal coordinates Polo has listed formulas for the $\underset{\sim}{\rho}$-vectors, expressed in terms of unit vectors parallel and perpendicular to the bonds of the undistorted molecule. In practice (56) is quite convenient, since most normal coordinates contain significant contributions from only a few internal coordinates. A good approximation can usually be obtained by taking no more than three of the transformation coefficients L_{ks} as nonzero. Furthermore, most of the internal coordinates are defined in terms of bonds and angles involving just 2, 3, or 4 atoms.

For symmetrical molecules, the calculations are simplified by use of symmetry coordinates formed from linear combinations of the internal coordinates.[18,41] If the sets of $\underset{\sim}{\rho}_{ik}$ vectors are chosen to have the appropriate symmetry, vibrations of each symmetry species can be considered separately. Also, the Eckart corrections in Eq. (47) vanish unless the corresponding translation or rotation has the same symmetry as the vibrational mode.

To find the appropriate $\underset{\sim}{\rho}_{ik}$ vectors, we have to displace the symmetrically equivalent atoms simultaneously, rather than proceeding atom-by-atom, but this is usually simple to do (as illustrated below). Whenever a symmetry species contains only one vibration, the Eckart expansion of that mode will depend only on the atomic masses

and molecular geometry. In this case Eq. (54) reduces to[42]

$$\phi_k = \mathcal{L}_{ks} Q_s$$

and the transformation coefficient,

$$\mathcal{L}_{ks} = (\mathcal{D}_{kk})^{1/2}, \tag{57}$$

involves just a diagonal element of Wilson's $\mathcal{D}$-matrix. When there are two or more vibrations of the same symmetry, the transformation coefficients also involve the vibrational force constants and must be found by solving a secular equation.[18] Other points which arise in the calculation of normal mode expansions will be bought out in the course of deriving formulas for some examples.

EXAMPLES

Linear WXYZ Molecule

If we choose the z-axis along the molecular axis, then for any linear molecule the following quantities all vanish:

$$\delta x_{is},\ \delta y_{is};\ \delta\tau_{xs},\ \delta\tau_{ys};\ \delta\vartheta_{xs},\ \delta\vartheta_{ys},\ \delta\vartheta_{zs},$$

for the stretching vibrations and

$$\delta z_{is};\ \delta\tau_{zs};\ \delta\vartheta_{zs},$$

for the bending vibrations. Fig. 4 shows the numbering of atoms and coordinates. We may consider the stretches and bends separately since they are in different symmetry species. The stretching coordinates are defined by

$$\begin{aligned} S_1 &= \delta z_2 - \delta z_1 \\ S_3 &= \delta z_3 - \delta z_2 \\ S_5 &= \delta z_4 - \delta z_3 \end{aligned} \tag{58}$$

Therefore we find the expansion to be

$$\delta z'_{1s} = 0$$
$$\delta z'_{2s} = L_{1s}$$
$$\delta z'_{3s} = L_{1s} + L_{3s}$$
$$\delta z'_{4s} = L_{1s} + L_{3s} + L_{5s}$$

for any one of the three stretching normal modes. After accounting for the Eckart conditions by use of (47), we have

$$\delta z_{is} = [(m_1 - M\bar{o}_{i1})L_{is} - (m_3+m_4)L_{3s} - m_4 L_{5s}]/M \qquad (59a)$$

for i = 1,2 and

$$\delta z_{is} = [m_1 L_{1s} + (m_1+m_2)L_{3s} - (m_4 - M\bar{o}_{i4})L_{5s}]/M \qquad (59b)$$

for i = 3,4. These results are readily visualized; for example, when the 1-2 bond is stretched an amount L_{1s}, we find atom 1 moves to the left a distance

$$[1-(m_1/M)]L_{1s} = [(m_2+m_3+m_4)/M]L_{1s}$$

and the other three atoms shift to the right a distance

$$(m_1/M)L_{1s}.$$

The bending coordinates in the xz plane are defined by

$$S_{2x} = (\delta x_2 - \delta x_1)/r_{12} + (\delta x_2 - \delta x_3)/r_{23} \qquad (60a)$$

$$S_{4x} = (\delta x_3 - \delta x_2)/r_{23} + (\delta x_3 - \delta x_4)/r_{34} \qquad (60b)$$

and analogous expressions (with x replaced by y) hold for the yz plane. The simplest way to obtain an expansion of a bending mode is to set all displacements equal to zero except

$$\delta x'_{1s} = - r_{12}L_{2s}, \quad \delta x'_{4s} = - r_{34}L_{4s}. \qquad (61)$$

The Eckart expansion is then found to be

$$\delta x_{is} = \left(\frac{m_1 - M\delta_{i1}}{M} + \frac{m_1 z_1 z_i}{I}\right) r_{12} L_{2s}$$

$$+ \left(\frac{m_4 - M\delta_{i4}}{M} + \frac{m_4 z_4 z_i}{I}\right) r_{34} L_{4s} \,, \qquad (62a)$$

for $i = 1,2,3,4$. These formulas can be readily specialized to simpler cases or extended to an even longer string of atoms.

Usually there are many possible alternative choices for the primed displacements. The corresponding formulas for the Eckart expansions will sometimes look quite different, but the various alternatives will give identical numerical results. The bending mode of a linear XYZ molecule provides a convenient example of this. (In applying the forgoing results, we disregard the fourth atom and set $L_{4s} = L_{5s} = 0$.) From Eq. (60) we see that instead of the choice given in (61) we could set all displacements equal to zero except

$$\delta x'_{2s} = R L_{2s} \,,$$

where $R = r_{12} r_{23} / (r_{12} + r_{23})$. This leads to

$$\delta x_{is} = -\left(\frac{m_2 - M\delta_{i2}}{M} + \frac{m_2 z_2 z_i}{I}\right) R L_{2s}, \qquad (62b)$$

$i = 1,2,3$, instead of Eq. (62a). However, the center of mass condition, $\Sigma_i m_i z_i = 0$, together with the definitions $r_{ij} = z_j - z_i$, yields the relations

$$M z_3 = (m_1 r_{13} + m_2 r_{23}) \,,$$

$$I = -(m_1 z_1 r_{13} + m_2 z_2 r_{23})$$

(and others obtained by cyclic permutation of subscripts) and from these we see that Eq. (62b) is actually identical to (62a).

To illustrate the use of symmetry coordinates, we may consider a linear X_2Y_2 molecule such as acetylene. Table VI gives the definitions of the symmetry coordinates, as obtained by the usual methods.[18] The species which have nonvanishing Eckart corrections are found from the character table of the $D_{\infty h}$ group. According to Eq. (55), we need to find displacements such that[42] $\delta_k = \mathcal{L}_{ks}$. By inspection of Table VI and Eq. (58) we see that for the two Σ_g^+ modes the appropriate displacements are

$$-\delta z_{1s} = \delta z_{4s} = 2^{-1/2}\, \mathcal{L}_{1s} + \tfrac{1}{2}\, \mathcal{L}_{2s} \tag{63}$$

$$-\delta z_{2s} = \delta z_{3s} = \tfrac{1}{2}\, \mathcal{L}_{2s}$$

and no Eckart corrections enter for this symmetry species. For the Σ_u^+ mode,

$$\delta z'_{1s} = \delta z'_{4s} = -2^{-1/2}\, \mathcal{L}_{3s} \tag{64}$$

$$\delta z'_{2s} = \delta z'_{3s} = 0\ ,$$

and after subtracting the translational correction of Eq. (47) we find the Eckart expansion is

$$\delta z_{1s} = \delta z_{4s} = 2^{1/2}(m_2/M)\, \mathcal{L}_{3s} \tag{65}$$

$$\delta z_{2s} = \delta z_{3s} = -2^{1/2}(m_1/M)\, \mathcal{L}_{3s}\ .$$

From Eq. (60) we obtain results of the same form as (64) but with z replaced by x, for the x-component of the Π_u mode; the results for

the Π_g mode also have this form except that the sign of $\delta x'_{4s}$ is reversed. Thus we find the following Eckart expansions for the bending vibrations:

$$\begin{aligned} -\delta x_{1s} &= \delta x_{4s} = 2^{1/2}(m_1 z_2^2/I)r\ \mathcal{L}_{4s} \\ \delta x_{2s} &= -\delta x_{3s} = 2^{1/2}(m_1 z_1 z_2/I)r\ \mathcal{L}_{4s} \end{aligned} \tag{66}$$

for the Π_g species and

$$\begin{aligned} \delta x_{1s} &= \delta x_{4s} = -2^{1/2}(m_2/M)r\ \mathcal{L}_{5s} \\ \delta x_{2s} &= \delta x_{3s} = 2^{1/2}(m_1/M)r\ \mathcal{L}_{5s} \end{aligned} \tag{67}$$

for the Π_u species. Only the Σ_g^+ modes require the solution of a secular equation; for the others the $\mathcal{L}_{ks}$ coefficients can be evaluated from Eq. (57) and the $\mathcal{D}$-matrix elements in Table VI.

