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May 1962

INFLUENCE OF VIBRATIONS ON MOLECULAR STRUCTURE DETERMINATIONS.

II. AVERAGE STRUCTURES DERIVED FROM SPECTROSCOPIC DATA.*

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Abstract

Formulas are given which enable structural parameters for the average molecular configuration in the ground vibrational state to be calculated for some simple types of molecules. The data required are the observed effective moments of inertia and harmonic force constants. No knowledge of anharmonic constants is necessary. The average structural parameters have a well defined physical meaning and are directly comparable with diffraction results. Polyatomic molecules for which explicit calculations are given are CO_2, CS_2, H_2O, SO_2, O_3, NO_2, CH_4, HCN, and C_2H_2. It is found that the average bond lengths involving H are usually 0.003-0.005 A longer than the corresponding D bond. For bonds involving heavier elements isotopic differences are smaller but nonetheless significant. Implications of the results for the general problem of structural determination are discussed.

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In Part I of this study[1] it has been shown that a good approximation to the moments of inertia of the average configuration of a molecule can be derived from the effective spectroscopic moments without knowledge of anharmonic potential constants. The effective moment of inertia for the ground vibrational state is related to the equilibrium moment by[2]

$$I_\alpha^o = I_\alpha^e + \frac{1}{2}\,\Sigma_s d_s \epsilon_s^\alpha\,, \tag{1}$$

where each vibrational mode (of degeneracy d_s) contributes a term. The vibration-rotation parameters ϵ_s^α may be separated into harmonic and anharmonic contributions,

$$\epsilon_s^\alpha = \epsilon_s^\alpha(\mathrm{har}) + \epsilon_s^\alpha(\mathrm{anhar}). \tag{2}$$

The moment of inertia of the average configuration is then given by

$$I_\alpha^* = I_\alpha^e + \frac{1}{2}\,\Sigma_s d_s \epsilon_s^\alpha(\mathrm{anhar}) \tag{3}$$

or

$$I_\alpha^* = I_\alpha^o - \frac{1}{2}\,\Sigma_s d_s \epsilon_s^\alpha(\mathrm{har}) \tag{4}$$

In the general formulation given in I the $\epsilon_s^\alpha(\mathrm{har})$ parameters are rather complicated functions but depend only on the harmonic force constants, molecular geometry, and atomic masses. For some of the simpler types of molecules explicit expressions for the ϵ_s^α(har) can be obtained. These are given in this paper, together with numerical results for a number of examples.

DIATOMIC MOLECULES

The relations among various bond length parameters, as formulated in I, have been examined for several molecules. Table I shows results obtained from spectroscopic values for B_o, α_e, and ω_e and the expressions given in I. There are several interesting features. First, $\langle r^2\rangle^{1/2} > \langle r\rangle > r_o > r_e$, as expected From Fig. 1 of I. For hydrides $r_o - r_e \approx 0.01$ A and $\langle r\rangle - r_e \approx 0.02$ A. Since electron diffraction "r_g" values[3,4] are essentially $\langle r\rangle$ we expect spectroscopic effective bond lengths and electron diffraction bond lengths to differ appreciably for hydrides. For heavier atoms the difference will be less but can still be significant. Another point of interest is the effect of isotopic substitution on the average bond length. Replacement of H by D causes a shortening of about 0.003 - 0.005 A in the various bond lengths r_o, $\langle r\rangle$, and $\langle r^2\rangle^{1/2}$. The heavier isotopic substitutions cause a shortening of about 0.0001 A, except where the heavy atom is bonded to H. Then the effect of heavy atom isotopic substitution is more or less negligible, since H does almost all of the vibrating.

