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STRUCTURE DETERMINATIONS III. INERTIAL DEFECTS

Berkeley, California

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Dudley R. Herschbach and Victor W. Laurie

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## INFLUENCE OF VIBRATIONS ON MOLECULAR STRUCTURE DETERMINATIONS.

## III. INERTIAL DEFECTS\*

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The relationships between various types of moments of inertia and vibration-rotation corrections are developed from general theory, with emphasis on the qualitative physical features and the quantities which may be calculated without knowledge of anharmonic force constants. The inertial defects of planar triatomic and tetratomic molecules and nonplanar molecules with a plane of symmetry are considered, and it is found that simple approximations, which depend mainly on the one or two modes of lowest frequency, give results within 10-20% of the experimental values. The application of inertial defect corrections in structure analysis is illustrated for the calculation of HH distances in  $\text{CH}_2\text{Cl}_2$ ,  $\text{SiH}_2\text{F}_2$ , and  $\text{CH}_3\text{CXO}$  molecules (X = H, F, Cl, Br).

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Spectroscopic determinations of molecular structure usually must make use of the "effective" moments of inertia of the ground vibrational state, as it is seldom feasible to evaluate experimentally the corrections for vibration-rotation interaction. Relations among the moments which hold only for a rigid body are assumed also to hold for the effective moments. In particular, it is often convenient to make use of a combination of the principal moments which gives the "second moment" of a coordinate axis,  $P_\gamma = \frac{1}{2}(I_\alpha + I_\beta - I_\gamma)$ . For a rigid molecule, this is given by

$$2P_\gamma = I_\alpha + I_\beta - I_\gamma = 2\sum_1 m_1 \gamma_1^2, \quad (1)$$

where  $\gamma_1$  is the distance of the 1th atom from the  $\alpha\beta$  plane and  $m_1$  is its mass ( $\alpha, \beta, \gamma$  may be permuted among  $x, y, z$ ). These quantities are especially useful if a molecule has a plane of symmetry. Also, in the "substitution method" of structure analysis, the isotopic differences of the second moments are the primary factors in the calculations.<sup>1,2</sup> Since it is usually necessary to employ the effective moments of inertia, however, the corresponding quantities contain contributions from vibration-rotation interactions and Eq.(1) is replaced by<sup>3</sup>

$$2P_\gamma = \mathcal{I}_\alpha + \mathcal{I}_\beta - \mathcal{I}_\gamma = 2P_\gamma - \Delta_\gamma. \quad (2)$$

The vibrational contributions are denoted by  $\Delta_\gamma$  and are termed "inertial defects."

For a planar molecule,  $P_y = 0$  for the out-of-plane direction (the c-axis) and the corresponding inertial defect becomes directly observable.<sup>4</sup> Thus,

$$\Delta = \mathcal{I}_c - (\mathcal{I}_a + \mathcal{I}_b), \quad (3)$$

where  $\mathcal{I}_c > \mathcal{I}_b > \mathcal{I}_a$ . It is found that for different molecules  $\Delta$  varies considerably in magnitude and may be either positive or negative. As first pointed out by Darling and Dennison,<sup>4</sup> for small amplitude vibrations of planar molecules  $\Delta$  may be calculated from the atomic masses and coordinates and the harmonic force constants, without knowledge of anharmonic force constants.<sup>5</sup> Further theoretical discussions have been given by Nielsen,<sup>6</sup> Posener,<sup>7</sup> and Oka and Morino.<sup>8</sup> Values of  $\Delta$  have been calculated for a number of small molecules<sup>8-10</sup> and the results are in excellent agreement with experiment.

In this paper the general inertial defects defined in Eq. (2) are studied. As in Parts I and II of this series,<sup>11,12</sup> particular attention is given to the role of anharmonicity and to features which affect the determination of the average structure of a molecule. Since the precise calculation of inertial defects becomes very laborious even for planar molecules when more than three atoms are involved, we have examined simple approximations which depend mainly on one or two modes of vibration and find that these provide reliable estimates of  $\Delta$  in many cases.

## GENERAL FORMULATION

Some results of the general theory of vibration-rotation interactions<sup>6,11</sup> will be restated briefly, in order to put them in a convenient form and to emphasize qualitative physical features. For small amplitude vibrations<sup>5,13</sup> a perturbation expansion up to terms linear in the vibrational quantum numbers gives the following relations:

$$\langle I_{\alpha}^{-1} \rangle^{-1} = 4 \sum_s \sum_t [(c_{st}^{\alpha})^2 \lambda_s / (\lambda_s - \lambda_t)] \langle Q_s^2 \rangle \quad (4)$$

$$\langle I_{\alpha}^{-1} \rangle^{-1} = \langle I_{\alpha} \rangle - \sum_s \sum_{\gamma} [(a_s^{\alpha\gamma})^2 / I_{\gamma}] \langle Q_s^2 \rangle \quad (5)$$

$$\langle I_{\alpha} \rangle = I_{\alpha} + \sum_s a_s^{\alpha\alpha} \langle Q_s \rangle + \sum_s A_{ss}^{\alpha\alpha} \langle Q_s^2 \rangle \quad (6)$$

In Eq. (4), the effective spectroscopic moment of inertia is seen to differ from the reciprocal of the average of the inverse of the instantaneous moment because of the contributions of Coriolis interactions. In Eq. (5), this "inverse of the average inverse" is converted to the direct vibrational average of the instantaneous moment of inertia by separating out the terms which arise in expanding the double inverse. Finally, in Eq. (6), the direct average moment is related to the moment of inertia for a particular rigid configuration of the atoms (termed the "standard" configuration<sup>3</sup>) by averaging an expansion of the instantaneous moment in powers of the normal coordinates. Up to terms linear in the vibrational quantum numbers, the quadratic averages  $\langle Q_s^2 \rangle$  depend only on the harmonic vibrational frequencies,

$$\langle Q_s^2 \rangle = (2K/d_s \omega_s) (v_s + \frac{1}{2} d_s), \quad (7)$$



where  $d_s$  is the degeneracy of the mode and  $K = h/8\pi^2 c = 16.8627$  amu A<sup>2</sup> cm.<sup>-1</sup> The linear averages  $\langle Q_s \rangle$  involve the anharmonic force constants (see Appendix C of Part I).

In Eq. (5) the origin of the "shrinkage" caused by inverse averaging is entirely analogous to that in the diatomic case,<sup>11</sup> for which

$$\langle r^{-2} \rangle^{-1} < \langle r^2 \rangle.$$

The Coriolis term in Eq. (4) may also be given a simple physical interpretation. The atoms are all vibrating relative to the principal axis system "fixed" to the rotating molecule,<sup>14</sup> and the slight angular momentum associated with these vibrations makes the observed rotational kinetic energy slightly larger than it would otherwise be.<sup>15</sup> Thus

$$\sum_{\alpha} \langle I_{\alpha}^{-1} \rangle M_{\alpha}^2 > \sum_{\alpha} \langle I_{\alpha}^{-1} \rangle M_{\alpha}^2,$$

and since the total angular momentum  $\mathcal{M}$  is a constant of the motion, this increase in the rotational energy appears as a slight shrinkage of the effective moments of inertia. While it is convenient to describe the terms involving  $\langle Q_s^2 \rangle$  in Eqs. (4)-(6) as due respectively to Coriolis coupling, inversion, and harmonic averaging of the moment of inertia, this classification should not be interpreted too rigidly. The conditions imposed when defining a set of rotating axes "fixed" to a vibrating molecule<sup>14</sup> imply relationships among the coefficients  $a_s^{\alpha\alpha}$ ,  $A_s^{\alpha\alpha}$ , and  $c_{st}^{\alpha}$ . One of the most useful of these relations<sup>8</sup> is

$$\sum_t (c_{st}^\alpha)^2 = A_{ss}^{\alpha\alpha} - \frac{1}{4} \sum_\gamma (a_s^{\alpha\gamma})^2 / I_\gamma. \quad (8)$$

In the sum of Eqs. (4)-(6), which relates the effective moment of inertia to that for the standard configuration of the molecule,

$$I_\alpha = I_\alpha + \sum_s a_s^{\alpha\alpha} \langle Q_s \rangle + \sum_s A_{ss}^{\alpha\alpha} \langle Q_s^2 \rangle, \quad (9)$$

we may use (8) to rewrite the coefficient of the harmonic term in a form which eliminates explicit reference to the term that arises from the inverse averaging. That is,

$$R_{ss}^{\alpha\alpha} = A_{ss}^{\alpha\alpha} - \sum_\gamma [(a_s^{\alpha\gamma})^2 / I_\gamma] - 4 \sum_t [(c_{st}^\alpha)^2 \lambda_s / (\lambda_s - \lambda_t)], \quad (10a)$$

may be rewritten as

$$R_{ss}^{\alpha\alpha} = -3A_{ss}^{\alpha\alpha} + 4 \sum_t [(c_{st}^\alpha)^2 \lambda_t / (\lambda_t - \lambda_s)]. \quad (10b)$$

We shall choose either the equilibrium or the average configuration of the atoms as the standard one, and make comparisons with the corresponding moments of inertia  $I_\alpha^e$  or  $I_\alpha^*$ , respectively. As shown in Part I, the various coefficients  $a_s^{\alpha\beta}$ ,  $A_{ss}^{\alpha\alpha}$ ,  $c_{st}^\alpha$ , the vibrational frequencies, and the harmonic averages  $\langle Q_s^2 \rangle$  all remain practically the same for any choice of the standard configuration. However, the anharmonic averages  $\langle Q_s \rangle$  are quite sensitive to this choice. In particular, when the average configuration is taken as the standard,

$$\langle Q_s \rangle = 0. \quad (11^*)$$

It should be emphasized that the moment of inertia  $I_\alpha^*$  for the average configuration is not equal to the average of the instantaneous moment, since  $\langle \alpha_i \rangle^2 \neq \langle \alpha_i^2 \rangle$ . Thus Eqs. (6) and (11<sup>\*</sup>) give

$$\langle I_\alpha \rangle = I_\alpha^* + \sum_s A_{ss}^{\alpha\alpha} \langle Q_s^2 \rangle. \quad (12^*)$$

Also from Eq. (9) we have

$$J_{\alpha} = I_{\alpha}^{*} + \sum_s A_{ss}^{\alpha\alpha} \langle Q_s^2 \rangle. \quad (13^{*})$$

These formulas, together with (4)-(7), show that the various kinds of moments of inertia,

$$J_{\alpha}, \langle I_{\alpha}^{-1} \rangle^{-1}, \langle I_{\alpha} \rangle, I_{\alpha}^{*}$$

may be interconverted by calculations which require only harmonic force constants, whereas to relate any of these to the equilibrium moment  $I_{\alpha}^e$  we must have the anharmonic force constants.