Branched WXYZ Molecule

When expressed in the vector notation of Eq. (56), the procedure indicated in Fig. 3 yields

$$\begin{aligned} \delta \underset{\sim}{r}'_{1s} &= 0 \\ \delta \underset{\sim}{r}'_{2s} &= \underset{\sim}{e}_{12} L_{15} \\ \delta \underset{\sim}{r}'_{3s} &= \delta \underset{\sim}{r}'_{2s} + \underset{\sim}{e}_{23} L_{2s} + (\underset{\sim}{e}_{\phi} \times \underset{\sim}{e}_{23}) r_{23} L_{3s}\ , \end{aligned} \tag{68}$$

where

$$\underset{\sim}{e}_{\phi} = (\underset{\sim}{e}_{21} \times \underset{\sim}{e}_{23}) \csc \phi_{123} \tag{69}$$

is a unit vector normal to the plane of the 1-2-3 angle. Addition of a fourth atom introduces the three new internal coordinates shown in Fig. 5(a). If the standard configuration of the molecule is planar,

we find

$$\delta \underset{\sim}{r}'_{4s} = \delta \underset{\sim}{r}'_{2s} + \underset{\sim}{e}_{24} L_{4s} + (\underset{\sim}{e}_{\phi} \times \underset{\sim}{e}_{24}) r_{24} L_{5s} + \underset{\sim}{e}_{\phi} r_{24} L_{6s}. \quad (70)$$

This follows from Eq. (56) and the three $\underset{\sim}{\rho}_{4k}$ vectors pictured in Fig. 5(b). The $\underset{\sim}{\rho}$ vectors for the 2-4 bond stretch and 1-2-4 angle bend are analogous to those in (68); that for the out-of-plane bend is perpendicular to the plane and of length r_{24}. If the molecule is nonplanar, the last two terms in (70) are replaced by[43]

$$\underset{\sim}{e}_{\phi'} \csc \psi_{143} r_{24} L_{5s} + (\underset{\sim}{e}_{24} \times \underset{\sim}{e}_{\vartheta}) r_{24} L_{6s}. \quad (71)$$

Here ψ_{143} is the dihedral angle between the 1-2-4 and 3-2-4 planes; $\underset{\sim}{e}_{\phi'}$ is given by (69) with the subscript 1 replaced by 4; and $\underset{\sim}{e}_{\vartheta}$ is a unit vector parallel to the 1-2-3 plane and perpendicular to the 2-4 bond. The $\underset{\sim}{\rho}_{4k}$ vectors are shown in Fig. 5(c). Note that the $\underset{\sim}{\rho}$-vector for the 1-2-4 angle bend no longer lies in the plane of the angle but now is normal to the plane of the adjacent 3-2-4 angle; its length is also increased by the factor $\csc \psi_{143}$.

Except when treating the simplest molecules, we have found it expedient to first evaluate the primed displacements numerically and then use Eq. (55), rather than derive analytic formulas for the Eckart expansions. For any planar molecule (with the out-of-plane axis taken as the z-direction), the C_s group character table shows that the following quantities vanish:

$$\delta z_{is};\ \delta \tau_{zs};\ \delta \vartheta_{xs},\ \delta \vartheta_{ys},$$

for the in-plane vibrations and

$$\delta x_{is},\ \delta y_{is};\ \delta \tau_{xs},\ \delta \tau_{yx};\ \delta \vartheta_{zs},$$

for the out-of-plane vibrations. As a planar molecule of four atoms has only one out-of-plane mode (s = 6), in this case it is preferable to work with the Eckart expansion, which is given by

$$\delta z_{i6} = \left[\left(\delta_{i4} - \frac{m_4}{M}\right) - \left(\frac{m_4 x_i x_4}{I_y} + \frac{m_4 y_i y_4}{I_x}\right)\right] r_{24} L_{66}, \qquad (72)$$

for i = 1,2,3,4.

In applying Eq. (56) to symmetrical molecules, we may take advantage of the fact that the symmetry coordinates are defined by an orthogonal transformation of the internal coordinates, $\underset{\sim}{\mathcal{S}} = \underset{\sim\sim}{U}\underset{\sim}{S}$. In most cases it is easy to choose the $\underset{\sim}{\rho}$-vectors for the internal coordinates so that under the group operations they transform in the same way as the internal coordinates. Then by simply forming the linear combinations dictated by the transformation $\underset{\sim}{U}$, we can construct the appropriate $\underset{\sim}{\rho}_{ik}$ vectors for each symmetry coordinate.

A planar WXY_2 molecule such as formaldehyde offers a simple example for this method. The symmetry coordinates are given in Table VII. The coordinate S_5' is the increment in the 3-2-4 angle; to bring out the symmetry it is used in preference to the coordinate S_3 shown in Fig. 5(a). The connection with the previous description is obtained from the redundancy relation,

$$S_3 + S_5 + S_5' = 0 \qquad (73)$$

By definition, the $\underset{\sim}{\rho}_{ik}$ vectors for a symmetry coordinate, for example,

$$\mathcal{S}_4 = 2^{-1/2}(S_1 - S_2),$$

must make $\mathcal{S}_4 = 1$ while the other symmetry coordinates remain zero. If we find the $\underset{\sim}{\rho}$-vectors for S_1 and $-S_2$ in the way already illustrated, the sum of these will give

$$\mathcal{S}_4 = 2^{-1/2}(1 + 1) = 2^{1/2}.$$

Hence, to get the desired result we merely have to renormalize the sum by dividing through by $2^{1/2}$. The orthogonality of the transformation guarantees that this procedure will alter only $\mathcal{S}_4$. The complete expansion generated from Table VII in this way is

$$\begin{aligned} \delta\underset{\sim}{r}'_{2s} &= 0 \\ \delta\underset{\sim}{r}'_{4s} &= \underset{\sim}{e}_{24}\mathcal{L}_{3s} + \underset{\sim}{e}_{\phi}\mathcal{L}_{6s} \\ \delta\underset{\sim}{r}'_{is} &= 2^{-1/2}\underset{\sim}{e}_{2i}(\mathcal{L}_{1s} \pm \mathcal{L}_{4s}) + 2^{-1/2}(\underset{\sim}{e}_{\phi} \times \underset{\sim}{e}_{2i})r(\mathcal{L}_{2s} \pm \mathcal{L}_{5s}), \end{aligned} \tag{74}$$

for $i = 1$ (upper sign) and $i = 3$ (lower sign).

This molecule is simple enough to make explicit formulation of the Eckart expansion worthwhile. The results can be tidily written by defining the quantities

$$X_{k\ell} = \sin\alpha\ \mathcal{L}_{ks} - r\cos\alpha\ \mathcal{L}_{\ell s}$$

$$Y_{k\ell} = \cos\alpha\ \mathcal{L}_{ks} + r\sin\alpha\ \mathcal{L}_{\ell s}$$

where α is one-half of the 1-2-3 angle. The components of the displacements parallel to the symmetry axis are, for the A_1 species:

$$\delta y_{is} = 2^{1/2}(m_1/M)Y_{12} + \left[\delta_{i4} - (m_4/M)\right]\mathcal{L}_{3s}\ , \tag{75a}$$

$i = 2,4$ and

$$\delta y_{is} = \delta y_{3s} = -2^{-1/2}\left[(m_2+m_4)/M\right]Y_{12} - (m_4/M)\mathcal{L}_{3s};$$

for the B_1 species:

$$\delta y_{2s} = \delta y_{4s} = 0 \tag{75b}$$

$$\delta y_{1s} = -\delta y_{3s} = -2^{-1/2}\left[\left(1 - \frac{2m_1x_1^2}{I_z}\right) Y_{45} + \frac{2m_1x_1y_1}{I_z} X_{45}\right]$$

The perpendicular components are, for the A_1 species:

$$\delta x_{2s} = \delta x_{4s} = 0$$

$$\delta x_{1s} = -\delta x_{3s} = -2^{-1/2}X_{12}\,, \tag{75c}$$

and for the B_1 species:

$$\delta x_{is} = 2^{1/2}\left[\left(\frac{m_1}{M} + \frac{m_1y_1y_i}{I_z}\right) X_{45} - \frac{m_1x_1y_i}{I_z} Y_{45}\right], \tag{75d}$$

$i = 2,4$ and

$$\delta x_{1s} = \delta x_{3s} = -2^{-1/2}\left[\left(\frac{m_2+m_4}{M} - \frac{2m_1y_1^2}{I_z}\right)X_{45} + \frac{2m_1x_1y_1}{I_z} Y_{45}\right]$$

Only the B_2 species has out-of-plane components and the formulas for these are included in Eq. (72).

To obtain the results for a bent XY_2 molecule from the forgoing, we discard terms involving $\mathcal{L}_{3s}$, $\mathcal{L}_{5s}$, $\mathcal{L}_{6s}$, and m_4. In addition, however, we must readjust the normalization of $\mathcal{L}_{2s}$. On substituting Eq. (73) into Table VII we see that

$$\mathcal{S}_2 = -2^{-1/2}S_3$$

and since $\mathcal{S}_2' = S_3$ is the proper symmetry coordinate for a bent XY_2 molecule, we need to replace $\mathcal{L}_{2s}$ by

$$\mathcal{L}_{2s}' = -2^{1/2}\mathcal{L}_{2s}.$$

Symmetric WXY_3 Molecule

Typical molecules of this type are the methyl halides, CH_3X. The H atoms are numbered 1,2,3; the C atom 4; the X atom 5. Bonds and angles are denoted by R for CX, r_i for CH_i, α_i for $HjCH_k$, and β_i for XCH_i. The general, nontetrahedral model will be considered.[44] The symmetry coordinates for the A_1 species are[45]

$$\mathcal{S}_1 = \Delta R$$

$$\mathcal{S}_2 = 3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$\mathcal{S}_3 = 6^{-1/2} f[\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3 - \gamma(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)]$$

$$= (2/3)^{1/2} f(\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3) ,$$

where the second form for $\mathcal{S}_3$ is obtained by use of the redundancy condition. The parameters f and γ, which are equal to unity for the tetrahedral case, are defined by

$$f = 2^{1/2}(1 + \gamma^2)^{-1/2}$$

and

$$\gamma = -3^{1/2} \cos\beta \sec\tfrac{1}{2}\alpha .$$

The coordinates for the degenerate E species consist of pairs, equivalent except for orientation.

$$\mathcal{S}_{4x} = 6^{-1/2}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$$

and

$$\mathcal{S}_{4y} = 2^{-1/2}(\Delta r_2 - \Delta r_3),$$

and the two remaining pairs of coordinates, $\mathcal{S}_5$ and $\mathcal{S}_6$, are defined by replacing Δr_i by $\Delta\alpha_i$ and $\Delta\beta_i$, respectively.