LINEAR XY_2 MOLECULES

For a linear XY_2 molecule in its ground vibrational state, Eq. (4) reduces to

$$I_b^* = I_b^o + K\left[\frac{3}{\omega_1} - \frac{1}{\omega_2} - \frac{1}{\omega_3} + \frac{4}{\omega_2 + \omega_3}\right] \qquad (5)$$

where $K = 16.863$ amu A^2 cm^{-1} and the vibrational frequencies ω_s are expressed in cm^{-1}. Using (5) and observed spectroscopic data the results of Table II are obtained. One interesting result is the <u>decrease</u> of both I^o and I^* when C^{12} is replaced by C^{13} in CO_2. For a rigid molecule isotopic substitution by a heavier atom would either <u>increase</u> the moment of inertia or for a molecule like CO_2 cause no change. However, the decrease in the average bond length actually causes a decrease in the moment of inertia. Although it is not an XY_2 molecule we have included $C^{12}S^{32}S^{34}$ for purposes of comparison with $C^{12}S_2^{32}$. The relations for an XYZ molecule given elsewhere in this paper were used in the calculations. There is some ambiguity in the listed r_{CS} since the bond with S^{34} has a slightly different value than the bond with S^{32}. However, the substitution of S^{34} for S^{32} definitely shortens the CS bond length by about 0.0001 A.

BENT XY_2 MOLECULES

For a bent XY_2 molecule the following relations are obtained:

$$I_a^* = I_a^o + 3K\left[\frac{\sin^2\chi}{\omega_1} + \frac{\cos^2\chi}{\omega_2} + \frac{I_a}{I_c}\right] \qquad (6)$$

$$I_b^* = I_b^o + 3K\left[\frac{\cos^2\chi}{\omega_1} + \frac{\sin^2\chi}{\omega_2} + \frac{I_b}{I_c}\right] \tag{7}$$

$$\begin{aligned} I_c^* = I_c^o - K\Bigg[&\frac{1}{\omega_1} + \frac{1}{\omega_2} + \frac{1}{\omega_3} - 4\zeta_{13}^2\left(\frac{1}{\omega_2} + \frac{1}{\omega_1+\omega_3}\right) \\ &- 4\zeta_{23}^2\left(\frac{1}{\omega_1} + \frac{1}{\omega_2+\omega_3}\right)\Bigg], \end{aligned} \tag{8}$$

where ζ_{13} and ζ_{23} are the Coriolis coupling constants and χ is a parameter determined from[5]

$$\cos^2\chi + 2\zeta_{23}(I_b/I_c)^{1/2}\cos\chi + [\zeta_{23}^2-(I_a/I_c)] = 0 \tag{9}$$

Here b denotes the symmetry axis and c the out-of-plane axis. The ζ's can be obtained by the methods of I or by the relation of Meal and Polo.[6] Using these relations and observed rotational constants and quadratic potential constants we have calculated average parameters for H_2O, SO_2, O_3, and NO_2. The results are given in Tables III and IV.

First we note that the ambiguities in effective parameters arising from the inertial defect[7] are absent in the average values. Within the experimental uncertainties in the rotational and potential constants used in the calculation the relation

$$I_c^* = I_a^* + I_b^*$$

is satisfied, as is necessary for any set of physically well defined moments of inertia. The observed small residual values of the inertial defects are a measure of the errors present in the calculated structural parameters, which should approximate very closely to actual averages.

Other points of interest are the fact that for water $\langle r_{OD}\rangle < \langle r_{OH}\rangle$ by 0.005 A and that I_b for SO_2 becomes smaller as we increase the mass of the S atom. Since S lies on the b axis, I_b for a rigid molecule would be unaffected but the small decrease in the average SO bond length causes a decrease in I_b for the average configuration. As we shall see later these small isotopic variations have an important effect on calculations of the positions of atoms near to a principal axis.

TETRAHEDRAL XY_4 MOLECULES

For molecules of the methane type

$$I_b^* = I_b^o + K\left[\frac{2}{\omega_1} + \zeta_{23}^2\left(\frac{1}{2\omega_3} + \frac{4}{\omega_2+\omega_3}\right) + \zeta_{24}^2\left(\frac{1}{2\omega_4} + \frac{4}{\omega_2+\omega_4}\right)\right.$$

$$\left. + 2\zeta_{34}^2\left(\frac{4}{\omega_3+\omega_4} - \frac{1}{\omega_3} - \frac{1}{\omega_4}\right)\right]. \qquad (10)$$

The Coriolis constants may be obtained from the relations

$$\zeta_{34} = \frac{3}{2}\zeta_{23}\zeta_{24} \qquad (11)$$

$$\zeta_{23}^2 + \zeta_{24}^2 = 1 \qquad (12)$$

and

$$\lambda_3\zeta_{24}^2 + \lambda_4\zeta_{23}^2 = \frac{8}{9}\left(1 + \frac{4m_Y}{m_X}\right)(r^2 f_r - 4r f_{\alpha r} + 4 f_\alpha)/I \qquad (13)$$

Here r is the average XY bond length, I is the moment of inertia,[5] and the force constants refer to the usual symmetry coordinates[8] of species F_2.