The "normal" order of the various moments of inertia is

$$\langle I_{\alpha} \rangle > I_{\alpha}^{*} > J_{\alpha} > I_{\alpha}^e. \quad (14)$$

This order, and the occasional deviations from it, may be understood by considering the signs of the various vibration-rotation terms. Among the harmonic terms, the inversion correction in Eq. (5) is always negative; in Eq. (6), however,

$$\sum_s A_{ss}^{\alpha\alpha} \langle Q_s^2 \rangle > 0, \quad (15)$$

since the definition of the coefficients requires

$$1 \geq A_{ss}^{\alpha\alpha} \geq 0 \quad (16)$$

[see Eq. (25)]. Thus we see from Eq. (12<sup>\*</sup>) that the inequality  $\langle I_{\alpha} \rangle > I_{\alpha}^{*}$  must always hold. For the ground vibrational state, the Coriolis contribution in Eq. (4) can be rewritten as

$$-4K \sum_s \sum_t [(c_{st}^{\alpha})^2 / (\omega_s + \omega_t)] \quad (17)$$

where now  $s > t$  in the summations (See Appendix B of Part I).

In Eq. (9), the harmonic contribution may likewise be rewritten with use of (10b) as

$$\sum_s \rho_{ss}^{\alpha\alpha} \langle Q_s^2 \rangle = -3K \sum_s (A_{ss}^{\alpha\alpha} / \omega_s) + 4K \sum_s \sum_t (c_{st}^\alpha)^2 \left[ \frac{1}{\omega_s} + \frac{1}{\omega_t} - \frac{1}{\omega_s + \omega_t} \right], \quad (18)$$

for the ground state, with  $s > t$ . These expressions show that "resonant" Coriolis interactions<sup>6,11</sup> will not influence the moments of inertia for the ground vibrational state. The contribution (17) is always negative. The first term in (18) is usually dominant, and therefore

$$\sum_s \rho_{ss}^{\alpha\alpha} \langle Q_s^2 \rangle < 0, \quad (19)$$

for the ground vibrational state. Accordingly, in Eq. (9) the negative Coriolis and inversion corrections determine the sign of the harmonic contributions, and the inequality  $I_\alpha^* > \mathcal{J}_\alpha$  holds whenever (19) does. The individual terms in the anharmonic contribution in Eqs. (6) and (9) may be either positive or negative. Analysis of experimental data for simple molecules has shown<sup>11,12</sup> that in most cases the stretching modes dominate and

$$\sum_s a_s^{\alpha\alpha} \langle Q_s \rangle > 0, \quad (20^e)$$

and  $\mathcal{J}_\alpha \approx I_\alpha^e$  usually holds because (20<sup>e</sup>) outweighs the harmonic contribution (19).

#### INERTIAL DEFECTS

From Eqs. (2) and (9) we obtain a general expression for the inertial defect as a sum of anharmonic and harmonic vibrational contributions,

$$\Delta_\gamma = \Delta_\gamma(\text{anhar}) + \Delta_\gamma(\text{har}), \quad (21)$$

where

$$-\Delta_Y(\text{anhar}) = \sum_s [a_s^{\alpha\alpha} + a_s^{\beta\beta} - a_s^{\gamma\gamma}] \langle Q_s \rangle \quad (22)$$

and, from Eq. (10b),

$$-\Delta_Y(\text{har}) = -3 \sum_s [A_{ss}^{\alpha\alpha} + A_{ss}^{\beta\beta} - A_{ss}^{\gamma\gamma}] \langle Q_s^2 \rangle \quad (23)$$

$$+4 \sum_s \sum_t [(c_{st}^\alpha)^2 + (c_{st}^\beta)^2 - (c_{st}^\gamma)^2] [\lambda_t / (\lambda_t - \lambda_s)] \langle Q_s^2 \rangle.$$

An equivalent but more cumbersome expression<sup>6,7</sup> for  $\Delta_Y(\text{har})$  may be obtained from Eq. (10a). The coefficients are defined in terms of derivatives of the Cartesian coordinates of the atoms with respect to the normal coordinates,

$$a_s^{\alpha\alpha} = 2 \sum_i m_i [\beta_i (\partial \beta_i / \partial Q_s) + \gamma_i (\partial \gamma_i / \partial Q_s)], \quad (24a)$$

$$a_s^{\alpha\beta} = -2 \sum_i m_i \alpha_i (\partial \beta_i / \partial Q_s) = -2 \sum_i m_i \beta_i (\partial \alpha_i / \partial Q_s) \quad (24b)$$

$$A_{ss}^{\alpha\alpha} = 1 - \sum_i m_i (\partial \alpha_i / \partial Q_s)^2, \quad (25)$$

$$c_{st}^\alpha = \sum_i m_i [(\partial \beta_i / \partial Q_s) (\partial \gamma_i / \partial Q_t) - (\partial \gamma_i / \partial Q_s) (\partial \beta_i / \partial Q_t)], \quad (26)$$

where

$$\sum_i m_i [(\partial \alpha_i / \partial Q_s)^2 + (\partial \beta_i / \partial Q_s)^2 + (\partial \gamma_i / \partial Q_s)^2] = 1, \quad (27)$$

and all quantities are evaluated for the standard configuration of the atoms. Thus (16) and several other useful relations are readily obtained:

$$a_s^{\alpha\alpha} + a_s^{\beta\beta} - a_s^{\gamma\gamma} = 4 \sum_i m_i \gamma_i (\partial \gamma_i / \partial Q_s), \quad (28)$$

$$A_{ss}^{\alpha\alpha} + A_{ss}^{\beta\beta} - A_{ss}^{\gamma\gamma} = 2 \sum_i m_i (\partial \gamma_i / \partial Q_s)^2, \quad (29)$$

$$A_{ss}^{\alpha\alpha} + A_{ss}^{\beta\beta} + A_{ss}^{\gamma\gamma} = 2, \quad (30)$$

$$2 \geq A_{ss}^{\alpha\alpha} + A_{ss}^{\beta\beta} - A_{ss}^{\gamma\gamma} \geq 0. \quad (31)$$

Planar Molecules

When all the atoms lie in the  $\alpha\beta$  plane, the coefficient (28) of the anharmonic part of  $\Delta_Y$  vanishes identically (since all  $\gamma_i = 0$ ), and

$$\Delta_Y = \Delta_Y(\text{har}). \quad (32)$$

Also, for in-plane vibrations,

$$(\partial\gamma_i/\partial Q_s) = 0 \quad (33a)$$

and for out-of-plane vibrations,

$$(\partial\alpha_i/\partial Q_s) = (\partial\beta_i/\partial Q_s) = 0. \quad (33b)$$

Thus the coefficient (29) also vanishes for in-plane vibrations, and it becomes equal to 2 for out-of-plane vibrations. Similarly, if both  $\omega_s$  and  $\omega_t$  are in-plane modes,  $c_{st}^\alpha = c_{st}^\beta = 0$ , whereas, if  $\omega_s$  is in-plane and  $\omega_t$  is out-of-plane,  $c_{st}^\gamma = 0$ . All the Coriolis coupling constants vanish if  $\omega_s$  and  $\omega_t$  are both out-of-plane.

The inertial defect may therefore be written as the sum of terms which refer to in-plane and out-of-plane vibrations,

$$\Delta = \Delta(1) + \Delta(0),$$

where

$$\begin{aligned} \Delta(1) = & \sum_s \{ 4 \sum_{s'} (c_{ss'}^c)^2 W_{ss'} - 4 \sum_t [(c_{st}^a)^2 + (c_{st}^b)^2] W_{st} \\ & + \frac{1}{I_a} [(a_s^{aa})^2 + (a_s^{ab})^2] + \frac{1}{I_b} [(a_s^{bb})^2 + (a_s^{ab})^2] \\ & - \frac{1}{I_c} (a_s^{cc})^2 \} \langle Q_s^2 \rangle \end{aligned} \quad (34a)$$

$$= 4 \sum_{\alpha} \{ \sum_{s'} (c_{ss'}^c)^2 W_{s's} - \sum_t [(c_{st}^a)^2 + (c_{st}^b)^2] W_{ts} \} \langle Q_s^2 \rangle \quad (34b)$$

and

$$\Delta(0) = -2 \sum_t \{ 1 - 2 \sum_s [(c_{st}^a)^2 + (c_{st}^b)^2] W_{ts} \} \langle Q_t^2 \rangle \quad (35a)$$

$$= 6 \sum_t \left( 1 - \frac{2}{3} \sum_s [(c_{st}^a)^2 + (c_{st}^b)^2] W_{st} \right) \langle Q_t^2 \rangle. \quad (35b)$$

Here  $W_{st} = \lambda_s / (\lambda_s - \lambda_t)$ , etc., and  $\underline{s}, \underline{s}'$  now refer to in-plane vibrations,  $\underline{t}$  to out-of-plane vibrations. The equivalent expressions obtained from (10a) as well as those from (10b) or (23) have been given, as these are more convenient for some purposes.

If out-of-plane vibrations are absent (as in a triatomic molecule) or "frozen", the inertial defect becomes

$$\Delta = \Delta(i) = 4 \sum_s \sum_{s'} (c_{ss'}^c)^2 \left\{ \frac{\lambda_{s'} \langle Q_s^2 \rangle - \lambda_s \langle Q_{s'}^2 \rangle}{\lambda_{s'} - \lambda_s} \right\}, \quad (36)$$

(where we now take  $s > s'$ ). This must be positive for the ground vibrational state since, as in (18), we may replace the factor within the curly brackets by

$$K \left[ \frac{1}{\omega_s} + \frac{1}{\omega_{s'}} - \frac{1}{\omega_s + \omega_{s'}} \right] > 0.$$

Also, from (6) and (28)-(33) we find

$$\langle I_c - (I_a + I_b) \rangle = 0, \quad (37)$$

as expected from Eq. (1) with all  $Y_1 = 0$ . In this case the contributions to  $\Delta(i)$  arise solely from the "shrinkage" effects which accompany the Coriolis interactions of (4) and the inverse averaging of (5); these effects, shown separately in (34a), have been amalgamated in (34b) and (36).