The form of the $\underset{\sim}{\rho}$-vectors for the internal coordinates has been illustrated in the previous examples. However, here we must take some care to start with a set which transforms under the group operations in the same way as the internal coordinates. As in Figs. 3(c) and 5(b) and Eq. (68), to increase Δr_i and $\Delta\beta_i$ by unity we shift atom H_i by

$$\underset{\sim}{\rho}_{ir} = \underset{\sim}{e}_{4i} \tag{76}$$

$$\underset{\sim}{\rho}_{i\beta} = [(\underset{\sim}{e}_{45} \times \underset{\sim}{e}_{4i}) \times \underset{\sim}{e}_{4i}]\, r \csc \beta. \tag{77}$$

These vectors obviously transform properly already, since they lie in the XCH_i symmetry planes. On the other hand, for $\Delta\alpha_i$ the $\underset{\sim}{\rho}$-vector used in Fig. 5(c) and Eq. (71) would move either H_j or H_k in an unsymmetrical fashion. Therefore, to increase $\Delta\alpha_i$ by unity, we shift both atoms by half the usual distance and thus maintain symmetry with respect to the XCH_i plane.

$$\underset{\sim}{\rho}_j(\Delta\alpha_i) = \tfrac{1}{2}(\underset{\sim}{e}_{4i} \times \underset{\sim}{e}_{4j})\, r \csc \psi \csc \alpha \tag{78a}$$

$$\underset{\sim}{\rho}_k(\Delta\alpha_i) = \tfrac{1}{2}(\underset{\sim}{e}_{4k} \times \underset{\sim}{e}_{4i})\, r \csc \psi \csc \alpha \tag{78b}$$

where i, j, k = 1, 2, 3 in cyclic order and ψ is the dihedral angle between successive H_iCX and H_jCX planes.

The $\underset{\sim}{\rho}$-vectors for the symmetry coordinates may now be constructed by the method illustrated with formaldehyde. For example, as the vector for $\mathcal{S}_{6x}$ we take

$$N_x(2\underset{\sim}{\rho}_{1\beta} - \underset{\sim}{\rho}_{2\beta} - \underset{\sim}{\rho}_{3\beta}).$$

This combination of displacements gives

$$\mathcal{S}_{6x} = N_x 6^{-1/2}(2 + 1 + 1)$$

(since the $\rho_{i\beta}$ are defined so that $\Delta\beta_i = 1$) and therefore the normalization constant is assigned the value

$$N_x = \tfrac{1}{2}(3/2)^{1/2} .$$

For the $\mathcal{S}_3$ coordinate, the use of Eqs. (78) leads to

$$N_3 \Sigma_i [\rho_i(\Delta\alpha_j) + \rho_i(\Delta\alpha_k)] ,$$

where $i = 1,2,3$ and $N_3 = 6^{-1/2}/f$. Thus in this case the displacement of each H atom must be obtained by addition of two vectors; it is readily shown that the resultant lies in the XCH_i plane and is given by

$$\rho_i(\Delta\alpha_j) + \rho_i(\Delta\alpha_k) = -\rho_{i\beta}/\gamma , \tag{79}$$

in conformity with the redundancy relation.

The expansion obtained for the A_1 modes is

$$\begin{aligned} \delta\underset{\sim}{r}'_{5s} &= \underset{\sim}{e}_{45}\mathcal{L}_{1s}; \quad \delta\underset{\sim}{r}'_{4s} = 0, \\ \delta\underset{\sim}{r}'_{is} &= \underset{\sim}{e}_{4i} N_2 \mathcal{L}_{2s} + \rho_{i\beta} N'_3 \mathcal{L}_{3s} , \end{aligned} \tag{80a}$$

$(i = 1,2,3)$ where $N_2 = 3^{-1/2}$ and $N'_3 = -6^{-1/2}/\gamma f$.

For the E_x components of the degenerate modes,

$$\begin{aligned} \delta\underset{\sim}{r}'_{1s} &= N_x\left[2\underset{\sim}{e}_{41}\mathcal{L}_{4s} + \rho_{1\beta}(\mathcal{L}_{5s}/\gamma + 2\mathcal{L}_{6s})\right] \\ \delta\underset{\sim}{r}'_{is} &= N_x\left[-\underset{\sim}{e}_{4i}\mathcal{L}_{4s} + \rho_{i\beta}(\mathcal{L}_{5s}/\gamma - \mathcal{L}_{6s}) + 3\rho_{i\alpha}\mathcal{L}_{5s}\right] \end{aligned} \tag{80b}$$

and $i = 2,3$. For the E_y components,

$$\delta\underset{\sim}{r}'_{1s} = N_y\left[\underset{\sim}{\rho}_1(\Delta\alpha_2) - \underset{\sim}{\rho}_1(\Delta\alpha_3)\right]\underset{\sim}{\ell}_{5s}$$

$$\delta\underset{\sim}{r}'_{is} = \mp N_y\left[\underset{\sim}{e}_{4i}\ell_{4s} + \underset{\sim}{\rho}_{i\beta}(\ell_{5s}/\gamma + \ell_{6s})\right] + \underset{\sim}{\rho}_{i\alpha}\ell_{5s}\ , \tag{80c}$$

with i = 2 (plus sign), i = 3 (minus sign), and $N_y = 2^{-1/2}$; $\underset{\sim}{\rho}_{i\alpha}$ denotes $\underset{\sim}{\rho}_i(\Delta\alpha_1)$, and the relation (79) has been used to simplify some terms. Atoms 4 and 5 have zero displacements.

Cartesian expressions for the $\underset{\sim}{e}_{4i}$ and $\underset{\sim}{\rho}_{i\beta}$ vectors are obtained easily, but those for the $\underset{\sim}{\rho}_i(\Delta\alpha_j)$ vectors are rather awkward. It is only necessary, however, to evaluate the components of $\underset{\sim}{\rho} = \underset{\sim}{\rho}_2(\Delta\alpha_1)$, which are

$$\begin{aligned}
\rho_x &= -\tfrac{1}{2}\, r \csc\psi \sin\psi' \cos\beta \\
\rho_y &= -\tfrac{1}{2}\, r \csc\psi \cos\psi \\
\rho_z &= \tfrac{1}{2}\, r \csc\psi \sin\psi' \sin\beta,
\end{aligned} \tag{81}$$

where ψ' is the dihedral angle between a XCH_1 plane and the adjacent H_iCH_j plane. The z-axis points along the 4-5 bond and the x-axis lies in the XCH_1 plane. By reversing the sign of the y-component in (81) $\underset{\sim}{\rho}_3(\Delta\alpha_1)$ is obtained and the relation

$$\underset{\sim}{\rho}_i(\Delta\alpha_j) = \underset{\sim}{\rho}_j(\Delta\alpha_1)$$

then provides the other coordinates that enter Eqs. (80). In terms of interbond angles, the dihedral angles are given by

$$\cos\psi = (\cos\alpha \mp \cos^2\beta)/\sin^2\beta$$

$$\cos\psi' = \cos\beta(1 - \cos\alpha)/(\sin\alpha \sin\beta).$$

The Eckart correction for the A_1 modes involves just translation along the symmetry axis,

$$\delta\tau_z = m_5 \mathcal{L}_{1s} - 3m_1(\cos\beta\, N_2 \mathcal{L}_{2s} + r \sin\beta\, N_3' \mathcal{L}_{3s}).$$

For the degenerate modes, the nonzero corrections are $\delta\tau_x$, $\delta\vartheta_y$ for E_x and $\delta\tau_y$, $\delta\vartheta_x$ for E_y.

The expressions given above may also be applied to symmetric pyrimidal XY_3 molecules. Terms arising from $\mathcal{S}_1$, $\mathcal{S}_6$, and m_4 are discarded; $\mathcal{S}_3$ is renormalized and accordingly $N_3 = \sqrt{3}N_3' = 3^{-1/2}$. It is convenient to retain the angles β_i, which are now defined with reference to the symmetry axis.

"Partly Frozen" Model; Group Vibrations

The one or two normal modes of lowest frequency are often found to contribute the dominant terms to vibration-rotation interactions. Examples which have been well characterized experimentally include the torsional oscillations of methyl groups,[46] the "warping" vibrations of planar rings,[47] and (as shown in Part III) a large class of inertial defects. Molecular models in which various parts are regarded as rigid have given good results for such cases. The form of Eqs. (47) and (56) makes it easy to derive a "partly frozen" approximation for any type of molecule. To freeze an atom, its displacement $\delta\mathbf{r}_{is}'$ is merely set equal to zero. In contrast to previous examples in which parts of a molecule were discarded, here the masses of the frozen atoms still enter, by way of the M and I_α elements in the Eckart corrections. When all the atoms involved in an internal coordinate are frozen, the coefficients for that coordinate vanish

(for all s). Moreover, the values of the $\mathcal{L}_{ks}$ for other coordinates are in general altered somewhat. These coefficients are most conveniently determined from a reduced vibrational secular equation involving the $\underset{\sim}{G}^{-1}$ elements for the unfrozen coordinates.[48] Fortunately, however, a matrix inversion can be avoided since Polo has derived the relation[40]

$$(G^{-1})_{kk} = \Sigma_i m_i (\underset{\sim}{\rho}_{ik})^2 . \qquad (82)$$

Here the Eckart corrections are to be included in the $\underset{\sim}{\rho}_{ik}$ and the sum must be extended over all the atoms (including the frozen ones).

The simplest example to consider has a single atom m_1 vibrating against the center of mass of a group. This is a useful approximation for the C-I stretch in CH_3I. Eq. (47) requires that

$$\delta\underset{\sim}{r}_{1s} = \underset{\sim}{e}_{1g} L$$

$$\delta\underset{\sim}{r}_{is} = -(m_1/m_g)\delta\underset{\sim}{r}_{1s}$$

where $i = 2,\ldots,N$, $m_g = \Sigma_i m_i$ is the mass of the group, and

$$L = [m_1 m_g/(m_1+m_g)]^{-1/2}.$$

Although L has the same form as for a diatomic molecule, the contributions to the vibration-rotation parameters also involve (via the $\underset{\sim}{e}_{1g}$ factor) the direction cosines between the principal axes and the line joining m_1 to the center of mass.

As another example, consider the symmetric bend ω_2 for planar WXY_2 or bent XY_2 molecules. This mode often accounts for most of the inertial defect, as shown in Part III. If the stretching vibrations of an XY_2 molecule are frozen, the secular equation reduces to

$$F_{22} - \lambda(G^{-1})_{22} = 0,$$

where F_{22} is the bending force constant and[40]

$$(G^{-1})_{22} = \tfrac{1}{2} m_Y r^2[1 - 2(m_Y/M) \sin^2\alpha] .$$

Eqs. (75a) and (75c) yield the same result for a WXY_2 molecule, except that the factor of $\frac{1}{2}$ is replaced by unity because of the change in normalization of $\mathcal{S}_2$. The corresponding values of

$$\mathcal{L}_{22} = (G^{-1})_{22}^{-1/2}$$

are used in Eqs. (75), with the other $\mathcal{L}_{ks} = 0$, in order to calculate the vibration-rotation constants for this model.