The average bond lengths derived for methane are given in Table V. Again deuteration is found to decrease the average bond length by about 0.003 A. The electron diffraction r_g values are seen to differ substantially from both r_o and $\langle r \rangle$. It can be shown[4] that the displacement of r_g from the equilibrium distance r_e is strongly dependent on the anharmonic potential constants, just as found in I for r_o. However, the difference $r_g - \langle r \rangle$, like $r_o - \langle r \rangle$, is practically independent of the anharmonic constants. Although r_g and $\langle r \rangle$ are identical for diatomic molecules[3] (after small corrections for centrifugal distortion and thermal vibration), they differ for polyatomic molecules because r_g represents an average of the instantaneous distance between atoms[4,9] whereas, as discussed in I, $\langle r \rangle$ is the average projection of the distance along the direction of the undisplaced bond. Procedures for deriving $\langle r \rangle$ from r_g are available.[9] Thus a precise comparison of the electron diffraction and spectroscopic results can be made in terms of $\langle r \rangle$ by means of calculations which involve just the harmonic force constants. A completely satisfactory check is obtained for methane, as the values of $\langle r \rangle$ derived[4,10] from r_g are identical to those in Table V.

LINEAR XYZ MOLECULES

For a linear XYZ molecule

$$I_b^* = I_b^o - K\left[\frac{1}{\omega_1} + \frac{1}{\omega_2} + \frac{1}{\omega_3} - 4\zeta_{12}^2\left(\frac{1}{\omega_3} + \frac{1}{\omega_1+\omega_2}\right) - 4\zeta_{23}^2\left(\frac{1}{\omega_1} + \frac{1}{\omega_2+\omega_3}\right)\right] \qquad (14)$$

The Coriolis coupling constants are readily evaluated from the relations

$$\zeta_{12}^2 + \zeta_{23}^2 = 1 \qquad (15)$$

and

$$\lambda_1\zeta_{23}^2 + \lambda_3\zeta_{12}^2 = (r_{XY}^2\, F_{11} + 2r_{XY}r_{YZ}\, F_{13} + r_{YZ}^2\, F_{33})/I_b \qquad (16)$$

where the quadratic potential constants for bond stretching are defined by the valence force field

$$2V(\text{stretching}) = F_{11}(\delta r_{XY})^2 + F_{33}(\delta r_{YZ})^2 + 2F_{13}\delta r_{XY}\delta r_{YZ} \qquad (17)$$

These relations have been applied to HCN and the results are given in Table VI. In this case the treatment is different from those hitherto discussed, however, in that more than one isotopic species is involved in the calculation of a given structural parameter. Since the average parameters vary slightly among isotopic species we no longer have the unique description possible with the calculations carried out for a single isotopic molecule. However, we expect C^{13} substitution to have a much smaller effect than deuteration and accordingly the pairs $HC^{12}N^{14}$, $HC^{13}N^{14}$, and $DC^{12}N^{14}$, $DC^{13}N^{14}$ have been treated separately. The results thus obtained are in accord with what one would expect. It is found that $\langle r_{CH} \rangle - \langle r_{CD} \rangle = 0.003$ A whereas $\langle r_{CN} \rangle$ is essentially the same for both HCN and DCN. Also the calculated $\langle r_{CN} \rangle$ and $\langle r_{CH} \rangle$ differ from the equilibrium values by amounts in accord with other calculations. Although our assumption that r_{CN} is unaffected by isotopic substitution introduces some error, as discussed later, the difference between $\langle r_{CH} \rangle$ and $\langle r_{CD} \rangle$ is certainly real.

If the "substitution" method,[11] which assumes $r_{CH} = r_{CD}$, is used to calculate a structure for HCN values of $r_{CH} = 1.063$ A and $r_{CC} = 1.155$ A are obtained. Since this r_s value for the CH bond is substantially less than the equilibrium value of $r_e = 1.066$ A, it violates Costain's rule[11] that $r_s > r_e$. However, the neglect of the bond shortening caused by deuterium substitution will always lead to an apparent bond length which is shorter than the average bond length for either the H or D species. This may sometimes, as in HCN, even be shorter than the equilibrium value.