If out-of-plane vibrations are present (37) becomes

$$\langle I_c - (I_a + I_b) \rangle = -2 \sum_t \langle Q_t^2 \rangle, \quad (38)$$

according to (29). In  $\Delta(0)$  this is always a negative contribution, and corresponds simply to averaging Eq. (1) over the nonplanar configurations attained during the vibrations.

There are in addition contributions to both  $\Delta(1)$  and  $\Delta(0)$  from Coriolis coupling between the in-plane and out-of-plane modes, as seen in (34a) and (35a). Often the out-of-plane modes are all lower in frequency than the in-plane ones; then all  $W_{ts} < 0$ , and these Coriolis terms reinforce (36) to make  $\Delta(1)$  more positive and reinforce (38) to make  $\Delta(0)$  more negative.

These general considerations do not indicate the sign of the total inertial defect. However, unless one or more out-of-plane modes are of very low frequency, we expect  $\Delta$  to be positive for the ground vibrational state, and this is found to be the case for almost all planar molecules thus far studied. The negative contribution of the out-of-plane modes accounts for the fact that planar ring compounds usually have rather small positive inertial defects. Examples are shown in Table I. These molecules have several low frequency out-of-plane modes which cancel much of the contribution from the in-plane modes.

#### Molecules with a Plane of Symmetry

When the only out-of-plane atoms are symmetrically equivalent pairs, the vibrations may be classified as either symmetric (+)



or antisymmetric (-) with respect to the plane of symmetry (taken as the  $\alpha\beta$  plane).<sup>16</sup> Thus, for an atom  $\underline{i}$  located on the symmetry plane, Eqs. (33a) and (33b) again hold for (+) and (-) vibrations respectively. For a symmetrically equivalent pair of atoms  $\underline{j}$ ,  $\underline{k}$  located out of the plane,

$$\alpha_j = \alpha_k, \beta_j = \beta_k, \gamma_j = -\gamma_k \quad (39a)$$

and

$$(\partial\gamma_j/\partial Q_s) = \mp (\partial\gamma_k/\partial Q_s) \quad (39b)$$

for (+) vibrations. As before, the in-plane atoms give no contribution to Eq. (22), the anharmonic part of the inertial defect. According to (39), the coefficient (28) of the anharmonic part also vanishes for (-) vibrations of the out-of-plane atoms, and for the (+) vibrations

$$a_s^{\alpha\alpha} + a_s^{\beta\beta} - a_s^{\gamma\gamma} = 8 \sum_j m_j \gamma_j (\partial\gamma_j/\partial Q_s), \quad (40)$$

where the sum extends over one member of each of the pairs of symmetrically equivalent out-of-plane atoms. Similarly, the harmonic coefficient (29) has no contributions from (+) vibrations of in-plane atoms, whereas the out-of-plane pairs give

$$A_{ss}^{\alpha\alpha} + A_{ss}^{\beta\beta} - A_{ss}^{\gamma\gamma} = 4 \sum_j m_j (\partial\gamma_j/\partial Q_s)^2. \quad (41)$$

For (-) vibrations both the in-plane and out-of-plane atoms contribute and (29) may differ greatly from the value of 2 obtained for planar molecules.

Instead of (37) or (38), for a nonplanar molecule the direct vibrational average of the second moment is given by

$$\langle I_\alpha + I_\beta - I_\gamma \rangle = 4 \sum_j m_j \gamma_j^2 + \sum_s^+ \Delta a_s \langle Q_s \rangle + \sum_s^+ \frac{1}{s} \Delta A_{ss} \langle Q_s^2 \rangle, \quad (42)$$

where  $\Delta a_s$  and  $\Delta A_{ss}$  denote (40) and (41), respectively, and  $Y_j$  is the coordinate of an out-of-plane atom in the standard configuration of the molecule.<sup>3</sup> The analogous expression for the effective moments of inertia is again obtained by adding the contributions from Coriolis coupling and inverse averaging as in Eq. (9); that is, by replacing the harmonic coefficient  $\Delta A_{ss}$  by  $\Delta \mathcal{A}_{ss}$ . Although (40) shows that relatively few terms contribute to the anharmonic part of the inertial defect, in practice there is no way to evaluate these. However, the effect of the anharmonic terms is simply to displace the coordinates for the average configuration of the molecule,  $Y_j^* = \langle Y_j \rangle$ , from those for the equilibrium configuration, as noted in Eq. (11\*). Thus, if we choose the average configuration as the standard,

$$\mathcal{I}_\alpha + \mathcal{I}_\beta - \mathcal{I}_\gamma = 4 \sum_j m_j \langle Y_j \rangle^2 - \Delta_\gamma(\text{har}). \quad (43^*)$$

For molecules which have a single pair of out-of-plane atoms, this relation enables the average value of the out-of-plane distance to be determined without knowledge of anharmonic force constants.

In the preceding discussion, we have ignored the nondiagonal terms in the effective moment of inertia tensor which appear in the general treatment of vibration-rotation interaction,<sup>6,11</sup>

$$\mathcal{I}_{\alpha\beta} = \sum_s (v_s + \frac{1}{2}d_s) c_s^{\alpha\beta}.$$

These terms vanish identically for molecules of orthorhombic symmetry (point groups  $C_{2v}$ ,  $D_2$ , or  $D_{2h}$ ). For a planar molecule,

$\mathcal{I}_{\beta\gamma}$  and  $\mathcal{I}_{\alpha\gamma}$  vanish, and  $\mathcal{I}_{\alpha\beta}$  does not contribute to the inertial defect because the sum of the in-plane moments,  $\mathcal{I}_{\alpha} + \mathcal{I}_{\beta}$ , is the same whether or not a transformation has been applied to eliminate the  $\mathcal{I}_{\alpha\beta}$  cross term. For nonplanar molecules without orthorhombic symmetry all the cross terms appear, but in the usual case for which  $\mathcal{I}_{\alpha} - \mathcal{I}_{\beta} \gg \mathcal{I}_{\alpha\beta}$ , etc., the diagonalizing transformation amounts to a very small second order perturbation correction, and since this is a quadratic function of  $(v_{\beta} + \frac{1}{2})$ , it may be disregarded.<sup>5</sup> In case two of the principal moments are equal or nearly equal, say  $\mathcal{I}_{\alpha} \approx \mathcal{I}_{\beta}$ , the transformation is

$$\mathcal{I}'_{\alpha}, \mathcal{I}'_{\beta} = \frac{1}{2}(\mathcal{I}_{\alpha} + \mathcal{I}_{\beta}) \pm \frac{1}{2}[(\mathcal{I}_{\alpha} - \mathcal{I}_{\beta})^2 + 4\mathcal{I}_{\alpha\beta}^2]^{\frac{1}{2}}, \quad (44)$$

where the minus sign refers to  $\mathcal{I}'_{\beta}$ . However, practically the only nonplanar molecules for which (44) would be required are symmetric tops, and for these it is conventional to retain  $\mathcal{I}'_{\alpha} = \mathcal{I}'_{\beta}$  and regard the  $\mathcal{I}_{\alpha\beta}$  correction as contributing to the degenerate Coriolis perturbation<sup>6,11</sup> rather than to the moments of inertia.

## EXAMPLES AND APPROXIMATIONS

### Bent Triatomic Molecules

A symmetrical bent  $XY_2$  molecule offers the simplest example of the inertial defect and most of the available calculations have dealt with this case.<sup>4,7,8,10</sup> A bent  $XYZ$  molecule is not much more complicated, however. The general expression (34b) reduces to six terms,

$$\Delta = 4\langle Q_1^2 \rangle [(\zeta_{12})^2 W_{21} + (\zeta_{13})^2 W_{31}] + 4\langle Q_2^2 \rangle [(\zeta_{12})^2 W_{12} + (\zeta_{23})^2 W_{32}] \\ + 4\langle Q_3^2 \rangle [(\zeta_{13})^2 W_{13} + (\zeta_{23})^2 W_{23}], \quad (45a)$$

where  $\langle Q_s^2 \rangle = 2(K/w_s)(v_s + \frac{1}{2})$ ;  $W_{st} = w_s^2 / (w_s^2 - w_t^2)$ , and the Coriolis constants satisfy a sum rule,

$$(\zeta_{12})^2 + (\zeta_{13})^2 + (\zeta_{23})^2 = 1. \quad (45b)$$

For the ground vibrational state the result reduces further to

$$\Delta = 4K(\zeta_{12})^2 \left( \frac{1}{w_1} + \frac{1}{w_2} - \frac{1}{w_1 + w_2} \right) + 4K(\zeta_{23})^2 \left( \frac{1}{w_2} + \frac{1}{w_3} - \frac{1}{w_2 + w_3} \right) \\ + 4K(\zeta_{13})^2 \left( \frac{1}{w_1} + \frac{1}{w_3} - \frac{1}{w_1 + w_3} \right). \quad (45c)$$

Here the Coriolis constants refer to the out-of-plane axis (the c-axis), and Eq. (45b) follows from Eqs. (8) and (33). For a bent  $XY_2$  molecule, one third of the terms in Eqs. (45) drop out, as  $\zeta_{12} = 0$  (where  $w_1$  denotes the symmetric stretching frequency,  $w_2$  the bend, and  $w_3$  the antisymmetric stretch).

The Coriolis coupling constants may be evaluated by means of a convenient matrix procedure due to Meal and Polo.<sup>17</sup> This gives the components along the Y-axis as

$$\underline{\zeta}^Y = \underline{L}^{-1} \underline{C}^Y (\underline{L}^\dagger)^{-1}, \quad (46)$$

in terms of the amplitude matrix  $\underline{L}$  which relates the internal displacement coordinates to the normal coordinates,  $\underline{S} = \underline{LQ}$ , and a matrix,  $\underline{C}^Y$ , which depends only on the atomic masses and geometrical parameters and can be evaluated from the usual  $\underline{g}$ -vectors employed in vibrational analysis.<sup>18</sup> In this way we obtain for the general bent XYZ molecule,

$$C_{12} = -C_{21} = \mu_2 \sin\phi \quad (47a)$$

$$C_{13} = -C_{31} = -\mu_1 \rho_{31} - \mu_3 (\rho_{31} - \rho_{32} \cos\phi) \quad (47b)$$

$$C_{23} = -C_{32} = -\mu_2 \rho_{32} - \mu_3 (\rho_{32} - \rho_{31} \cos\phi), \quad (47c)$$

and  $C_{11} = C_{22} = C_{33} = 0$ . For the bent  $XY_2$  case, the calculation of  $\zeta^Y$  reduces to a very simple formula, given by Meal and Polo,<sup>17</sup> which requires only a knowledge of the harmonic stretching force constants, and not the normal coordinate transformation or the  $\underline{L}$  matrix elements.