Vibrational frequencies characteristic of a particular functional group appear in many molecules. From Eq. (45) it is seen that the contributions of these group frequencies to ϵ(harmonic) can be considered separately, provided that the Coriolis constants ζ_{st} connecting the group and framework vibrations are sufficiently small. Even when this does not hold, the calculations can often be simplified by use of the treatment of group frequencies recently presented by King and Crawford.[49]

APPENDIX A

VIBRATION-ROTATION HAMILTONIAN

Previous treatments[5] have all been based on Eckart's expression for the classical kinetic energy,

$$2T = \underset{\sim}{\omega}^{\dagger}\underset{\sim}{A}\underset{\sim}{\omega} + 2\underset{\sim}{\omega}^{\dagger}\underset{\sim}{B}\dot{\underset{\sim}{Q}} + \dot{\underset{\sim}{Q}}^{\dagger}\underset{\sim}{C}\dot{\underset{\sim}{Q}} \tag{A1}$$

and the Hamiltonian derived from this by Wilson and Howard,[4]

$$2H = (\underset{\sim}{m}-\underset{\sim}{m})^{\dagger}\mu(\underset{\sim}{m}-\underset{\sim}{m}) + \underset{\sim}{P}^{\dagger}\underset{\sim}{P} + 2V \tag{A2}$$

where

$$\begin{aligned} \underset{\sim}{m} &= \underset{\sim}{B}\underset{\sim}{C}^{-1}\underset{\sim}{P} \\ \mu &= (\underset{\sim}{A}-\underset{\sim}{B}\underset{\sim}{C}^{-1}\underset{\sim}{B}^{\dagger})^{-1}. \end{aligned} \tag{A3}$$

Here the matrix $\underset{\sim}{A}$ is $\underset{\sim}{I}$, the moment of inertia tensor, and for the usual choice of normal coordinates $\underset{\sim}{C}$ is just $\underset{\sim}{E}$, the unit matrix. The matrix $\underset{\sim}{B}$ involves the Coriolis coupling coefficients and is a linear function of the normal coordinates. The fact that the matrix μ is not merely the inverse of the moment of inertia tensor has complicated the formulation and interpretation of vibration-rotation perturbations. This difficulty can be avoided by expressing the Hamiltonian in another form,

$$2H = \underset{\sim}{m}^{\dagger}\underset{\sim}{A}^{-1}\underset{\sim}{m} + (\underset{\sim}{P}-\underset{\sim}{\varrho})^{\dagger}\underset{\sim}{R}^{-1}(\underset{\sim}{P}-\underset{\sim}{\varrho}) + 2V \tag{A5}$$

where

$$\underset{\sim}{\varrho} = \underset{\sim}{B}^{\dagger}\underset{\sim}{A}^{-1}\underset{\sim}{m} \tag{A6}$$

$$\underset{\sim}{R} = \underset{\sim}{C}-\underset{\sim}{B}^{\dagger}\underset{\sim}{A}^{-1}\underset{\sim}{B}\ . \tag{A7}$$

The derivation proceeds from (A1) and the definitions

$$\mathcal{m}_\alpha = \partial T/\partial\omega_\alpha \text{ and } P_s = \partial T/\partial\dot{Q}_s ,$$

which yield

$$\underset{\sim}{\mathcal{m}} = \underset{\sim\sim}{A}\omega + \underset{\sim\sim}{B}\dot{Q} \tag{A8a}$$

$$\underset{\sim}{P} = \underset{\sim}{B}^{\dagger}\omega + \underset{\sim\sim}{C}\dot{Q} . \tag{A8b}$$

Thus the total angular momentum $\underset{\sim}{\mathcal{m}}$ of the vibrating rotor contains a contribution from the internal motion; likewise, the vibrational momentum $\underset{\sim}{P}$ includes contributions dependent on the velocity of overall rotation. For a rigid rotor the quantity

$$\underset{\sim}{\mathcal{m}}^{\dagger}\underset{\sim}{I}^{-1}\underset{\sim}{\mathcal{m}}$$

would be equal to twice the kinetic energy ($\dot{Q} = 0$); for the vibrating rotor we find

$$2T - \underset{\sim}{\mathcal{m}}^{\dagger}\underset{\sim}{I}^{-1}\underset{\sim}{\mathcal{m}} = \dot{\underset{\sim}{Q}}^{\dagger}[\underset{\sim}{C}-\underset{\sim}{B}^{\dagger}\underset{\sim}{I}^{-1}\underset{\sim}{B}]\dot{\underset{\sim}{Q}} . \tag{A9}$$

The matrix $\underset{\sim}{R}$, defined by the terms within square brackets, may be regarded as a reduced mass matrix associated with the vibrations. This suggests that we write

$$\underset{\sim}{P} = \underset{\sim\sim}{R}\dot{Q} + \underset{\sim}{\mathcal{P}} \tag{A10}$$

in which $\underset{\sim}{\mathcal{P}}$ represents the part of the total vibrational momentum that arises from the rotation (via Coriolis interaction). A comparison of (A8) with (A10) shows that $\underset{\sim}{\mathcal{P}}$ must be defined as in (A6). Substitution of (A10) into (A9) then yields the desired form of (A5).

As shown by Eckart,[2] the elements of the matrices $\underset{\sim}{A}$ (3x3), $\underset{\sim}{B}$ (3x3N-6) and $\underset{\sim}{C}$ (3N-6x3N-6) are defined by

$$A_{\alpha\beta} = \Sigma_i m_i [r_i^2 \delta_{\alpha\beta} - \alpha_i \beta_i]_*$$

$$B_{\alpha s} = \Sigma_i m_i [\alpha_i (\partial \beta_i / \partial Q_s) - \beta_i (\partial \alpha_i / \partial Q_s)]_* \qquad \text{(A11)}$$

$$C_{st} = \Sigma_{\alpha\, i} m_i (\partial \alpha_i \partial Q_s)_* (\partial \alpha_i / \partial Q_t)_*$$

It may be remarked that these expressions and the Hamiltonian forms (A2) or (A5) are quite general, and still hold (i) when the normal coordinates are replaced by any set of internal coordinates; (ii) when a configuration other than the equilibrium one is chosen as the standard; and (iii) whether or not Eckart's second condition, Eq. (17), is applied. If internal coordinates are used the $\underset{\sim}{C}$ matrix becomes Wilson's $\underset{\sim}{G}^{-1}$ matrix.[18] When the second Eckart condition is imposed, the $\underset{\sim}{B}$ matrix becomes a linear function of the normal coordinates. Accordingly $\underset{\sim}{R}$ and $\underset{\sim}{\varrho}$ as well as $\underset{\sim}{I}$ are quadratically dependent on the normal coordinates. However, for a treatment in which only the vibration-rotation interactions correct to terms linear in $(v_s + \frac{1}{2})$ are required, it is sufficient to use just the leading terms

$$\underset{\sim}{R} = \underset{\sim}{E} + \ldots \qquad \text{(A12)}$$

$$\underset{\sim}{\varrho} = \underset{\sim\alpha}{\Sigma} \underset{\sim}{\zeta}^{\alpha} \underset{\sim}{Q} \underset{\sim}{m}_{\alpha} / \underset{\sim\alpha}{I} + \ldots \qquad \text{(A13)}$$

This is the case dealt with in the text and in Appendix B.

To obtain the corresponding quantum mechanical Hamiltonian, it is necessary to evaluate the proper Laplacian operator. This is awkward since the coefficients of the momenta are not constants and the rotational momenta used are not conjugate to any coordinates. It has been verified that the procedures used by Wilson and Howard,[4,18]

can be applied to (A5) with $\underset{\sim}{m}$ and $\underset{\sim}{P}-\underset{\sim}{Q}$ taken as the quantum mechanical operators. [The result has a form analogous to Eq. (10), p. 280, of reference 18, with the determinant of $\underset{\sim}{I}^{-1}$ replacing that of $\underset{\sim}{\mu}$.] However, in the perturbation treatment what is actually used is an expansion of the Hamiltonian up to terms quadratic in Q and P. It is found that to this order the correct results are obtained by merely symmetrizing products such as $P_s Q_s$ in the classical Hamiltonian.

APPENDIX B

TREATMENT OF CORIOLIS TERMS

The perturbation treatment of the Hamiltonian given in (A5) conveniently separates into two parts. In the text the contributions from the leading term have been evaluated by simply calculating the vibrational average of the inverse moment of inertia. Here we shall derive the additional contributions that arise from the second term and involve the Coriolis constants. In the approximation represented by Eq. (29) of the text, only those terms proportional to both $\underset{\sim}{m}^{\dagger}\underset{\sim}{m}$ and to $(v_s + \frac{1}{2})$ will contribute to the effective moment of inertia. Contributions of this form are contained in the term

$$\underset{\sim}{\rho}^{\dagger}\underset{\sim}{\rho} \tag{B1}$$

and in the cross term

$$-(\underset{\sim}{\rho}^{\dagger}\underset{\sim}{P} + \underset{\sim}{P}^{\dagger}\underset{\sim}{\rho}). \tag{B2}$$