LINEAR X_2Y_2 MOLECULES

For this case

$$I_b^* = I_b^o - K\left[\frac{1}{\omega_1} + \frac{1}{\omega_2} + \frac{1}{\omega_3} + \frac{1}{\omega_4} + \frac{1}{\omega_5} - \frac{4}{\omega_3+\omega_5} - 4\zeta_{14}^2\left(\frac{1}{\omega_2} + \frac{1}{\omega_1+\omega_4}\right) - 4\zeta_{24}^2\left(\frac{1}{\omega_1} + \frac{1}{\omega_2+\omega_4}\right)\right] \tag{18}$$

The Coriolis constants are determined from the relations

$$\zeta_{14}^2 + \zeta_{24}^2 = 1 \tag{19}$$

and

$$\lambda_1\zeta_{24}^2 + \lambda_2\zeta_{14}^2 = (2r_{XY}^2\mathcal{F}_{11} + 2^{\frac{1}{2}}r_{XY}r_{XX}\mathcal{F}_{12} + r_{XX}^2\mathcal{F}_{22})/I \tag{20}$$

where the quadratic force constants refer to the symmetry coordinates given in Table VI of Part I.

For C_2H_2 and C_2D_2 the vibration-rotation parameters and the equilibrium structure have been determined.[12] The contributions from each vibrational mode are shown in Table VII, and may be compared with the data for linear triatomic molecules given in Tables II and IV of Part I. In this case, it is found that I^o and I^* are very nearly equal, as the negative contributions to ϵ(har) from the stretching modes are only slightly outweighed by the positive contributions from the bending modes. The anharmonic contributions also largely cancel.

If we assume that $r_{CH} > r_{CD}$ by 0.003 A, we calculate $\langle r_{CH}\rangle = 1.065$ A and $\langle r_{CC}\rangle = 1.206$ A. The equilibrium values[12] are $r_{CH}^e = 1.058$ A and $r_{CC}^e = 1.205$ A. The usual assumption that $r_{CH} = r_{CD}$ has two unsatisfactory consequences: it yields $r_{CH}^o = 1.057$ A, a value too close to (and <u>less</u> than) the equilibrium value; and it requires the anomalous conclusion[13] that the CH bond becomes shorter in excited vibrational states.

DISCUSSION

There are several advantages in basing spectroscopic structure determinations on the I^* rather than the I^o moments. First, the inconsistencies which must be accepted when the I^o moments are used in relations that hold only for genuine moments of inertia are largely eliminated by the use of the I^* moments. For example, the problems arising from quantum defects in planar molecules are avoided, as illustrated in Table III. Another important advantage is the physically well-defined meaning of the average structural parameters. This makes them a convenient basis for the precise correlation of electron diffraction and spectroscopic results, as discussed under Table V. The "effective" or "substitution" parameters commonly derived from spectroscopic measurements are defined only by the operational procedures used to obtain them. The relation of r_s parameters, in particular, to the electron diffraction r_g parameters is extremely complex, and $r_g - r_s$ depends strongly on the anharmonic force constants. Furthermore, the r_o and r_s bond lengths can be longer or shorter than the equilibrium values, whereas the average bond lengths are consistently longer. The average parameters should therefore offer a more reliable means for comparison of molecules, and should be preferred whenever, as is usually the case, the equilibrium structures are not available.

As we have seen, for the simple molecules considered in this paper the I^* moments can be derived from the observed I^o values without a normal coordinate analysis. Additional formulas, intended for applications which require the contributions from the individual vibrational modes, are collected in the Appendix.

In practice the complete calculation of an average structure is unfortunately limited to small molecules, not much larger than those treated here. Although only the harmonic force constants are required, even these are only available for fairly simple molecules. However, as shown in Parts III and IV of this study, it is sometimes feasible and useful to treat portions of larger molecules.

A fundamental difficulty which affects the calculation of the average structural parameters, as well as the effective and substitution parameters, is the ambiguity introduced when it is necessary to combine data from several isotopic species. These parameters all differ slightly for different isotopic species, as illustrated in several of the examples we have considered.