The calculations which have been carried out for several bent  $XY_2$  molecules<sup>4,7,8,10</sup> (listed as "exact" in Table II) have given good agreement with the observed inertial defects. For the ground vibrational state, the calculated inertial defects are not very sensitive to substantial variations in the vibrational force constants and Coriolis coupling parameters. Thus it is of interest to examine approximate forms of Eqs. (45) which require only the vibrational frequencies.

According to Eq. (26), the Coriolis coupling constants which link modes  $w_s$  and  $w_t$  represent the components of a vector cross product,

$$\zeta_{st} = \sum_i m_i (\delta \underline{r}_{is} \times \delta \underline{r}_{it}), \quad (48)$$

where the atomic displacement vectors for each normal mode have the components  $\partial \alpha_i / \partial Q_s$ , etc. As noted by Darling and Dennison,<sup>4</sup> in the normal vibrations of  $H_2O$  and other symmetric hydride

molecules, the hydrogen atoms move almost parallel (for  $\omega_1$  and  $\omega_3$ ) or perpendicular (for  $\omega_2$ ) to the bonds. The Coriolis coupling between the bending mode and the antisymmetric stretch is then almost maximal ( $\zeta_{23}^c \approx 1$ ), and there is little coupling between the symmetric and antisymmetric stretching modes ( $\zeta_{13}^c \approx 0$ ). This situation persists for other  $XY_2$  molecules and even XYZ molecules as long as the central atom is much heavier than the end atoms. On the other hand, if the central atom is the lightest one, or all three have about the same mass, as in  $Cl_2O$  or  $O_3$ , the atomic displacements deviate considerably from the bond directions and the Coriolis coupling between the various modes becomes roughly uniform (within the restrictions imposed by the molecular symmetry).

For the ground vibrational state, the limit of "dominant coupling" ( $\zeta_{23} \approx 1$ ) gives

$$\Delta \approx 4K \left( \frac{1}{\omega_2} + \frac{1}{\omega_3} - \frac{1}{\omega_2 + \omega_3} \right) \quad (49a)$$

whereas the limit of "uniform coupling" gives

$$\Delta \approx \frac{4K}{3} \left( \frac{2}{\omega_1} + \frac{2}{\omega_2} + \frac{2}{\omega_3} - \frac{1}{\omega_1 + \omega_2} - \frac{1}{\omega_2 + \omega_3} - \frac{1}{\omega_1 + \omega_3} \right) \quad (49b)$$

for an XYZ molecule [each  $\zeta^2$  factor in Eq. (45c) is replaced by  $\frac{1}{3}$ ] or

$$\Delta \approx 2K \left( \frac{1}{\omega_1} + \frac{1}{\omega_2} + \frac{2}{\omega_3} - \frac{1}{\omega_2 + \omega_3} - \frac{1}{\omega_1 + \omega_3} \right) \quad (49c)$$

for an  $XY_2$  molecule (each  $\zeta^2 \approx \frac{1}{2}$ ). In view of the sum rule for the Coriolis coefficients, Eq. (45b), these approximations may both be written in the form

$$\Delta = 4K/\Omega_{SS'} \quad (50a)$$

by replacing the frequency terms in Eq. (45c) with an average value,

$$\frac{1}{\Omega_{SS'}} = \left\langle \frac{1}{\omega_S} + \frac{1}{\omega_{S'}} - \frac{1}{\omega_S + \omega_{S'}} \right\rangle_{Av} \quad (50b)$$

In the dominant coupling limit, only one term is retained; in the uniform coupling limit all the terms are averaged, three terms in the case of an XYZ molecule, two for an  $XY_2$  molecule.

In Fig. 1 and Table II the results obtained from these approximations are compared with the observed inertial defects for triatomic molecules. As expected, the dominant coupling approximation (open squares in Fig. 1) is quite accurate for the hydride molecules, but considerably overestimates the inertial defects for other molecules, whereas the uniform coupling approximation (open circles) is often an underestimate. For either approximation the bending frequency predominates in the average value of Eq. (50b), as indicated in the upper panel of Fig. 1; hence an even simpler approximation is

$$\Delta \approx 4K/\omega_2 \quad (50c)$$

This usually falls between the dominant and uniform coupling limits (heavy dashed diagonal line in Fig. 1).

For an excited vibrational state the inertial defect is more sensitive to the nature of the Coriolis coupling. If the bending mode is excited, the approximations corresponding to Eqs. (49) and (50) give

$$\Delta \approx \Delta_0 + (8K/\omega_2)W_{32} \quad (49a')$$

$$\Delta \approx \Delta_0 + \frac{4}{3}(2K/\omega_2)(W_{12} + W_{32}) \quad (49b')$$

$$\Delta \approx \Delta_0 + (4K/\omega_2)(W_{12} + W_{32}) \quad (49c')$$

and

$$\Delta \approx 3\Delta_0, \quad (50c')$$

where  $\Delta_0$  is the inertial defect for the ground state. Again, the data for hydride molecules<sup>8</sup> are found to conform accurately to the dominant coupling approximation, Eq. (49a'). The  $S_2O$  molecule (bottom entry in Table II) is the only other example available at present.

#### Planar Tetratomic Molecules

For a planar tetratomic molecule with no other symmetry elements there are 20 distinct nonvanishing Coriolis coefficients and hence the general expression for the inertial defect, Eqs. (34b) and (35b), has 41 terms. The exact calculation is still quite arduous for molecules with  $C_{2v}$  symmetry such as formaldehyde, which have 11 Coriolis constants. However, recently Oka and Morino<sup>9</sup> have carried through a complete normal coordinate analysis and obtained good agreement with the observed inertial defects for several of these molecules. Their calculations enable us to make a detailed analysis of simple approximations similar to Eqs. (50), which we again find to yield surprisingly



good results (see Fig. 2 and Table III).

For the ground vibrational state the general formula gives

$$\Delta = \Delta^+ + \Delta^- \quad (51a)$$

where

$$\Delta^+ = 4K \sum_s \sum_{s'} (\zeta_{ss'}^c)^2 \left( \frac{1}{\omega_s} + \frac{1}{\omega_{s'}} - \frac{1}{\omega_s + \omega_{s'}} \right) \quad (51b)$$

$$\Delta^- = \frac{-2K}{\omega_6} - 4K \sum_s [(\zeta_{s6}^a)^2 + (\zeta_{s6}^b)^2] \left( \frac{1}{\omega_s} - \frac{1}{\omega_s + \omega_6} \right), \quad (51c)$$

and the sum rules are

$$\sum_s \sum_{s'} (\zeta_{ss'}^c)^2 = 2 \quad (52a)$$

$$\sum_s (\zeta_{s6}^a)^2 = 1; \quad \sum_s (\zeta_{s6}^b)^2 = 1. \quad (52b)$$

Here  $s, s' = 1$  to  $5$  denote the in-plane modes ( $s < s'$  in the double sums) and  $\omega_6$  is the frequency of the out-of-plane bending mode. For molecules with  $C_{2v}$  symmetry  $\zeta_{ss'}^c$  is nonzero only for the coupling of the  $A_1$  modes ( $s = 1, 2, 3$ ) and the  $B_1$  modes ( $s' = 4, 5$ );  $\zeta_{s6}^a$  is nonzero only for  $B_1$  modes, and  $\zeta_{s6}^b$  only for  $A_1$  modes (provided the two-fold symmetry axis is the  $a$ -axis; the reverse holds if it is the  $b$ -axis). Thus for  $C_{2v}$  molecules Eq. (51a) reduces to 12 terms rather than 21 and the sum rules become

$$\sum_s (\zeta_{s4}^c)^2 = 1; \quad \sum_s (\zeta_{s5}^c)^2 = 1 \quad (53a)$$

and

$$\sum_{s'} (\zeta_{s'6}^a)^2 = 1; \quad \sum_s (\zeta_{s6}^b)^2 = 1. \quad (53b)$$

From these sum rules and the average frequency approximation we obtain, for the general case,

$$\Delta^+ \approx 8K/\Omega_{s5}, \quad (54a)$$

$$\Delta^- \approx -(2K/\omega_6) - (4K/\Omega_{s6a}) - (4K/\Omega_{s6b}), \quad (54b)$$

and, for  $C_{2v}$  symmetry,

$$\Delta^+ \approx (4K/\Omega_{s4}) + (4K/\Omega_{s5}) \quad (55a)$$

$$\Delta^- \approx -(2K/\omega_6) - (4K/\Omega_{s6a}) - (4K/\Omega_{s6b}), \quad (55b)$$

where the  $\Omega_{s5}$  terms are defined as in Eqs. (50), and the  $\Omega_{s6}$  terms are given by

$$\frac{1}{\Omega_{s6}} = \left\langle \frac{1}{\omega_s} - \frac{1}{\omega_s + \omega_6} \right\rangle_{Av}. \quad (56)$$

In Eq. (53a) ten terms contribute to the average frequency and in (53b) five terms to each of the two average frequencies. Thus it is quite unlikely that the dominant coupling approximation would be a realistic approximation for an unsymmetrical molecule. In Eqs. (55), it will sometimes apply in the  $\Omega_{s6}$  average, to which only two terms contribute, but will hold less often for the other  $\Omega$ 's, to which three terms contribute.

Situations where dominant coupling should apply can usually be recognized from a qualitative inspection of the form of the normal coordinates. For example, Eq. (48) indicates that for  $X_2CO$  or  $XNO_2$  molecules  $\Omega_{s6}^a$  should be small, since in the  $\omega_5$  mode the "outside" atoms (X or O atoms) move approximately parallel to the symmetry axis (a-axis) and the contributions from the axial atoms tend to cancel out.<sup>19</sup>

Fig. 2 and Table III include all the available experimental data on ground state inertial defects of planar tetratomic molecules. The observed values (solid triangles in Fig. 1) are

again found to correlate with  $4K/\omega_1$  (heavy dashed diagonal line), where  $\omega_1$  denotes the lowest in-plane bending frequency, but several examples show marked deviations, particularly  $F_2CO$ ,  $ClNO_2$ , and  $BrF_3$ . The dominant coupling approximation (open squares) evaluated for the two lowest in-plane frequencies is given merely to provide an empirical comparison; except for  $F_2CO$ , it is much too high, as would be expected since this makes no allowance for the negative  $\Delta^-$  contribution. The uniform coupling approximation (open circles) is again an underestimate and is quite low for the  $X_2CO$ ,  $XNO_2$ , and  $BrF_3$  molecules.