According to (A13), the term (B1) can be averaged directly to give

$$\langle Q_s^2\rangle \zeta_{st}^{\alpha}\zeta_{st}^{\beta} m_{\alpha} m_{\beta}/I_{\alpha}I_{\beta} \tag{B3}$$

where s, t, α, and β are all summed over. (For convenience the summation variables have been reshuffled to put s first.) The cross term (B2) must be evaluated as a second order perturbation since it has only nondiagonal vibrational matrix elements,

$$\langle v_s v_t | v_s+1, v_t+1\rangle = Z(-iK)(\omega_s-\omega_t)[(v_s+1)(v_t+1)/\omega_s\omega_t]^{1/2} \tag{B4a}$$

$$\langle v_s v_t | v_s+1, v_t-1\rangle = Z(-iK)(\omega_s+\omega_t)[(v_s+1)v_t/\omega_s\omega_t]^{1/2} \tag{B4b}$$

with

$$Z = \Sigma_\alpha \zeta^\alpha_{st}\ \alpha/I_\alpha.$$

The two terms in (B2), one with $\zeta_{st}P_sQ_t$ and the other with $\zeta_{ts}P_tQ_s$, have been combined using the relation $\zeta_{ts} = -\zeta_{st}$. The second order perturbation sum reduces to the same form as (B3) with one more factor

$$(3\lambda_s + \lambda_t)/(\lambda_s - \lambda_t)\ . \qquad \text{(B5)}$$

The total Coriolis contribution to the effective rotational Hamiltonian of Eq. (27) thus contains the factor

$$1 + (3\lambda_s + \lambda_t)/(\lambda_s - \lambda_t) = 4\lambda_s/(\lambda_s - \lambda_t)$$

and in the coefficients of Eq. (36) appears as

$$\epsilon^{\alpha\beta}_s(\text{Coriolis}) = -(8K/\omega_s)\Sigma_t \zeta^\alpha_{st}\zeta^\beta_{st}\lambda_s/(\lambda_s - \lambda_t). \qquad \text{(B6)}$$

In the effective moments of inertia for the ground state ($v_s=v_t=\ldots=0$) pairs of terms ϵ_s and ϵ_t may be added together to give

$$\frac{K}{\omega_s}\frac{\lambda_s}{\lambda_s-\lambda_t} + \frac{K}{\omega_t}\frac{\lambda_t}{\lambda_t-\lambda_s} = \frac{K}{\omega_s+\omega_t}\ . \qquad \text{(B7)}$$

This shows that "resonant" Coriolis perturbations will not appear in the ground vibrational state.

It should be mentioned that other Coriolis effects[5,29] are present for degenerate vibrations. These show up in separate terms involving the angular momentum of the degenerate vibrations, and therefore are not regarded as part of the effective moment of inertia. Thus in the forgoing the constants ζ_{st} which connect different components of a degenerate vibration are ignored. There are, however, useful relations between (B6) and the coefficients associated with the degenerate Coriolis perturbations.[25,30]

APPENDIX C

ANHARMONIC VIBRATIONAL AVERAGES

In our treatment the linear and cubic terms in the potential function of Eq. (20) are regarded as the primary perturbations. The first-order perturbed vibrational wavefunction obtained from Eq. (23) is then used to average the interaction terms in the kinetic energy, a procedure equivalent to a second-order perturbation treatment of the Hamiltonian.[50] As shown in the text, the calculation reduces just to evaluating

$$\langle Q^n \rangle = \langle \psi_{vib} | Q_s^n | \psi_{vib} \rangle \tag{C1}$$

for $n = 1,2$. Only an approximation which yields the leading terms, proportional to the vibrational quantum numbers, is required.

In $\psi_{vib} = \psi_h + \psi_a$ the unperturbed or "harmonic" part is the product of harmonic oscillator functions, one for each normal mode:

$$\psi_h = |v_s\rangle \Pi_t |v_t\rangle, \tag{C2}$$

(where $t = s$) for a given vibrational state with quantum numbers $v_1, \ldots, v_s, \ldots, v_{3N-6}$. The "anharmonic" part ψ_a consists of a linear combination of many nondiagonal terms in which one or more of the vibrational quantum numbers differ from those in ψ_h. However, the only terms which enter in the evaluation of (C1) are of the type

$$\psi_a = [A_+ |v_s + 1\rangle + A_- |v_s - 1\rangle] \Pi_t v_t\rangle. \tag{C3}$$

The coefficients

$$A_\pm = \langle v_s | \mathcal{V}_s | v_s \pm 1 \rangle / (\mp \hbar\omega_s)$$

are formed from matrix elements of those perturbation terms that are linear or cubic functions of the $\underline{s}^{th}$ normal coordinate,

$$\mathcal{V}_s = \tfrac{1}{2} V_s Q_s + \tfrac{1}{2} k_{sss} Q_s^3 + \tfrac{3}{2} \Sigma_t k_{tts} Q_t^2 Q_s .$$

When v_s is even (or odd), ψ_h is an even (or odd) function of Q_s and ψ_a is an odd (or even) function. Therefore in (C1) we find

$$\langle Q_s \rangle = \langle \psi_h | Q_s | \psi_a \rangle + \langle \psi_a | Q_s | \psi_h \rangle$$

and

$$\langle Q_s^2 \rangle = \langle \psi_h | Q_s^2 | \psi_h \rangle + \langle \psi_a | Q_s^2 | \psi_a \rangle .$$

The anharmonic part of $\langle Q_s^2 \rangle$ is dropped, since it contains only terms at least quadratic in $v + \frac{1}{2}$. Thus we are left with just the result for a simple harmonic oscillator,

$$\langle Q_s^2 \rangle = (2K/\omega_s)(v_s + \tfrac{1}{2}) .$$

The two terms in $\langle Q_s \rangle$ are equal and we find

$$\langle Q_s \rangle = 2[A_+ \langle v_s | Q_s | v_s + 1 \rangle + A_- \langle v_s | Q_s | v_s - 1 \rangle] .$$

After introducing the harmonic oscillator matrix elements and the relation $K/\omega_s = \frac{1}{2}(h\omega_s/\lambda_s)$, we can reduce this to

$$\langle Q_s \rangle = - \tfrac{3}{2} [k_{sss} \langle Q_s^2 \rangle + \Sigma_t k_{tts} \langle Q_t^2 \rangle + \tfrac{1}{3} V_s]/\lambda_s \qquad (C4)$$

This becomes Eq. (34) of the text when (21) is taken into account.

It is interesting to note that if we separate the potential energy into harmonic and anharmonic parts,

$$2V_h = \Sigma_s \lambda_s Q_s^2$$

$$2V_a = \Sigma_s V_s Q_s + \Sigma_s k_{sss} Q_s^3 + \cdots ,$$

then (C4) is equivalent to the condition

$$\lambda_s \langle Q_s \rangle = \langle \partial V_h / \partial Q_s \rangle = -\langle \partial V_a / \partial Q_s \rangle$$

or

$$\langle \partial V / \partial Q_s \rangle = 0.$$

(Again, just terms linear in $v + \frac{1}{2}$ are retained.)

Often it is convenient to express the potential energy in terms of internal coordinates rather than normal coordinates, by use of Eq. (54). When transforming results from one basis to the other, it again proves useful to consider the expansion of a mode, as the following relations hold:

$$\begin{aligned} \lambda_s &= 2\, V_h(\ddagger) \\ k_{sss} &= 2\, V_a(\ddagger) \\ 3k_{sst} &= 2(\partial V_a / \partial Q_t)_{\ddagger} \\ &= 2\Sigma_k (\partial V_a / \partial S_k)_{\ddagger}\, L_{kt}. \end{aligned} \tag{C5}$$

Here the symbol "‡" indicates that the function is evaluated at the configuration specified in Eq. (55).

Footnotes

1. H. B. G. Casimir, The Rotation of a Rigid Body in Quantum Mechanics, (Leyden Thesis; J. B. Wolter's, The Hague, 1931); C. Eckart, Phys. Rev. 46, 383 (1934); J. H. Van Vleck, ibid. 47, 487 (1935).

2. C. Eckart, Phys. Rev. 47, 552 (1935). See also S. M. Ferigle and A. Weber, Am. J. Phys. 21, 102 (1953).

3. In this paper we shall be concerned with small amplitude vibrations. Phenomena such as inversion, internal rotation, and the like present special problems and will not be considered here.

4. E. B. Wilson and J. B. Howard, J. Chem. Phys. 4, 260 (1936).

5. Extensive reviews have been given by H. H. Nielsen, Rev. Mod. Phys. 23, 90 (1951); Handbuch der Physik, 37, 173 (Springer Verlag, Berlin, 1959).

6. For examples see C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill, New York, 1955), pp 42 and 54.

7. C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. 74, 1113 (1948).

8. M. W. P. Strandberg, T. Wentink, and R. L. Kyhl, Phys. Rev. 75, 270 (1949).

9. R. J. Myers and W. D. Gwinn, J. Chem. Phys. 20, 1420 (1952).

10. V. W. Laurie, J. Chem. Phys. 28, 704 (1958).

11. T. Oka, J. Phys. Soc. Japan 15, 2274 (1960).

12. C. C. Costain, J. Chem. Phys. 29, 864 (1958). See also J. K. Brown and A. P. Cox, Spect. Acta 17, 1230 (1961).

13. J. Kraitchman, Am. J. Phys. 21, 17 (1953).

14. L. Pierce, J. Mol. Spect. 3, 575 (1959).

15. R. A. Bonham, L. S. Bartell, and D. A. Kohl, J. Am. Chem. Soc. 81, 4765 (1959).

16. D. R. Lide, J. Chem. Phys. 33, 1514, 1519 (1960).

17. D. R. Herschbach and V. W. Laurie, Bull. Am. Phys. Soc. 5, 500 (1960). Oka has also reached this conclusion by physical arguments. He has calculated the average structure of formaldehyde in reference 11, and that of hydrogen selenide in T. Oka and Y. Morino, J. Molec. Spect. (to be published.)

18. E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Company, New York, 1955).

19. N. F. Ramsey, Phys. Rev. 87, 1075 (1952); J. A. Ibers and D. P. Stevenson, J. Chem. Phys. 28, 929 (1958); 33, 762 (1960).

20. It may be noted that $r_e^2\langle\xi^2\rangle$ is equal to the mean square harmonic vibrational amplitude u^2 (evaluated at T = 0°K) which has been tabulated for many molecules by A. Reitan, Acta. Chem. Scand. 12, 131 (1958); Det Kgl. Norska Videnskabers Selskabs Skrifter Nr. 2 (1958); S. J. Cyvin, ibid., Nr. 2 (1959).

21. L. S. Bartell, J. Chem. Phys. 23, 1219 (1955); K. Kuchitsu and L. S. Bartell, ibid. 35, 1945 (1961).

22. P. Thaddeus, J. Loubser, A. Javan, L. Krisher, and H. Lecar, in Quantum Electronics, C. H. Townes, Ed. (Columbia University Press, New York, 1960); J. Chem. Phys. 31, 1677 (1959).