Since deuterium substitution shortens the average bond length by 0.003-0.005 A, structures obtained by ignoring this difference have to be interpreted with some care. For example, anomalous results were obtained for HCN and C_2H_2 even though, according to the criterion adopted in the substitution method,[11] neither of these molecules has an atom dangerously near to the center-of-mass. The consistent differences found empirically in Tables I and IV to VI would seem to justify replacing the conventional assumption that $r_{XD} = r_{XH}$ by $r_{XD} = r_{XH} - \delta$, with $\delta = 0.003$ A; and in any case it would be desirable to include the effect of varying δ from zero to perhaps 0.005 A when reporting results derived from deuterium substitution.

The decrease in an average bond length on isotopic substitution of a heavier atom is only of the order of 0.0001 A. This is, however, enough to account for the "wrong-way" change in the moments of inertia of $C^{13}O_2$ and $S^{34}O_2$ noted in Tables II and III. Furthermore, the neglect of even such small isotopic variations can have a relatively large effect on the calculated structure. We shall illustrate this here for the simple case of a linear XYZ molecule, and in Part IV discuss the problem again in more detail. If an isotopic substitution is made on the ith atom, the coordinate z_i of the atom (in the principal axis system of the parent molecule) is related to the change in the moment of inertia by

$$\Delta I = \mu z_i^2 \tag{21}$$

where $\mu = M\Delta m_i/(M + \Delta m_i)$ and M is the mass of the parent molecule. This relation holds only if the bond lengths are unchanged by isotopic substitution. If we assume that the substituion shrinks the bonds slightly,

$$r'_{12} = z'_2 - z'_1 = r_{12} - \delta_1 \qquad (22a)$$

and

$$r'_{23} = z'_3 - z'_2 = r_{23} - \delta_3 \qquad (22b)$$

then Eq. (21) must be replaced by

$$\Delta I(i=1) = \mu z_1^2 + 2(m'_1 z'_1 \delta_1 - m_3 z'_3 \delta_3) \qquad (23a)$$

$$\Delta I(i=2) = \mu z_2^2 + 2(m_1 z'_1 \delta_1 - m_3 z'_3 \delta_3) \qquad (23b)$$

$$\Delta I(i=3) = \mu z_3^2 + 2(m_1 z'_1 \delta_1 - m'_3 z'_3 \delta_3) \qquad (23c)$$

where primes refer to the substituted species and terms quadratic in the increments δ_1 and δ_3 have been neglected. According to the definitions (22), the coordinate z'_1 is negative, z'_3 is positive, and δ_1 and δ_3 will be positive when a heavier isotope is substituted. Therefore we see from Eqs. (23) that for all three atoms the apparent z_i^2 calculated from Eq. (21) will be too small. This occurs simply because the decrease in bond lengths makes ΔI smaller than it would be for a rigid molecule. Although this shows that a "substitution" coordinate will always be smaller in absolute magnitude than the actual coordinate, a bond length can involve either the sum or difference of the absolute magnitudes of two coordinates, and hence a "substitution" bond length can be either too short or too long.

The discrepancy to be expected is readily estimated from Eqs. (23). For example, if we consider substitution on one of the end atoms (i=1) and take

$$\mu \approx 1$$
$$m_1 \approx m_3 \approx 20 \text{ g mole}^{-1}$$
$$-z_1' \approx z_3' \approx 1.2 \text{ A}$$
$$\delta_1 \approx 10^{-4} \text{ A}, \ \delta_3 \approx 0$$

we find that the apparent $|z_1|$ coordinate calculated from Eq. (21) will be too small by about 0.002 A. Here an isotopic variation of only 0.01 % in the bond length introduces an 0.2% error in the substitution coordinate. The discrepancy can vary over a wide range, and differ considerably for substitutions on different atoms in the same molecule.

For substitutions on the middle atom (i=2), this effect can be greatly magnified, as Eq. (23b) predicts that the discrepancy will increase strongly as z_2 is decreased. This is illustrated in Table VIII, which gives results calculated for several molecules on the assumption that $\delta_1 = \delta_3 = 10^{-4}$ A. To these examples we may add CO_2 as a limiting case. Eq. (23b) becomes in this limit

$$\Delta I = -4mr\delta \tag{24}$$

and in Table II we noted that C^{13} substitution gave $\Delta I^* = -0.004$ amu A^2. Thus we find $\delta = 5 \times 10^{-5}$ A for CO_2, about the expected magnitude.[14] From these results, and other evidence discussed in Part IV, we may conclude that the slight isotopic variations in the average bond lengths are responsible, at least in large part, for the appearance of imaginary coordinates and other notorious difficulties associated with substitution of atoms near a principal axis.