However, a comparison with the normal coordinate calculations which Oka and Morino<sup>9</sup> carried out for six  $C_{2v}$  molecules shows that the uniform approximation actually gives fairly reliable results for the individual terms in Eqs. (55) except for the  $\Omega_{s,6}$  average in those cases for which  $\zeta_{56}^a$  is expected to be very small. Since  $\omega_4$  is considerably larger than  $\omega_5$  in these cases, the uniform coupling approximation makes  $\Delta^-$  much too negative, as shown in Fig. 3. Results very close to the "exact" calculations are obtained simply by using a mixed coupling approximation (crosses in Figs. 2 and 3) which employs dominant coupling ( $\zeta_{46}^a = 1$ ) for the  $\Omega_{s,6}$  term and uniform coupling for the others.

An exception to this is the  $Br_2CO$  molecule, for which the uniform coupling approximation considerably overestimates the  $\Omega_{s,4}$  term, as seen in Fig. 3. Again, the discrepancy could be anticipated, since qualitative considerations indicate that  $\zeta_{14}^c$  should approach unity for  $X_2CO$  molecules as the mass of the X atoms increases. However, in this case we find that no simple correction

is feasible. By use of the sum rule,

$$\frac{4K}{\Omega_{s4}} = \frac{4K}{\omega_4} + 4K \sum_s (\zeta_{s4}^c)^2 \left( \frac{1}{\omega_s} - \frac{1}{\omega_s + \omega_4} \right). \quad (57)$$

Although  $\zeta_{14} \gg \zeta_{24}$  and  $\zeta_{34}$ , this is offset by the frequency factors, (see Fig. 4) since  $\omega_1$  and  $\omega_4 \gg \omega_2$  and  $\omega_3$ , and all three terms in the sum give comparable contributions. Thus the dominant coupling approximation would considerably overestimate the sum and uniform coupling considerably underestimate it; the values obtained are 0.011 and 0.140, respectively, compared with  $0.032 \text{ amu } \text{Å}^2$  from use of the calculated Coriolis constants. Fortunately, the other term,  $4K/\omega_4 = 0.089 \text{ amu } \text{Å}^2$ , is independent of the nature of the coupling, and is large enough to damp out much of the uncertainty in the total result. For the other molecules shown in Fig. 3, it is also found that in the various averages one of the three contributing Coriolis constants often outweighs the others, but the frequency distributions and damping effects are such that the deviations in  $\Omega_{s4}$  and  $\Omega_{s5}$ , for example practically balance out.

The only other molecule for which the experimental result differs from the uniform or mixed coupling approximation by more than about 10% is  $\text{BrF}_3$ . In this case, the approximations agree closely with the "exact" calculation (open triangle in Fig. 2), and the disagreement with the experimental inertial defect may be due to inaccuracies in the vibrational assignment. For the other molecules considered here the observed frequencies were used, but the assignment for  $\text{BrF}_3$  is tentative and was derived

mainly from a normal coordinate calculation based on the  $\text{ClF}_3$  force constants.<sup>20</sup>

It is interesting to note that for the unsymmetrical molecules in both Figs. 1 and 2 the simple uniform coupling approximation gives particularly good results, only slightly low.

Another empirical approximation applicable to certain unsymmetrical molecules was suggested by Oka and Morino<sup>9</sup>, who take the geometric mean of the inertial defects for related symmetric molecules. These values, which are listed under "exact calculation" in Tables II and III, come out a bit high.

At first glance it is surprising that even for the tetratomic molecules, for which several terms appear in Eqs. (54) and (55), the simple  $4K/\omega_\ell$  approximation should be so nearly equivalent to uniform coupling. Some qualitative features that contribute to this may be understood from Fig. 4. As illustrated by the upper curve, the effective frequency  $\omega_{SS'}$ , associated with the coupling of two in-plane modes, defined by

$$\frac{1}{\omega_{SS'}} = \left( \frac{1}{\omega_S} + \frac{1}{\omega_{S'}} - \frac{1}{\omega_{S+S'}} \right), \quad (58)$$

is such that  $\omega_{SS'}$  is always less than either  $\omega_S$  or  $\omega_{S'}$ . The frequency  $\Omega_{SS'}$ , obtained from averaging a set of these terms lies between the minimum and maximum value of  $\omega_{SS'}$ . In the absence of strong contrary bias by the Coriolis constants, the inverse averaging favors the minimum value of  $\omega_{SS'}$ , which lies between  $\frac{2}{3}\omega_\ell$  and  $\omega_\ell$ . The former limit obtains when the next highest frequency is near  $\omega_\ell$ , the latter when it is very far above  $\omega_\ell$ . Thus, if all the coupled terms are averaged, we may expect  $\Omega_{SS'}$  to be near  $\omega_\ell$  and hence  $\Delta^+ \approx 8K/\omega_\ell$ . As seen in

Fig. 3, this holds accurately for  $\text{H}_2\text{CO}$ ,  $\text{D}_2\text{CO}$ , and  $\text{F}_2\text{CO}$ . For the heavier molecules the ratios of the other frequencies to  $\omega_\ell$  increase, consequently  $\Omega_{SS}$  becomes substantially larger than  $\omega_\ell$ , and  $\Delta^+$  falls well below  $8K/\omega_\ell$ . In the exact calculations, this trend is accentuated by the Coriolis bias illustrated below Eq. (57). A similar rough analysis accounts for the qualitative behavior of the terms involving the out-of-plane vibration. The lower curve in Fig. 4 shows that only those in-plane modes with frequencies less than or comparable to  $\omega_6$  will give substantial contributions. This usually includes about half of the in-plane modes (see upper panel of Fig. 2). Also, to allow for the rapid drop-off of the frequency factor in Fig. 4, we roughly approximate the contribution of these modes as half of that for the lowest mode. This gives

$$\Delta^- \approx -\frac{2K}{\omega_6} - \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\frac{8K}{\omega_\ell}, \quad (59)$$

which is  $-4K/\omega_\ell$  when  $\omega_\ell \approx \omega_6$  and is less negative when  $\omega_\ell < \omega_6$ , in accord with the results of Fig. 3. Although these arguments are quite crude, they do closely simulate the behavior of the exact calculations and also emphasize that the simple  $4K/\omega_\ell$  approximation actually represents an average over all the frequencies rather than neglect of all except  $\omega_\ell$ .

The inertial defects of the  $\omega_3$  and  $\omega_5$  excited vibrational states (the lowest in-plane modes) of  $\text{F}_2\text{CO}$  have been measured recently.<sup>21</sup> These frequencies differ by only  $43 \text{ cm}^{-1}$  and good agreement with the data for both states is obtained from a "resonant coupling" approximation,

$$\Delta \approx \Delta_0 + (8K/w_s)(\zeta_{ss'}^c)^2 [\omega_{s'}^2 / (\omega_{s'}^2 - \omega_s^2)], \quad (60)$$

(where  $s' = 5, 3$  for  $s = 3, 5$ ). This omits all terms in the general expression, Eq. (34b), except those with  $(\omega_3^2 - \omega_5^2)$  in the denominator. The experimental inertial defects correspond to  $(\zeta_{35}^c)^2 = 0.741$  and  $0.724$  for the  $s = 3$  and  $s = 5$  states, compared with the value  $0.647$  obtained from the normal coordinate analysis.<sup>9</sup>

### APPLICATIONS TO STRUCTURE ANALYSIS

The errors and inconsistencies introduced in structure analysis by the neglect of inertial defects can be quite substantial.<sup>22</sup> Often these can be markedly reduced by the use of  $\Delta$ 's having only the 10-20% accuracy given by the simple  $4K/w_s$  approximation. In particular, the magnitude of the observed inertial defect usually offers the most conclusive test of the planarity of a molecule.<sup>9</sup> Here we shall consider examples of non-planar molecules for which Eq. (43\*) may be used to determine the average value of the distance between a pair of out-of-plane hydrogen atoms. In these cases the hydrogen parameters derived from the effective moments of inertia show anomalously large changes on isotopic substitution. These variations arise primarily from the vibrations of heavy in-plane atoms rather than changes in the average hydrogen coordinates,<sup>22</sup> and they disappear when the inertial defect correction is included.

X<sub>2</sub>YZ<sub>2</sub> Molecules

For the CH<sub>2</sub>Cl<sub>2</sub> molecule, the average out-of-plane coordinate (y-coordinate) of the H atoms is given by

$$I_a + I_b - I_c = 4m_H \langle y_H \rangle^2 - \Delta_y (\text{har}). \quad (61)$$

The inertial defect  $\Delta_y$  perpendicular to the ClCCl plane (xz plane) is dominated by the low-frequency Cl atom vibrations, in particular the ClCCl symmetrical bend at  $\omega_4 = 283 \text{ cm}^{-1}$ . Since the next lowest vibration is at  $704 \text{ cm}^{-1}$ , we expect the inertial defect to be close to  $4K/\omega_4 = 0.238 \text{ amu A}^2$ .