23. D. R. Herschbach and V. W. Laurie, J. Chem. Phys. 35, 458 (1961). In Eq. (3) of this paper the minus sign should be omitted.

24. J. Plíva, Coll. Czech. Chem. Commun. 23, 777, 1839 (1958).

25. For a linear XYZ molecule the harmonic contribution to the correction for the bending mode, $d_2\alpha_2$, is equal to the ℓ-type doubling constant, q_ℓ, which has been measured for several molecules (see reference 6).

26. That is, we shall restrict attention to configurations close enough to the equilibrium one to make an expansion to terms linear in $v + \frac{1}{2}$ an adequate approximation.

27. We shall not consider the small contributions to the effective moments of inertia which arise from centrifugal distortion (treated in references 4, 11, and 33) and from electronic-rotational interactions (treated in reference 6, pp. 15-18 and 212-215, and in reference 11).

28. These various contributions are linked by the Eckart conditions, as illustrated in Eq. (45).

29. J. H. Meal and S. R. Polo, J. Chem. Phys. 24, 1119, 1126 (1956).

30. T. Oka and Y. Morino, J. Molec. Spect. 6, 472 (1961).

31. A matrix method has been given in references 30 and 38,

$$\underset{\sim}{\ell} = \underset{\sim}{M}^{-1/2} \underset{\sim}{B}^{\dagger} \underset{\sim}{G}^{-1} \underset{\sim}{U}^{\dagger} \underset{\sim}{L} ,$$

where $\underset{\sim}{M}$ is a diagonal matrix with elements m_i and the other matrices are defined in reference 18.

32. In Eqs. (46) and elsewhere we write expressions corresponding to just one coordinate direction; the others can be obtained by cyclic permutations of α, β, γ.

33. D. Kivelson and E. B. Wilson, J. Chem. Phys. 21, 1229 (1953). For other applications of Eq. (47) see references 40 and J. M. Dowling, R. Gold, and A. M. Meister, J. Molec. Spect. 1, 265 (1957); 2, 9, 411 (1958).

34. The coordinates obtained by use of Eq. (47) are referred to the center of mass of the expanded configuration, but not to its principal axes. In practice the contributions with $\alpha \neq \beta$ can often be neglected.

35. K. S. Pitzer, J. Chem. Phys. 8, 711 (1940).

36. D. R. Herschbach, H. S. Johnston, and D. Rapp, J. Chem. Phys. 31, 1652 (1959).

37. The procedure is particularly convenient for computing machines. R. H. Schwendeman, J. Molec. Spect. 6, 301 (1961) has described a program for moment of inertia calculations which can be adapted to evaluate Eqs. (50) and (51).

38. This has been pointed out by Plíva in reference 24. He has derived a treatment of triatomic molecules in which the internal coordinates are defined by the general nonlinear relations. The distinction is also important in the analysis of vibrational effects in electron diffraction; see Y. Morino and E. Hirota, J. Chem. Phys. 23, 737 (1955).

39. Similar considerations are involved in the derivation of Eqs. (48) and (49).

40. S. R. Polo, J. Chem. Phys. 24, 1133 (1956).

41. For symmetrical molecules certain of the coefficients in Eqs. (48) and (49) must vanish, according to rules summarized in reference 30.

42. Quantities which refer to symmetry coordinates will be distinguished by script letters.

43. Eq. (71) may be derived by combining Eq. (A5) of reference 40 with Eq. (26a) of reference 36; in the latter the last subscript should read "δ" rather than "γ".

44. The tetrahedral case has been discussed briefly by Polo in reference 40. His results agree with ours but are considerably different in form, since he treats symmetry coordinates differently.

45. The vibrational analysis of the nontetrahedral model is treated by G. W. Bethke and M. K. Wilson, J. Chem. Phys. 26, 1118 (1957) and W. T. King, I. M. Mills, and B. L. Crawford, ibid., 27, 455 (1957).

46. C. C. Lin and J. D. Swalen, Rev. Mod. Phys. 31, 841 (1959).

47. S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, J. Chem. Phys. 33, 1643 (1960); 34, 1319 (1961).

48. See reference 18, p. 75.

49. W. T. King and B. L. Crawford, J. Molec. Spect. 5, 421 (1960).

50. See, for example, L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1949), p. 152.

Table I. Comparison of bond lengths for diatomic molecules.[a]

Bond length	$\kappa = r/r_e$
Effective, $r_v = \langle r^{-2}\rangle^{-1/2}$	$1+\langle\xi\rangle-\frac{3}{2}\langle\xi^2\rangle$
Average, $\langle r\rangle$	$1+\langle\xi\rangle$
RMS, $\langle r^2\rangle^{1/2}$	$1+\langle\xi\rangle+\frac{1}{2}\langle\xi^2\rangle$
Inverse cube, $\langle r^{-3}\rangle^{-1/3}$	$1+\langle\xi\rangle-2\langle\xi^2\rangle$
Substitution, r_s	$1+f(\langle\xi\rangle-\frac{3}{2}\langle\xi^2\rangle)$

[a]The quantities $\langle\xi\rangle$, $\langle\xi^2\rangle$, and f are defined in Eqs. (4) and (12) of the text.

Table II. Ratio of anharmonic to harmonic contribution to moment of inertia.[a]

Molecule	ϵ_1	ϵ_2	ϵ_3	$\Sigma_s d_s \epsilon_s$
CO_2	-2.86	- 3.48	- 8.22	-6.72
CS_2	-2.45	- 7.66	-15.08	-5.40
OCS	-3.32	- 4.33	-10.41	-7.26
OCSe	-3.53	- 5.40	-	
SCTe	-	-10.84	-	
HCN	-2.46	- 2.07	- 3.59	-4.83
ClCN	-	- 5.37	-	
BrCN	-3.51	- 6.90	-	
ICN	-2.96	- 8.08	-	
NNO	-3.04	- 2.04	- 7.63	-9.03
H_2O				
c-axis	-2.42	- 0.316	- 1.82	-5.18
b-axis	-2.09	- 0.392	- 1.37	-1.23
a-axis	-2.86	0.669	- 4.16	-0.637

[a]References to experimental data are given under Table III of Part II.

Table III. Formulas for linear symmetric XY_2 molecule.[a]

$$2V_{har} = F_{11}(S_1^2 + S_3^2) + 2F_{12}S_1S_3 + F_{22}(S_{2a}^2 + S_{2b}^2)$$

$$2V_{anhar} = F_{111}(S_1^3 + S_3^3) + 3F_{113}(S_1^2S_3 + S_1S_3^2) + 3F_{122}(S_1+S_3)(S_{2a}^2 + S_{2b}^2)$$

$$\lambda_1 = (F_{11} + F_{13})/m,\ \lambda_2 = 4F_{22}/\mu r^2,\ \lambda_3 = 2(F_{11} - F_{13})/\mu$$

$$H_1 = 1\ ,\ H_2 = (3\lambda_2 + \lambda_3)/(\lambda_3 - \lambda_2)\ ,\ H_3 = (3\lambda_3 + \lambda_2)/(\lambda_3 - \lambda_2)$$

$$A_1 = r(F_{111} + 3F_{113})/(F_{11} + F_{13}),\ A_2 = (\lambda_2/\lambda_1)(4rF_{122}/F_{22}),$$

$$A_3 = (\lambda_3/\lambda_1)r(F_{111} - F_{113})/(F_{11} - F_{13})$$

$$\langle\xi\rangle = -(3B_e/\omega_1)\left[A_1(v_1 + \tfrac{1}{2}) + \tfrac{1}{2}(\omega_1/\omega_2)A_2(v_2 + 1) + (\omega_1/\omega_3)A_2(v_3 + \tfrac{1}{2})\right]$$

$$\langle\xi^2\rangle = (2B_e/\omega_1)(v_1 + \tfrac{1}{2})$$

[a] $S_1 = \delta r_{XY}$; $S_2 = \delta$; $S_3 = \delta r_{XY'}$; $\xi = \frac{1}{2}(S_1 + S_3)$. Mass of X atom is M, of Y atom m, and $\mu = 2mM/(2m+M)$.

Table IV. Vibration-rotation parameters for CO_2.[a]

Mode	Harmonic	Anharmonic	Total
1	-0.0747	0.213	0.139
2,2'	0.0673	-0.234	-0.167
3	-0.0470	0.386	0.339
Sum	-0.0544	0.365	0.311

[a]The tabulated quantities are the contributions to $\frac{1}{2}\epsilon = I_o - I_e$ (in amu A^2 units). Data used is from C. P. Courtoy [Can. J. Phys. 35, 608 (1957)]: $B_e = 0.39162_5$, $\alpha_1 = 0.00126$, $\alpha_2 = -0.00076$, $\alpha_3 = 0.003088$, $\omega_1 = 1354.9$, $\omega_2 = 673.02$, $\omega_3 = 2396.4$ (all in cm^{-1} units).

Table V. Notation and units.

$\alpha_i, \beta_i, \gamma_i$	=	coordinates of i^{th} atom with respect to principal axis system, chosen from x,y,z in cyclic order (Å).
Q_s	=	normal coordinates ($g^{1/2}$ $mole^{-1/2}$ Å)
P_s	=	total vibrational momentum associated with s^{th} normal coordinate
ρ_s	=	part of vibrational momentum which arises from Coriolis interaction, defined in Eq. (A6) of Appendix A.
π_α	=	components of total angular momentum along the principal axes
ω_s	=	harmonic vibrational frequency (cm^{-1})
$\lambda_s = 4\pi^2 c^2 m_H \omega_s^2$	=	5.8893×10^{-7} ω_s^2 (10^5 dynes cm^{-1} g^{-1} mole)
k_{sst}	=	cubic anharmonic vibrational constant (10^{-11} ergs $g^{-3/2}$ $mole^{3/2}$ $Å^{-3}$)
$K = h/8\pi^2$	=	16.863 g $mole^{-1}$ $Å^2$ cm^{-1}

Table VI. Symmetry analysis for a linear X_2Y_2 molecule.[a]

Symmetry Species	Eckart Corr.	Mode No.	$\mathcal{S}_k$	$\mathcal{S}_{kk}$
Σ_g^+		s=1	$2^{-1/2}(S_1+S_5)$	$(2/m_1)+(2/m_2)$
		2	S_3	$2/m_2$
Σ_u^+	$\delta\tau_z$	3	$2^{-1/2}(S_1-S_5)$	$(1/m_1)+(1/m_2)$
Π_g	$\delta\vartheta_x, \delta\vartheta_y$	4	$2^{-1/2}(S_2-S_4)$	$(1/m_1r^2)+\frac{1}{m_2}(\frac{1}{r}+\frac{2}{R})^2$
Π_u	$\delta\tau_x, \delta\tau_y$	5	$2^{-1/2}(S_2+S_4)$	$(\frac{1}{m_1}+\frac{1}{m_2})\frac{1}{r^2}$

[a]Here $r=r_{12}=r_{34}$; $R=r_{23}$; $m_1=m_4$; $m_2=m_3$. The non-diagonal element $\mathcal{S}_{12}$ for the Σ_g^+ modes has the value $-2/m_2$.