As we have seen, the errors caused by isotopic variations are appreciable even for atoms fairly distant from an axis, and structures obtained by simply neglecting these variations often contain spurious features. It would be very useful, particularly when comparing structural parameters for different molecules, to be able to estimate corrections by means of a set of empirically[15] determined δ's for various bonds and angles. Whether it is feasible to establish such a set of δ's or similar parameters is not yet clear, and cannot be settled without more data on simple molecules. However, the physical interpretation of average structural parameters suggests that the δ's may prove to be roughly characteristic of bonds and transferable between molecules.

APPENDIX. HARMONIC TERMS IN VIBRATIONAL CORRECTIONS

As shown in Eq. (13) of Part I, the vibration-rotation parameters may be written as $d_s\epsilon_s=-(6K/\omega_s)(H_s+A_s)$, so that the harmonic and anharmonic contributions are given by the dimensionless quantities H_s and A_s, respectively. Formulas for the H_s coefficients are given below for the types of molecules treated in this paper. In addition to the notation employed in the text, it has been convenient to define the function $\xi_{st} = \frac{4}{3}\lambda_s/(\lambda_s-\lambda_t)$.

Molecule	H_1	H_2	H_3
Linear XY_2	1	$1-\xi_{32}$	$1-\xi_{23}$
Linear XYZ	$1-\zeta_{12}^2\xi_{21}$	$1-\zeta_{12}^2\xi_{12}-\zeta_{32}^2\xi_{32}$	$1-\zeta_{32}^2\xi_{23}$
Bent XY_2			
a-axis	$\sin^2\chi$	$\cos^2\chi$	I_a/I_c
b-axis	$\cos^2\chi$	$\sin^2\chi$	I_b/I_c
c-axis	$1-\zeta_{13}^2\xi_{31}$	$1-\zeta_{23}^2\xi_{32}$	$1-\zeta_{13}^2\xi_{13}-\zeta_{23}^2\xi_{23}$

Molecule	H_1	H_2	H_3	H_4	H_5
Linear X_2Y_2	$1-\zeta_{14}^2\xi_{41}$	$1-\zeta_{24}^2\xi_{42}$	$1-\xi_{53}$	$1-\zeta_{14}^2\xi_{14}-\zeta_{24}^2\xi_{24}$	$1-\xi_{35}$
Tetrahedral XY_4	$\frac{2}{3}$	$\zeta_{24}^2\xi_{24}+\zeta_{23}^2\xi_{23}$	$\zeta_{23}^2(\frac{3}{2}-\xi_{23})$ $+ 2\zeta_{34}^2(1-\xi_{43})$	$\zeta_{24}^2(\frac{3}{2}-\xi_{24})$ $+ 2\zeta_{34}^2(1-\xi_{34})$	

FOOTNOTES

1. D. R. Herschbach and V. W. Laurie, J. Chem. Phys., 37, 000 (1962), preceding paper, hereafter referred to as I.
2. The nondiagonal elements $\epsilon_s^{\alpha\beta}$ which appear in the general formulas of Eqs. (36) and (37) in I vanish identically for all types of molecules considered in this paper. The numbering of the vibrational modes used here conforms to that of G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand Company, New York, 1945).
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5. In Eq. (9) and elsewhere the moments of inertia for the average configuration (which is here the "standard" configuration defined in Part I) should be used, but the observed effective moments give sufficient accuracy.
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Footnotes (cont)

13. J. Overend, Trans. Far. Soc. 56, 310 (1960).

14. A value somewhat less than 10^{-4} is also indicated for nitrous oxide, since the z_2 found by the substitution method,[11] although very small, is not yet imaginary as predicted in Table VIII. Substitution of the middle atom in $N^{15}N^{14}O^{16}$ does given an imaginary z_2, however.

15. We must rely mainly on empirical analysis, since the dominant contributions to the isotopic variations come from vibrational anharmonicity, as shown in Part IV.