Another estimate of  $\Delta_y$  (har) may be obtained from the apparent difference in the H and D coordinates derived from the effective moments of inertia of the CH<sub>2</sub>Cl<sub>2</sub><sup>35</sup> and CD<sub>2</sub>Cl<sub>2</sub><sup>35</sup> species. If Eq. (61) is used with  $\Delta_y = 0$ , the effective HH distance is calculated to be 0.023 A shorter than the DD distance.<sup>23</sup> However, the difference in the true average coordinates is expected to make the HH distance longer than the DD by about 0.006 A, as in methane.<sup>12</sup> The presence of the inertial defect is thus the main source of the observed isotopic difference in the effective parameters. Since deuteration has little effect on  $\omega_4$ , we may neglect the isotopic variation of  $\Delta_y$  and evaluate it by applying Eq. (61) to the effective moments of CH<sub>2</sub>Cl<sub>2</sub><sup>35</sup> and CD<sub>2</sub>Cl<sub>2</sub><sup>35</sup>. In a previous treatment,<sup>22</sup> this was done assuming  $\langle y_H \rangle = \langle y_D \rangle$ . A better estimate is obtained by transferring the methane result, and this gives  $\Delta_y = 0.19 \text{ amu A}^2$ . Unfortunately, there is an uncertainty of several hundredths of an Angstrom from the uncertainties of 1 Mc



in the rotational constants.<sup>23</sup> For example, if the data for the  $\text{CH}_2\text{Cl}^{35}\text{Cl}^{37}$  and  $\text{CD}_2\text{Cl}^{35}\text{Cl}^{37}$  species are used, we obtain  $\Delta_y = 0.24$  amu  $\text{A}^2$ .

The average H atom coordinates calculated for the various estimates of the inertial defect are given in Table IV.

A similar calculation has been done for  $\text{SiH}_2\text{F}_2$ , with  $\omega_4 = 322 \text{ cm}^{-1}$ . Again we have adopted the methane variation in analyzing the isotopic data.<sup>24</sup> Rotational constants for both  $\text{SiH}_2\text{F}_2$  and  $\text{SiD}_2\text{F}_2$  are also available for the first excited state of the  $\omega_4$  vibration. For this in Eq. (61) we take  $\Delta_y \approx 3\Delta_0$ , where  $\Delta_0$  is the inertial defect of the ground state; also we assume that  $\langle y_H \rangle - \langle y_D \rangle$  is the same as in the ground state, since  $\langle y_H \rangle$  is expected to be relatively insensitive to the  $\text{FSiF}$  bending mode. The results of these calculations are also included in Table IV.

### $\text{CH}_3\text{CXO}$ Molecules

Another class of molecules to which Eq. (61) may be applied has a methyl group attached to a planar framework so that only two of the methyl hydrogens are out-of-plane. In the series of acetyl molecules  $\text{CH}_3\text{CXO}$ , with  $X = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CN}, \text{etc.}$ , the effective HH distance of the methyl group is found to decrease markedly as X becomes larger.<sup>22</sup> Thus in acetaldehyde the effective HH distance is 1.761 Å whereas in acetyl chloride it is 1.712 Å and in acetyl cyanide 1.703 Å. This apparent decrease in the size of the methyl group disappears when the inertial defect is taken into account, and the trend in the effective HH distance is seen to be due to the increase in  $\Delta_y$  as the vibrations involving the X atom shift to lower frequencies.

The calculations are summarized in Table V. Again the estimates of  $\Delta_y$  obtained from rotational data for the  $\text{CH}_3\text{CXO}$  and  $\text{CD}_3\text{CXO}$  species agree satisfactorily with those from vibrational frequencies. The latter estimates include a contribution of  $-0.015 \text{ amu } \text{A}^2$  from the out-of-plane torsion (internal rotation) of the methyl group; this was obtained from an approximate treatment given previously.<sup>25</sup> For acetaldehyde the contribution of in-plane vibrations was taken as  $4K/\omega_2$ , with  $\omega_2 = 512 \text{ cm}^{-1}$ , the lowest in-plane frequency, since the next lowest is at  $911 \text{ cm}^{-1}$ . For the acetyl halides, the lowest two in-plane frequencies were used: in  $\text{CH}_3\text{COF}$ , 434 and  $590 \text{ cm}^{-1}$ ; in  $\text{CH}_3\text{COCl}$ , 348 and  $436 \text{ cm}^{-1}$ ; and in  $\text{CH}_3\text{COBr}$ , 304 and  $338 \text{ cm}^{-1}$ .

In addition to eliminating the apparent shrinkage in the methyl group size for the heavier members of the acetyl series, the inertial defect corrections yield parameters quite close to those for methyl groups in other molecules. For example,  $\langle y_H \rangle = 0.896 \text{ A}$  in methane.<sup>12</sup>

## APPENDIX

Because of the large number of references from which vibrational and rotational data were taken we have found it convenient to collect many of the references in one list. References from which vibrational data were taken are marked by V; those from which rotational data were taken are marked by R. Molecules are listed in the order in which they appear in Tables II - V.

$H_2O$ ,  $HDO$ ,  $D_2O$  (V,R): W. S. Benedict, N. Gailar, and E.K. Plyler, J. Chem. Phys. 24, 1139(1956).

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$H_2Se$ ,  $D_2Se$  (V,R): T. Oka and Y. Morino, J. Mol. Spectroscopy 8, 300(1962).

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Table I. Inertial defects of planar ring compounds.

Molecule	$\Delta$ (amu $\text{A}^2$ )
Pyridine <sup>a</sup>	0.032
Benzonitrile <sup>b</sup>	0.073
Furan <sup>c</sup>	0.048
Thiophene <sup>d</sup>	0.065
Thiazol <sup>e</sup>	0.073
Thiadiazole <sup>f</sup>	0.084
Pyrrole <sup>g</sup>	0.076
Fluorobenzene <sup>h</sup>	0.027

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Table II. Inertial defects of triatomic molecules ( $\text{amu } \text{\AA}^2$ ).

Molecule <sup>a</sup>	Exact Calc.	Approx. Calc. Eqs. (49) <sup>b</sup>	Calc. Eq. (50c)	Obs. $\Delta$
H <sub>2</sub> O	0.0460	0.0459	0.0408	0.0486
HDO	0.0545 <sup>c</sup>	0.0548	0.0468	0.0537
D <sub>2</sub> O	0.0627	0.0635	0.0557	0.0648
H <sub>2</sub> S	0.0631	0.0631	0.0555	0.0660
D <sub>2</sub> S	0.0879	0.0861	0.0751	----
H <sub>2</sub> Se	0.0736	0.0739	0.0652	0.0744
D <sub>2</sub> Se	0.1034	0.1032	0.0910	0.1045
NO <sub>2</sub>	0.0936	0.0849	0.0891	0.072
O <sub>3</sub>	0.1107	0.1077	0.0957	0.1018
SO <sub>2</sub>	0.1376	0.1439	0.1303	0.1348
ClO <sub>2</sub>	0.1602	0.1652	0.1481	0.1561
F <sub>2</sub> O	0.1496	0.1456	0.1463	0.1491
Cl <sub>2</sub> O	0.187	0.179	0.211	0.197
Cl <sub>2</sub> S	0.286	0.276	0.324	----
NOF	----	0.134	0.129	0.113
NSF	----	0.173	0.184	0.187
S <sub>2</sub> O	----	0.173	0.174	0.176
S <sub>2</sub> O <sup>d</sup>	----	0.475	0.522	0.507

<sup>a</sup>References are given in the Appendix. The calculated values represent the vibrational contributions to the inertial defect, and neglect small contributions from centrifugal distortion and electronic-rotational interactions. The data refer to the most abundant isotopic species.

<sup>b</sup>For the hydride molecules, SO<sub>2</sub> and ClO<sub>2</sub> the dominant coupling approximation was used; for all others the uniform coupling approximation was used.

<sup>c</sup>Approximated by the geometric mean of  $\Delta$  (H<sub>2</sub>O) and  $\Delta$  (D<sub>2</sub>O); see reference 9.

<sup>d</sup>For the excited bending mode; the approximate values were obtained from Eqs. (49b') and (50c') respectively.

Table III. Inertial defects of planar tetratomic molecules ( $\text{amu } \text{A}^2$ ).

Molecule <sup>a</sup>	Exact Calc.	Approx. Calc.		Obs. $\Delta$
		Av. Freq. <sup>b</sup>	$4K/w_1$	
H <sub>2</sub> CO	0.0597	0.0548	0.0542	0.0574
HDCO	0.0711	0.0617	0.0648	0.0679
D <sub>2</sub> CO	0.0810	0.0691	0.0682	0.0777
HFCO	0.0919	0.0861	0.1021	0.0903
DFCO	0.1078	0.0932	0.1026	0.1020
F <sub>2</sub> CO	0.1554	0.1625	0.1153	0.1556
Cl <sub>2</sub> CO	0.2628	0.276	0.237	0.252
Br <sub>2</sub> CO	0.3296	0.417	0.372	---
FNO <sub>2</sub>	0.159	0.160	0.147	---
ClNO <sub>2</sub>	0.215	0.220	0.184	0.208
ClF <sub>3</sub>	0.202	0.119	0.207	0.194
BrF <sub>3</sub>	0.220	0.214	0.225	0.260

<sup>a</sup>References are given in the Appendix. The "exact" calculations are from reference 9; the values for HDCO, HFCO, and DFCO were obtained from the geometric mean approximation, however, and for FNO<sub>2</sub>, ClF<sub>3</sub>, and BrF<sub>3</sub> substantial approximations in the normal coordinate analyses were necessary.

<sup>b</sup>The uniform coupling approximation was used for all terms in Eqs. (54) and (55) except for the  $\Omega_{s,6}$  terms for the X<sub>2</sub>CO and XNO<sub>2</sub> molecules, for which the dominant coupling approximation was used.



Table IV. Calculations on  $X_2YZ_2$  molecules.<sup>a</sup>

Method	$\Delta$	$\langle y_H \rangle$
$CH_2Cl_2$		
b	0.24 amu $\text{\AA}^2$	0.913 $\text{\AA}$
c	0.19	0.906
d	0.24	0.912
$SiH_2F_2$		
b	0.209	1.240
e	0.207	1.240
f	0.192	1.243

<sup>a</sup>References are given in the Appendix.

<sup>b</sup>From  $\Delta = 4K/w_4$ .

<sup>c</sup>From  $CH_2Cl_2^{35}$  and  $CD_2Cl_2^{35}$ .

<sup>d</sup>From  $CH_2Cl^{35}Cl^{37}$  and  $CD_2Cl^{35}Cl^{37}$ .

<sup>e</sup>From ground state rotational data on  $SiH_2F_2$  and  $SiD_2F_2$ .

<sup>f</sup>From rotational data for the state  $v_4 = 1$  for  $SiH_2F_2$  and  $SiD_2F_2$ .

Table V. Calculations on  $\text{CH}_3\text{CXO}$  molecules.<sup>a</sup>

X	Method	$\Delta$	$\langle y_H \rangle$
H	b	0.100 amu $\text{A}^2$	0.894 A
	c	0.117	0.896
F	b	0.202	0.891
	c	0.204	0.891
Cl	b	0.249	0.891
	c	0.262	0.896
Br	b	d	d
	c	0.316	0.900

<sup>a</sup>References are given in the Appendix.