Table VII. Symmetry coordinates for a planar WXY_2 molecule.[a]

Species	Eckart Corr.	Mode No.	$\mathcal{S}_k$
A_1	$\delta\tau_y$	1	$2^{-1/2}(S_1+S_2)$
		2	$2^{-1/2}(S_5+S_5')$
		3	S_4
B_1	$\delta\tau_x, \delta\vartheta_z$	4	$2^{-1/2}(S_1-S_2)$
B_2	$\delta\tau_z, \delta\vartheta_x$	6	S_6

[a] $R = r_{24}$; $r = r_{12} = r_{23}$; $m_1 = m_3$; the z-axis is out-of-plane, the y-axis along the symmetry axis.

Captions for Figures

Fig. 1. Relative deviations from r_e for various types of average bond lengths as a function of the anharmonic constant. Ordinate scale is in multiples of the mean square harmonic vibrational amplitude.

Fig. 2. Comparison of vibrational contributions to effective moment of inertia. Abscissa and dashed line show sum of corrections for stretching modes. Solid circles show total correction, the sum of bending and stretching terms. Open circles show sum obtained by assigning to each bond the observed correction for the corresponding diatomic molecule.

Fig. 3. Construction of a normal mode expansion.

Fig. 4. Internal coordinates for a linear WXYZ molecule.

Fig. 5. Internal coordinates and displacement vectors for a branched WXYZ molecule.

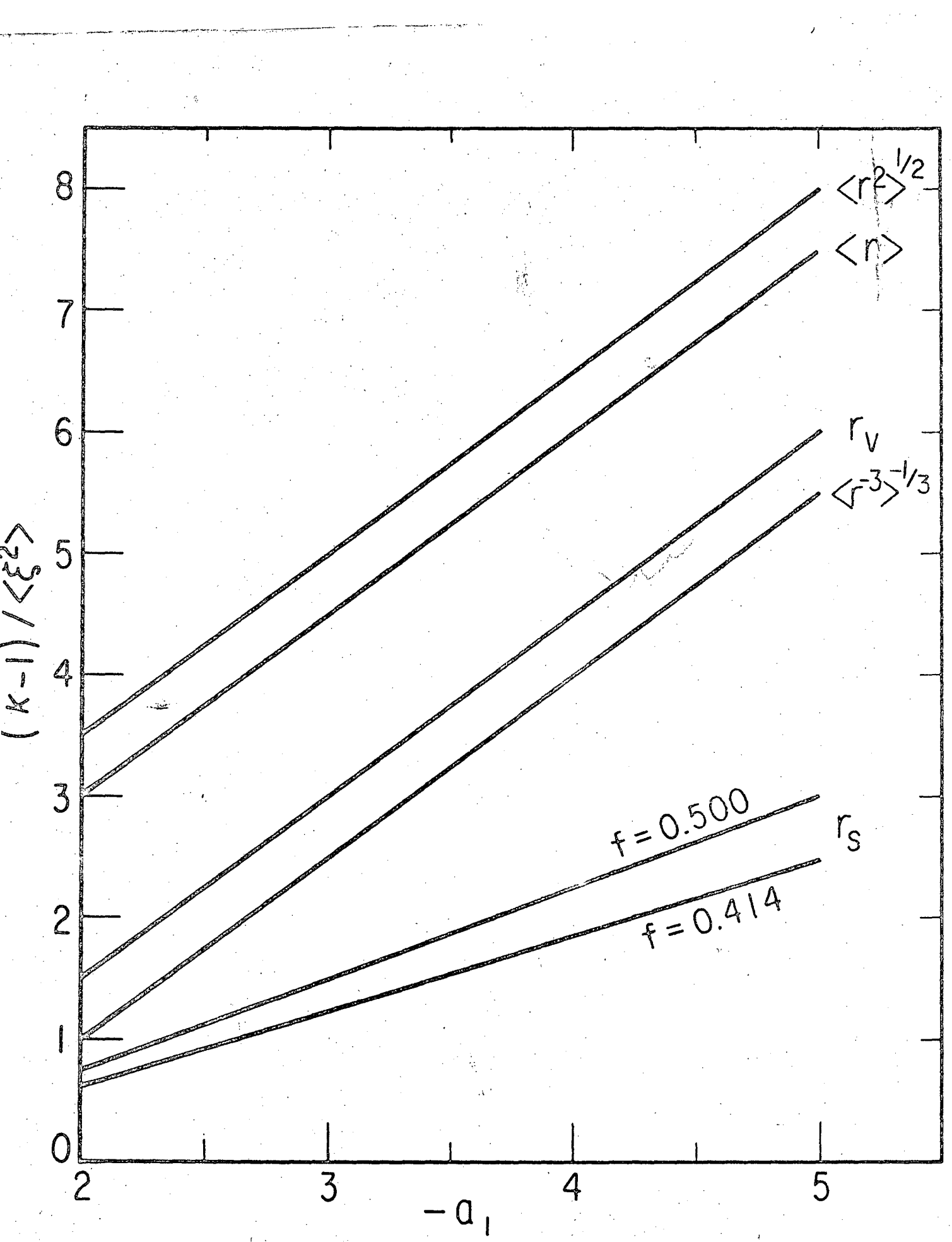
8
7
6
5
4
3
2
1
0
2
3
4
5
$-a_1$
$(\kappa-1)/\langle\xi^2\rangle$
$\langle r^2\rangle^{1/2}$
$\langle r\rangle$
r_v
$\langle r^{-3}\rangle^{-1/3}$
r_s
f = 0.500
f = 0.414

Fig. 1

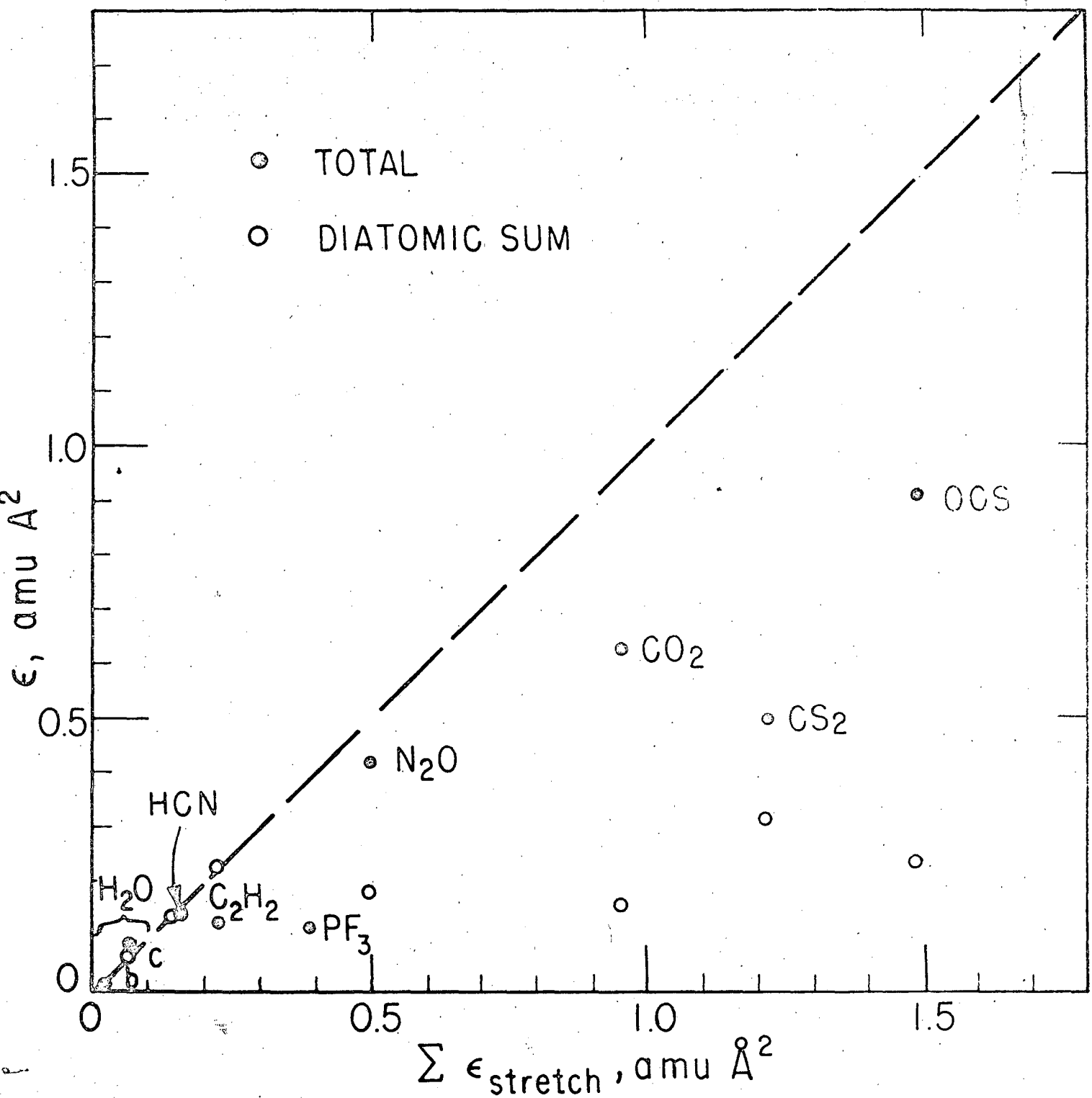
TOTAL
DIATOMIC SUM
OCS
CO_2
CS_2
N_2O
HCN
H_2O
C_2H_2
PF_3
C
0
0.5
1.0
1.5
ϵ, amu A^2
$\Sigma \epsilon_{stretch}$, amu $Å^2$