Table I. Various bond lengths (Å) of some selected diatomic molecules

Molecule	r_o	r_e	$\langle r^2 \rangle^{1/2}$	$\langle r \rangle$	Ref.
HF	0.9257	0.9170	0.9349	0.9326	a
DF	0.9234	0.9171	0.9300	0.9284	b
TF	0.9230	0.9177	0.9286	0.9272	c
$O^{16}H$	0.9800	0.9707	0.9897	0.9873	d
$O^{16}D$	0.9772	0.9700	0.9843	0.9825	d
$C^{12}H$	1.1303	1.1187	1.1415	1.1388	d
$C^{12}H$	1.1265	1.1188	1.1348	1.1327	d
HCl^{35}	1.2837	1.2745	1.2926	1.2904	e
HCl^{37}	1.2837	1.2746	1.2926	1.2904	e
DCl^{35}	1.2813	1.2744	1.2889	1.2858	f
DCl^{37}	1.2813	1.2744	1.2889	1.2858	f
TCl^{35}	1.2800	1.2746	1.2871	1.2853	g
TCl^{37}	1.2800	1.2746	1.2871	1.2853	g
$C^{12}O^{16}$	1.1335	1.1283	1.1407	1.1402	h
$C^{13}O^{16}$	1.1333	1.1283	1.1405	1.1400	h
$Cl^{35}F$	1.6352	1.6283	1.6372	1.6368	h
$Cl^{37}F$	1.6351	1.6283	1.6371	1.6367	h
$I^{127}Cl^{35}$	2.3236	2.3209	2.3250	2.3246	h
$I^{127}Cl^{37}$	2.3235	2.3209	2.3249	2.3245	h

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[g] C. A. Burrus, W. Gordy, B. Benjamin, and R. Livingston, Phys. Rev. 97, 1661 (1955).

[h] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Company, Inc., N. Y., 1955).

Table II. I_b^* and bond lengths for CO_2^a and CS_2^b

Molecule	I_b^o	I_b^*	r_e	r_o	$\langle r \rangle$
$C^{12}O_2^{16}$	43.214	43.242	1.1600	1.1621	1.1625
$C^{13}O_2^{16}$	43.211	43.238	1.1600	1.1620	1.1624
$C^{12}S_2^{32}$	154.563	154.620	1.5532	1.5545	1.5548
$C^{12}S^{32}S^{34}$	159.252	159.309	1.5532	1.5544	1.5547

[a] Derived from data of C. P. Courtoy, Ann. Soc. Scien. Bruxelles, Serie I, 73, 5 (1959).

[b] Derived from data of A. H. Guenther, J. Chem. Phys. 31, 1095 (1959).

Table III. Moments of inertia for some bent XY_2 molecules (amu A^2).

Molecule	I_a	I_b	I_c	$I_c-I_a-I_b$
H_2O				
equilibrium[a]	0.61590	1.15621	1.77025	-0.00186
effective[a]	0.60488	1.16348	1.81575	0.04738
average	0.63433	1.19073	1.82712	0.00209
D_2O				
equilibrium[a]	1.1078	2.3133	3.4167	-0.0044
effective[a]	1.0961	2.3190	3.4799	0.0648
average	1.1347	2.3580	3.4945	0.0018
$S^{32}O_2$				
effective[b]	8.31756	48.9946	57.4470	0.1348
average	8.3972	49.0934	57.4881	-0.0026
$S^{33}O_2$				
effective[c]	8.44572	48.9941	57.5761	0.1363
average	8.5264	49.0931	57.6171	-0.0024
$S^{34}O_2$				
effective[c]	8.56959	48.9931	57.6998	0.1371
average	8.6510	49.0921	57.7407	-0.0024
O_3				
effective[d]	4.74523	37.8708	42.7175	0.1015
average	4.8024	37.9715	42.7728	-0.0091
$N^{14}O_2$				
effective[e,f]	2.1093	38.906	41.087	0.072
average	2.1582	38.992	41.134	-0.015

[a] W. S. Benedict, N. Gailar, and E. K. Plyler, J. Chem. Phys. 24, 1139 (1956).

[b] D. Kivelson, J. Chem. Phys. 22, 904 (1954).