<sup>b</sup>From rotational data for  $\text{CH}_3$  and  $\text{CD}_3$  species.

<sup>c</sup>From vibrational approximation.

<sup>d</sup>No data on  $\text{CD}_3\text{COBr}$ .

## Footnotes

1. J. Kraitchman, Am. J. Phys. 21, 17(1953).
2. C.C. Costain, J. Chem. Phys. 29, 864(1958).
3. We shall use script letters to denote effective moments of inertia obtained from experimental values of spectroscopic rotational constants. The moments corresponding to a standard, rigid configuration of the atoms will be denoted by Roman I's; a superscript "e" will be added when a formula holds only for the equilibrium configuration. When no superscript is used, a formula holds for any choice of the standard configuration.
4. This quantity was first discussed by B.T. Darling and D.M. Dennison, Phys. Rev. 57, 128(1940), in their study of the H<sub>2</sub>O molecule and was termed the "quantum defect", to suggest its origin in zero-point vibration. However, as atomic spectroscopy has prior claim to this name, it seems preferable to use again the general term "inertial defect", with the convention that for planar molecules this means  $\Delta = \Delta_c$  unless  $\Delta_a$  or  $\Delta_b$  is explicitly indicated.
5. This holds in the usual approximation in which only terms linear in the vibrational quantum numbers are included in  $\Delta$ .
6. H.H. Nielsen, Revs. Mod. Phys. 23, 90(1951).
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8. T. Oka and Y. Morino, J. Mol. Spectroscopy 6, 472(1961); 8, 9(1962).

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11. D.R. Herschbach and V.W. Laurie, *J. Chem. Phys.* 37, 1668 (1962), referred to as Part I.
12. V.W. Laurie and D.R. Herschbach, *J. Chem. Phys.* 37, 1687 (1962), referred to as Part II.
13. Small contributions arising from centrifugal distortion and electronic-rotational interactions are not considered here, as these have been treated by Oka and Morino in reference 8.
14. See, for example, E.B. Wilson, J.C. Decius, and P.C. Cross, Molecular Vibrations (McGraw-Hill Book Company, New York, 1955), p. 13.
15. This statement follows from Eqs. (9) and (12) of Appendix A, Part I.
16. Molecules belonging to point groups  $C_s$ ,  $C_{nv}$ ,  $C_{nh}$ ,  $D_2$ ,  $D_{nd}$ , or  $D_{nh}$  are of this type. For  $m > 2$  such molecules possess doubly degenerate vibrations whose normal coordinates, as usually defined, may not be simply symmetric or antisymmetric to the  $\alpha\beta$  plane. Linear combinations which have this symmetry are readily constructed, however, and the discussion of the text applies to these. See, for example, G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand, Co., Inc., New York, 1945), pp. 83 - 98.
17. J. H. Meal and S.R. Polo, *J. Chem. Phys.* 24, 1126(1956).

18. Reference 14, p. 56. In Eqs. (47) the standard notation of this reference is used: The internal coordinates are  $S_1 = \delta r_{31}$ ,  $S_2 = \delta r_{32}$ , and  $S_3 = \delta \phi$ ; the vertex atom is number 3; the bond angle is  $\phi$ ; and  $\mu_i$  and  $\rho_{ij}$  are reciprocals of the atomic masses and bond lengths.
19. The qualitative form of the  $\omega_4$  and  $\omega_5$  normal vibrations for these molecules corresponds approximately to the sum and difference of the diagrams given on page 65 of reference 16 (see also page 171), as these are strongly "mixed" unless the outside atoms are hydrogens.
20. H.H. Claassen, B. Weinstock, and J.G. Malm, J. Chem. Phys. 28, 285(1958).
21. V.W. Laurie and D.T. Pence, J. Mol. Spectroscopy 10, 155(1963).
22. V.W. Laurie, J. Chem. Phys. 28, 704(1958).
23. R.J. Myers and W.D. Gwinn, J. Chem. Phys. 20, 1420(1952).
24. Although there is no experimental data on  $\langle y_H \rangle - \langle y_D \rangle$  for Si compounds, the weaker bonding might be expected to make the isotopic difference somewhat larger than for C compounds. However, the use of 0.004 A instead of the 0.003 A obtained from methane would increase the H coordinates given for  $\text{SiH}_2\text{F}_2$  in Table IV by only 0.002 A.
25. D.R. Herschbach, J. Chem. Phys. 31, 91(1959).

## Captions for Figures

- Fig. 1. Experimental inertial defects (solid triangles) compared with values calculated from the dominant coupling approximation (open squares) and the uniform coupling approximation (open circles). Light dashed lines show the rough correlation between these approximations and the bending frequency,  $\omega_2$ ; the heavy dashed line is the simple  $4K/\omega_2$  approximation. The upper panel gives the vibrational frequencies for each molecule (solid circles or squares) and the average frequencies (open circles) which correspond to  $\Omega_{SS}$ , for the uniform coupling approximation.
- Fig. 2. Comparison of experimental inertial defects with approximate calculations. Notation is defined under Fig. 1 or in the text.
- Fig. 3. Comparison of results obtained from the complete normal coordinate calculations of Oka and Morino<sup>9</sup> (triangles) with the uniform coupling approximation (circles) and the mixed coupling approximation (crosses). Solid figures give the total inertial defect; open figures in the upper and lower panels give the  $\Delta^+$  and  $\Delta^-$  contributions. The dotted lines are proportional to the reciprocal of the lowest in-plane frequency, and diamonds give the leading term in the  $\Delta^-$  contribution,  $-2K/\omega_6$  for the out-of-plane bending frequency.
- Fig. 4. Dimensionless plot of frequency terms which contribute to the inertial defect. The ordinate scale is in multiples of  $4K/\omega_l$ , where  $\omega_l$  denotes the frequency of the lower of the two coupled modes. The upper abscissa scale gives the ratio of  $\omega_l$  to the higher frequency.