Fig. 2

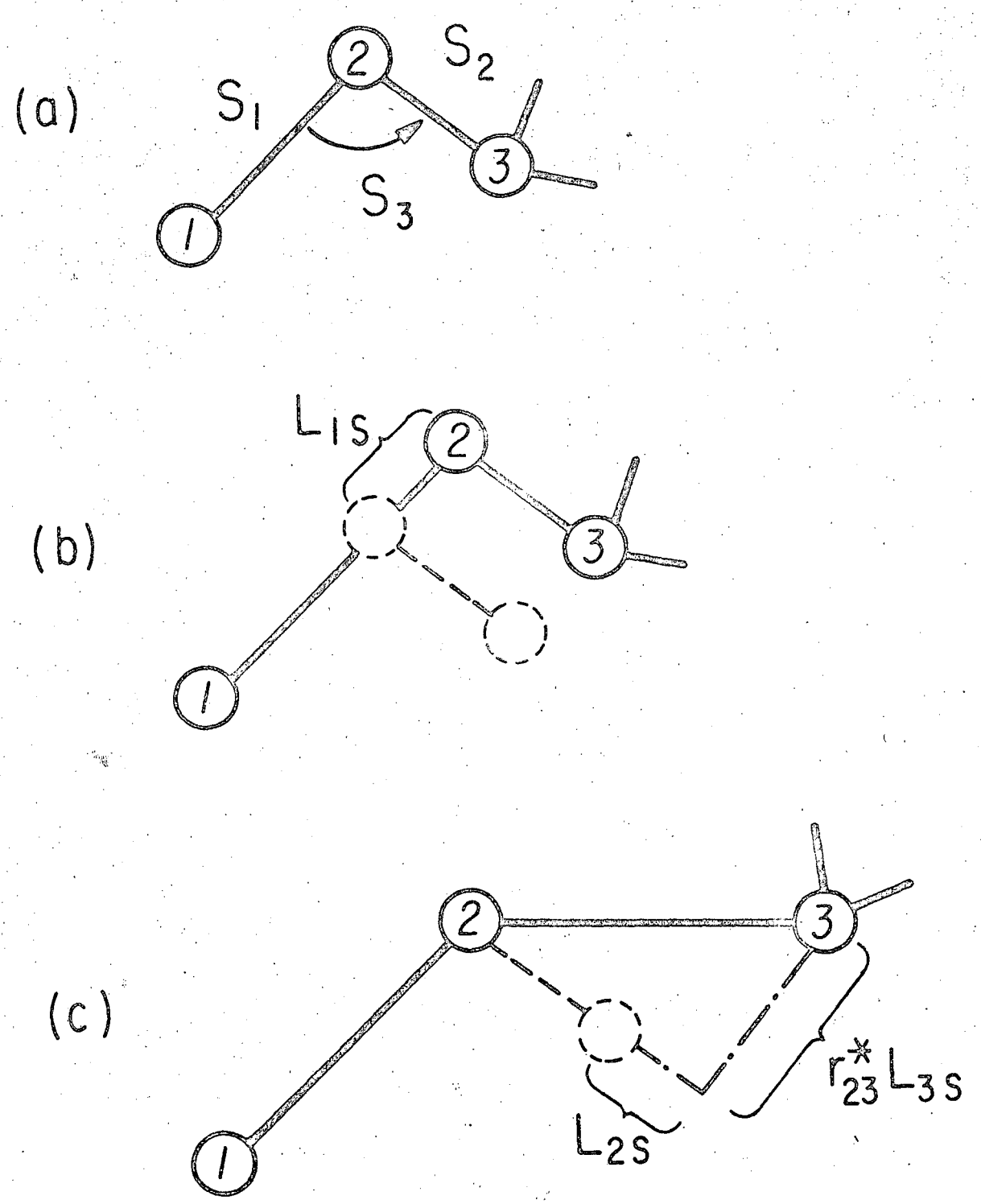

Fig. 3

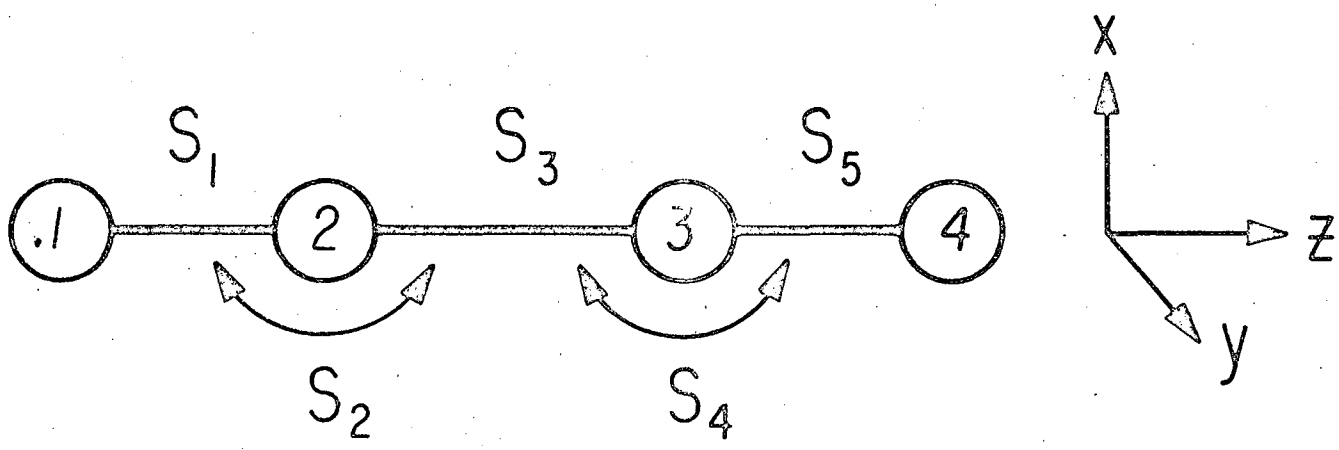

Fig. 4

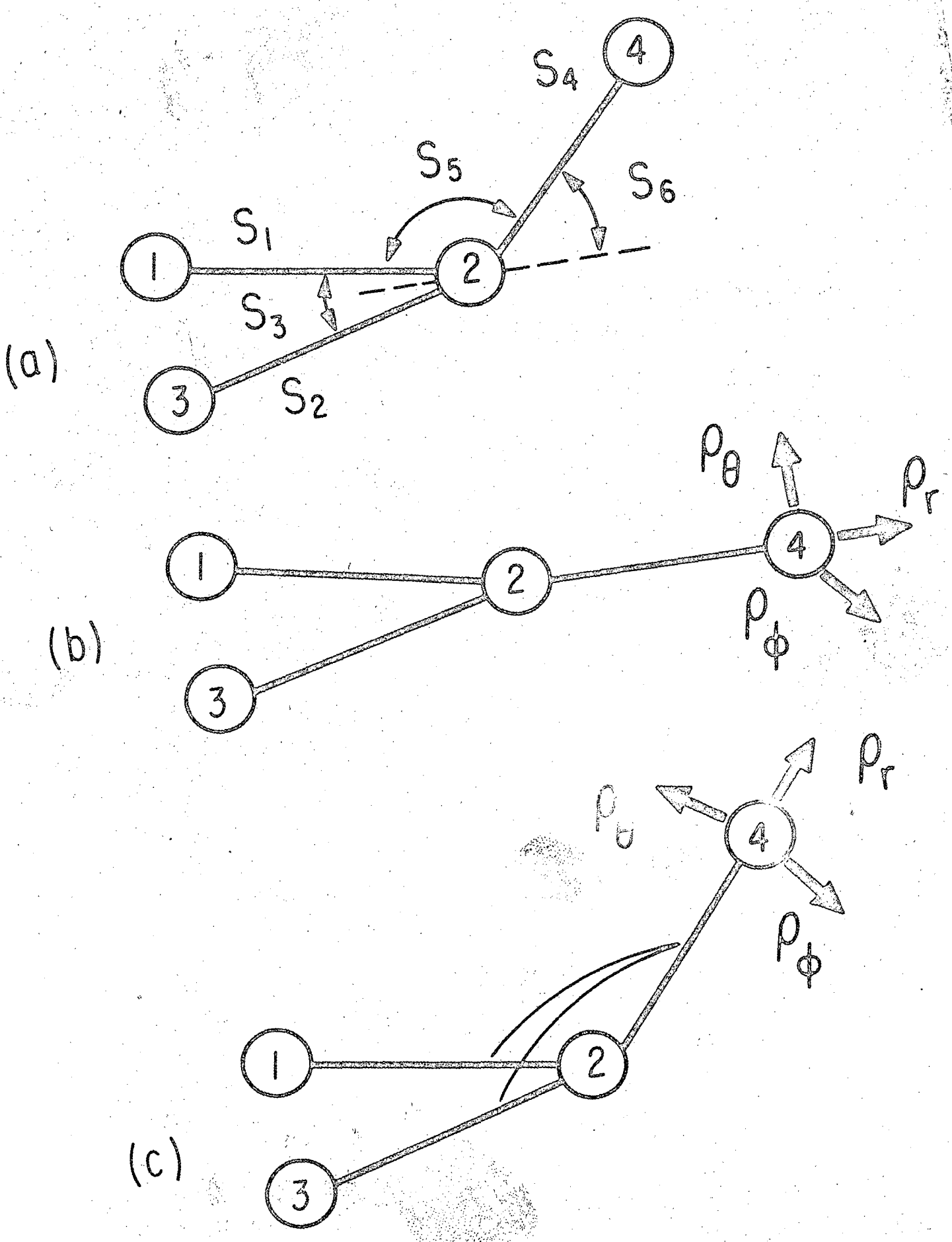
(a)
1
2
3
4
S_1
S_2
S_3
S_4
S_5
S_6
(b)
ρ_θ
ρ_r
ρ_ϕ
(c)
ρ_θ
ρ_r
ρ_ϕ

Fig. 5

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