[c] W. E. Smith, Austral. J. Phys. 2, 109 (1959).

[d] L. Pierce, J. Chem. Phys. 24, 139 (1956).

[e] G. R. Bird, J. Chem. Phys. 25, 1040 (1956).

[f] E. T. Arakawa and A. H. Nielsen, J. Mol. Spect. 2, 413 (1958).

Table IV. Structural parameters of some bent XY_2 molecules

Molecule	r_o	$\langle r \rangle$	θ_o	$\langle \theta \rangle$
H_2O	0.9579	0.9735	104°56'	104°16'
D_2O	0.9571	0.9683	104°52'	104°22'
$S^{32}O_2$	1.4321	1.4350	119°32'	119°21'
$S^{33}O_2$	1.4322	1.4350	119°32'	119°21'
$S^{34}O_2$	1.4321	1.4350	119°32'	119°21'
O_3^{16}	1.2760	1.2794	116°58'	116°44'
$N^{14}O_2^{16}$	1.1967	1.2000	134°15'	133°48'

Table V. Bond lengths for methane.

	r_o	r_g	$\langle r\rangle$
CH_4	1.094[a]	1.107[c]	1.099[a,d]
CD_4	1.092[b]	1.102[c]	1.096[b,d]

[a] Based on the rotational analysis of K. T. Hecht, J. Mol. Spectroscopy 5, 335 (1960).

[b] Rotational constant $B_o = 2.631$ cm^{-1} taken from G. S. Shepard and H. L. Welsh, J. Mol. Spectroscopy 1, 227 (1957).

[c] From reference 10.

[d] Harmonic force constants taken from L. H. Jones and R. S. McDowell, J. Mol. Spectroscopy 3, 632 (1959).

Table VI. Bond lengths for HCN.[a]

Molecule	r^{e}_{CH}	r^{e}_{CN}	r^{o}_{CH}	r^{o}_{CN}	$\langle r_{CH} \rangle$	$\langle r_{CN} \rangle$
$HC^{12}N^{14}$ $HC^{13}N^{14}$	1.0659	1.1531	1.0676	1.1558	1.073_9	1.157_4
$DC^{12}N^{14}$ $DC^{13}N^{14}$	1.0659	1.1531	1.0657	1.1557	1.070_6	1.157_0

[a] Derived from data of D. H. Rank, G. Skorinko, D. P. Eastman, and T. A. Wiggins, J. Opt. Soc. Am. 50, 421 (1960).

Table VII. Vibration-rotation parameters for acetylene.[a]

Mode	$\frac{1}{2}d_s\epsilon_s$(har)	$\frac{1}{2}d_s\epsilon_s$(anhar)	ϵ(anhar)/ϵ(har)
		C_2H_2	
1	-0.01566	0.0575	-3.67
2	-0.02560	0.0639	-2.50
3	-0.01645	0.0496	-3.02
4	0.03172	-0.0583	-1.84
5	0.02791	-0.0533	-1.91
Sum	0.00192	0.0595	31.1
$I_b^o = 14.332$, $I_b^* = 14.330$, $I_b^e = 14.270$			
		C_2D_2	
1	-0.01984	0.0883	-4.45
2	-0.02883	0.0656	-2.28
3	-0.02248	0.0731	-3.25
4	0.03803	-0.0881	-2.32
5	0.03822	-0.0872	-2.28
Sum	0.00510	0.0517	10.1
$I_b^o = 19.893$, $I_b^* = 19.888$, $I_b^e = 19.825$			

[a] Derived from data of reference 12.

Table VIII. Effect of isotopic variations on calculated coordinate.[a]

Molecule	Actual z_2	Apparent z_2	Difference
$Br^{79}CN$	1.1910	1.1840	0.0070
$OCSe^{80}$	1.0952	1.0873	0.0079
$Cl^{35}CN$	0.6679	0.6588	0.0091
OCS	0.5224	0.5106	0.0118
FCN	0.1694	0.1438	0.0256
NNO	0.0726	imaginary	

[a] Calculations based on data from C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Company, New York, 1955), except for FCN, which is from J. Sheridan and J. K. Tyler, Nature 185, 96 (1960). The apparent z_2 coordinate was determined from substitution of the middle atom, an N^{15} substitution for NNO, a C^{13} substitution for the other molecules.