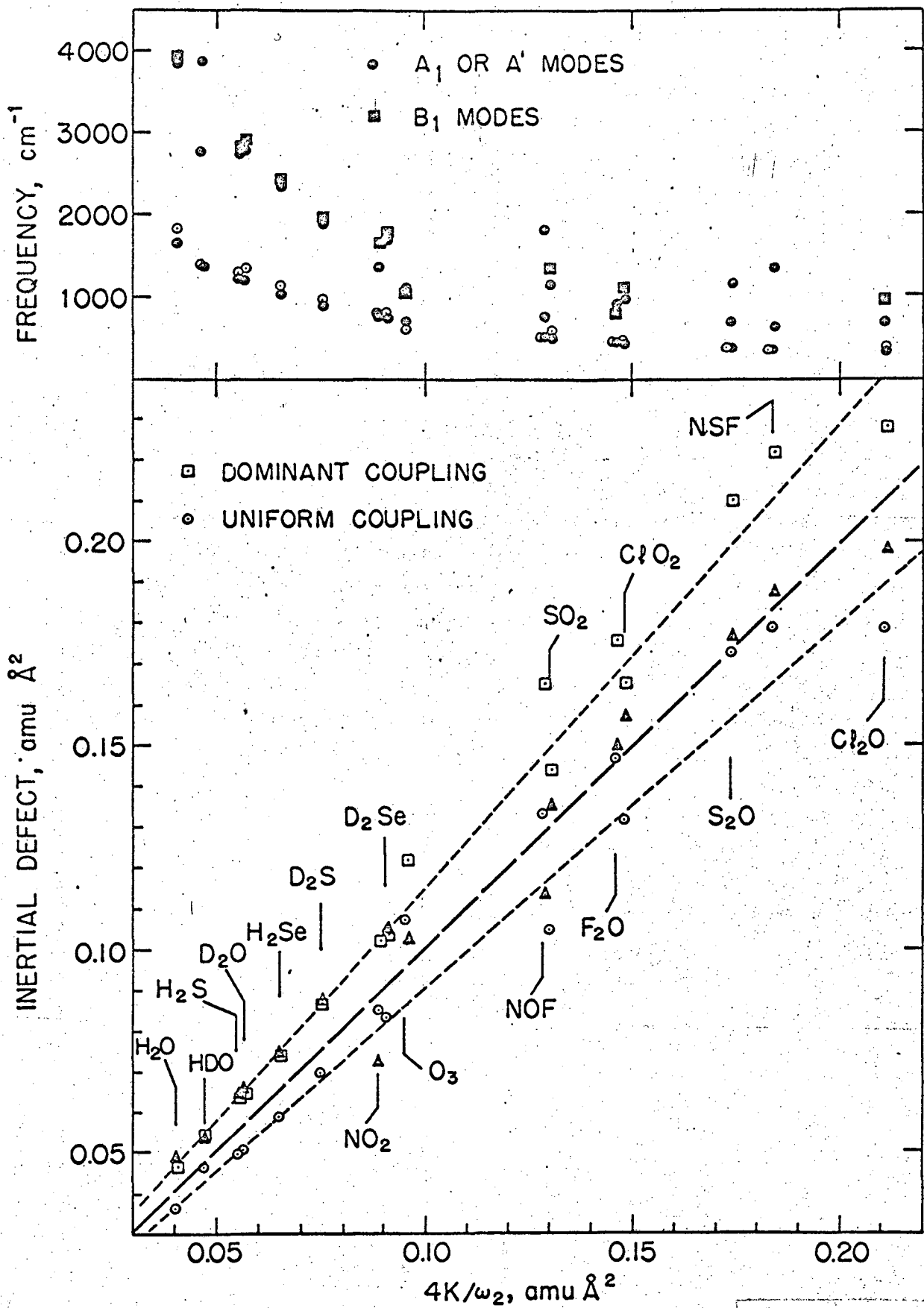


Fig. 1

MU-33218

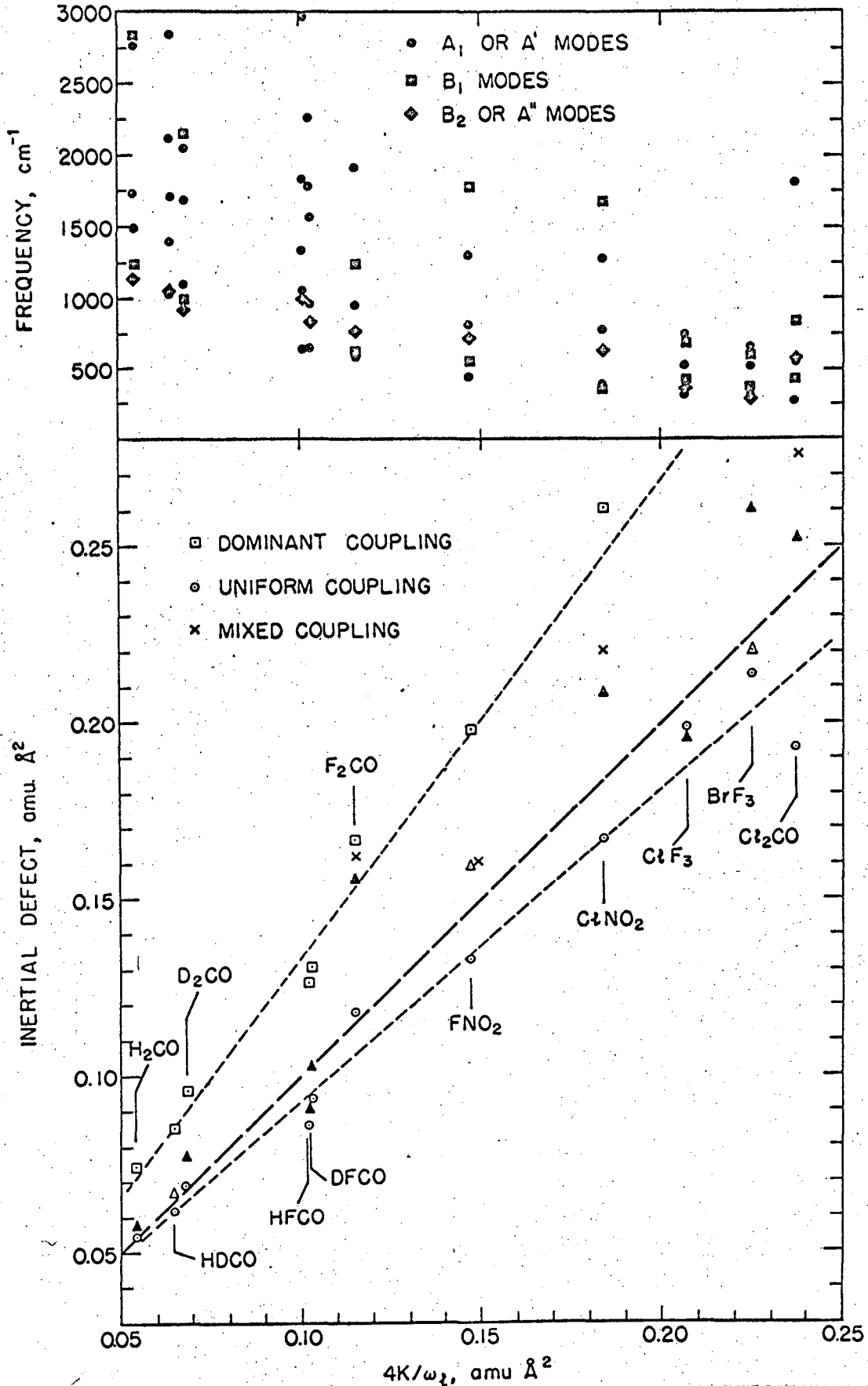


Fig. 2

MU-33219



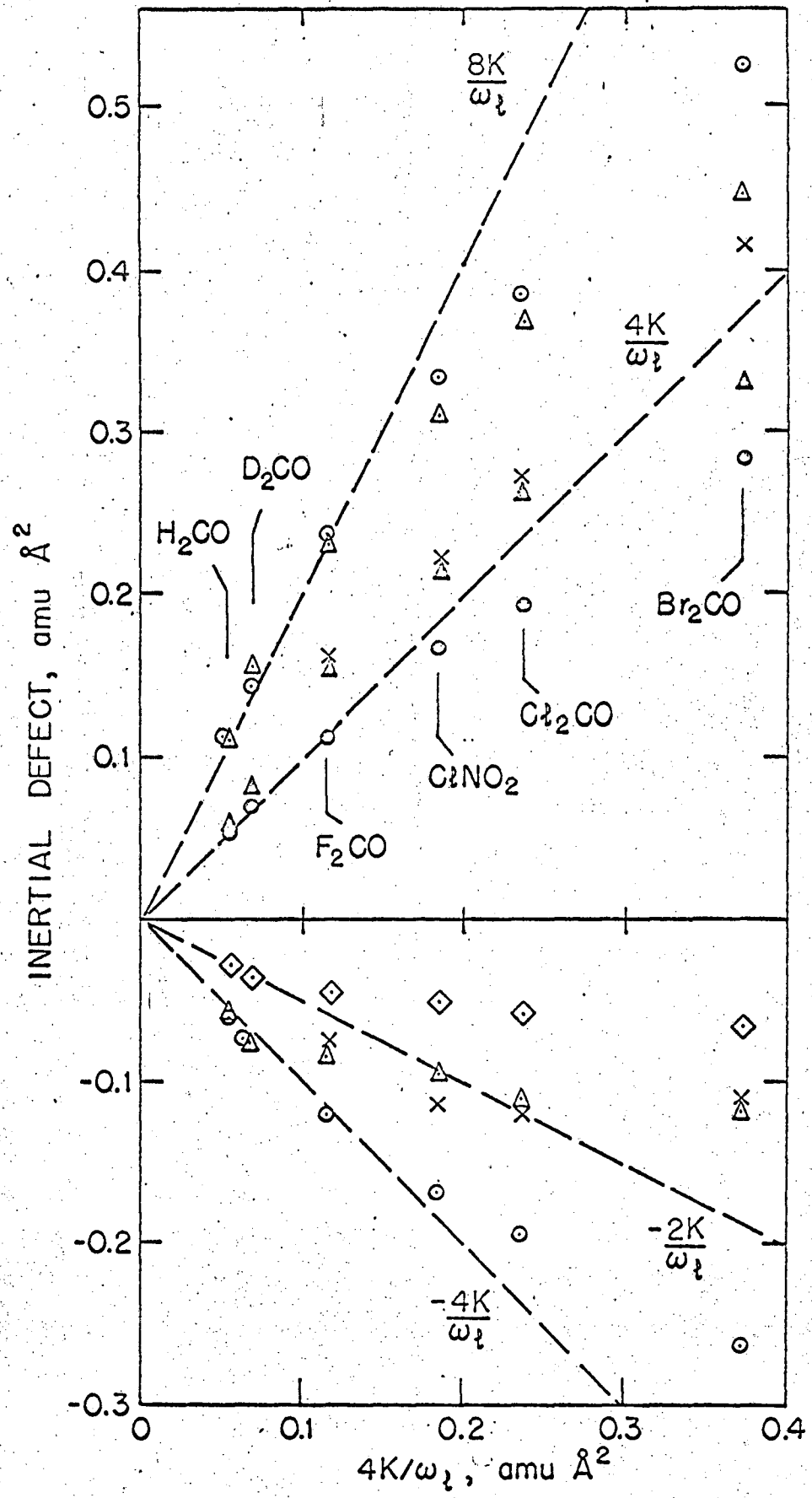


Fig. 3

MU-33220

*Lorchbach and Laurie - Fig. 3*

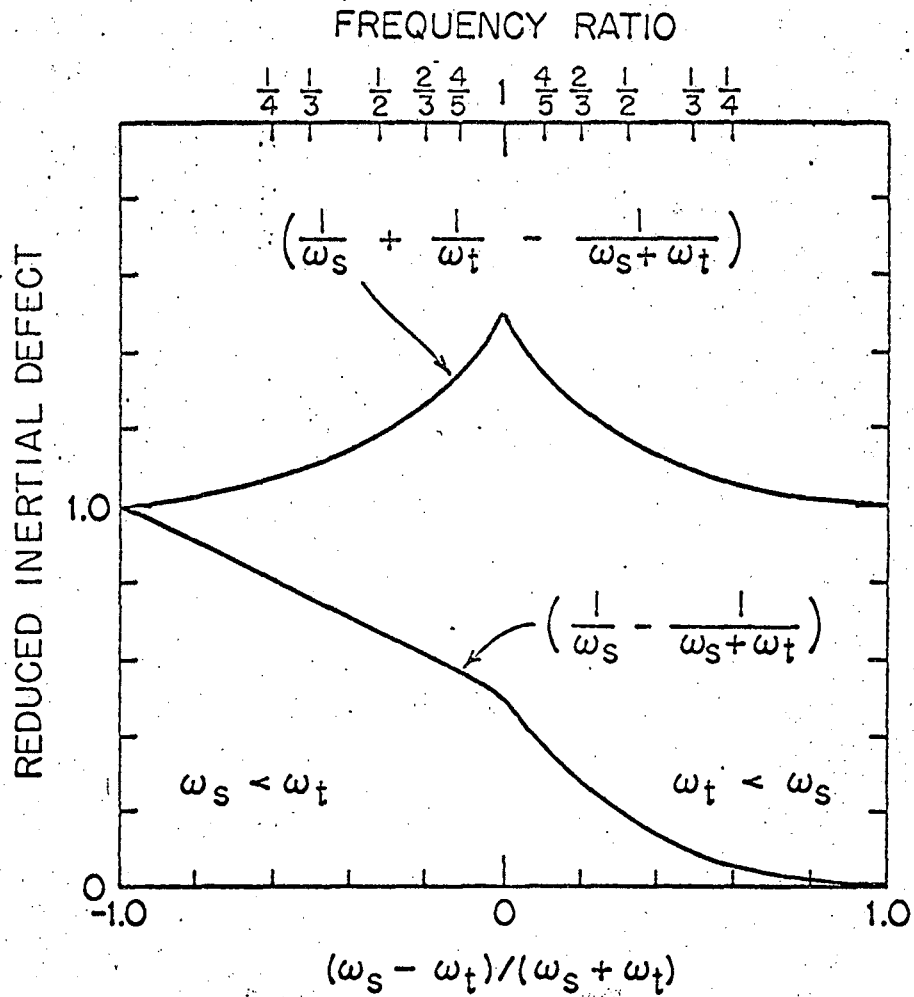


Fig. 3.

MU-33221

Herschbach and Laurie - Fig. 4

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