

The Vibration-Rotation Problem in Triatomic Molecules Allowing for a Large-Amplitude Bending Vibration

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In this paper we derive an expression for the vibration-rotation Hamiltonian of a triatomic molecule. In the derivation we use a curvilinear bending coordinate and two rectilinear stretching coordinates in such a way that the Hamiltonian obtained is applicable for any triatomic molecule, linear or bent, and allows for large displacements of the bending coordinate (sometimes said to result from the molecule being "quasi-linear" but, in fact, of general occurrence). We derive a zeroth-order Hamiltonian to describe the energy levels associated with the bending vibration, and are able to fit the experimental results on HCN and DCN better than if we had used the standard formalism of rectilinear (and small) displacements. We also use the formalism to describe the dependence of the rotational constant B on the bending vibrational quantum number and apply the results to the microwave data on CsOH and CsOD.

I. INTRODUCTION

Two separate vibration-rotation formalisms are commonly used for polyatomic molecules, depending on whether the molecule under consideration is linear or nonlinear. It is often unsatisfactory to be committed to one or the other of these two limiting formalisms. The vibration-rotation formalism considered in this paper is designed for triatomic molecules and allows for large amplitude excitation of the bending vibration. The treatment leads to a Hamiltonian which can be applied equally well to both linear and bent triatomic molecules.

The form of the vibration-rotation Hamiltonian is a direct consequence of the coordinates and coordinate axis systems chosen to describe the configuration of the molecule at any instant. Since many distinct choices of coordinates and axes exist, many distinct Hamiltonian derivations are possible (1, 2, 3). The coordi-

nates that we use allow us to follow a derivation of the Hamiltonian which is as parallel as possible to the standard derivation (4).

The derivation presented here for a molecule undergoing a large-amplitude bending vibration is very similar to that presented earlier for a molecule undergoing nearly free internal rotation (5, 6). These derivations can be generalized and extended to apply to a molecule having several large-amplitude vibrational motions (7).

The curvilinear coordinate system to be used is defined in Sect. II. In Sect. III a derivation of the kinetic energy operator is presented, analogous to that of Wilson and Howard (8) and the Wilson FG matrix formalism (4) is introduced. The bending vibration is considered by itself in Sect. IV, where a numerical integration procedure is described which allows one to obtain bending vibrational energy levels and wave functions for any potential function (algebraic or numerical). In Sect. V we compare the traditional cubic bend-stretch interaction constants for a given potential function written in three different coordinate systems. The dependence of the rotational constant B on the bending vibrational quantum numbers is investigated in Sect. VI; and in Sect. VII this treatment is applied to the microwave data on CsOH.

II. COORDINATES AND AXES

Before considering the derivation of the Hamiltonian, we shall consider carefully the definition of the various coordinates and constraints used. Such an approach is more satisfying from one point of view, i.e., one is never working with undefined coordinates, but less satisfying from another, i.e., the relative merits of one set of coordinates (and constraints) versus another in simplifying the general Hamiltonian expression cannot easily be determined.

Three parameters are necessary to describe the shape of a triatomic molecule: e.g., r_{12} and r_{32} , the instantaneous values of the two bond lengths, and $\tilde{\gamma}$, the instantaneous value of the angle between the two bonds (see Fig. 1). From the point of view of intramolecular force fields, a particularly appropriate set of three parameters consists of the deviations Δr_{12} , Δr_{32} , $\Delta \tilde{\gamma}$ of these three quantities from some reference values. We shall call this latter set of parameters the *true valence coordinates* for a triatomic molecule.

However, in the vibration-rotation Hamiltonian it is normal to use as shape coordinates three rectilinear displacements of the molecule from equilibrium. We shall call this set of coordinates the *linearized valence coordinates*. In the limit of small amplitudes, these coordinates become the true valence coordinates. Plíva (9, 10) has shown, for both bent and linear triatomic molecules, how the quadratic, cubic, and quartic potential constants of a force field expressed in terms of the true valence coordinates are related to the quadratic, cubic, and quartic potential constants of that same force field expressed in terms of the linearized valence coordinates. It is well known that rectilinear displacement co-

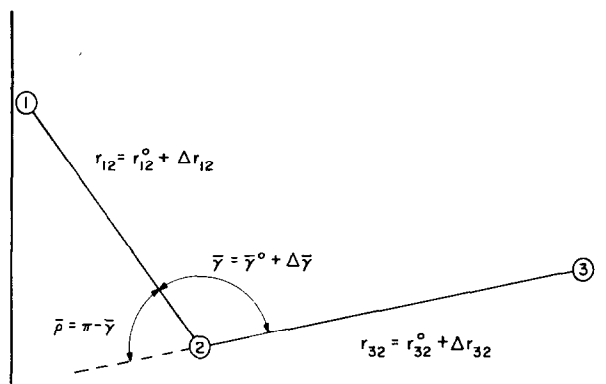


FIG. 1. True valence coordinates for a triatomic molecule. Each of the true valence coordinates (Δr_{12} , Δr_{32} , $\Delta \bar{\gamma}$) represents the difference between an instantaneous value (r_{12} , r_{32} , $\bar{\gamma}$) and a reference value (r_{12}^0 , r_{32}^0 , $\bar{\gamma}^0$).

ordinates are inappropriate for vibrational motion in triatomic molecules when the amplitude of the bending vibration becomes large, because no single rectilinear coordinate can describe large changes in the bending angle without simultaneously introducing large changes in one or both bond distances.

The coordinates used here consist of two linearized valence coordinates S_1 and S_3 , corresponding to the two bond-stretching motions, and one curvilinear coordinate γ , which for small S_1 and S_3 is very nearly, but not exactly, equal to the instantaneous bending angle $\bar{\gamma}$. (As shown below, the angle γ is equal to the instantaneous bending angle of a *reference configuration* for the molecule, whereas the angle $\bar{\gamma}$ is equal to the instantaneous bending angle of the molecule itself.) The precise nature of the coordinates used here can be understood by examining Eq. (1) below and Appendix I of Ref. (4).

$$\mathbf{r}_i = \mathbf{R} + S^{-1}(\chi\theta\phi) \cdot [\mathbf{a}_i(\rho) + \mathbf{d}_i]. \quad (1)$$

The quantity \mathbf{r}_i on the left side of Eq. (1) is a column matrix containing the three coordinates of the i th nucleus in an axis system (XYZ) fixed in the laboratory ($i = 1, 2, 3$). These three laboratory-fixed coordinates are also given by the expression on the right side of Eq. (1). The quantities there are somewhat more obscure, however, and we now consider them one by one.

\mathbf{R} is a column matrix containing the three laboratory-fixed coordinates of the origin of the molecule-fixed axis system. The vector \mathbf{R} is defined as a function of the \mathbf{r}_i by Eqs. (8) below.

The form of each element of the 3×3 direction cosine matrix $S(\chi\theta\phi)$ is given in Table I-1 of Ref. (4). The inverse of this matrix is used in Eq. (1) to convert from vector components in a molecule-fixed axis system to vector components in a laboratory-fixed axis system. The matrix $S(\chi\theta\phi)$ is defined as a function of the \mathbf{r}_i by Eqs. (8) below.

The three components of $\mathbf{a}_i(\rho) + \mathbf{d}_i$ are the molecule-fixed coordinates of the

atoms. The $\mathbf{a}_i(\rho)$ represent a reference configuration from which the small-amplitude displacement vectors \mathbf{d}_i are measured. This reference configuration is a function of $\rho \equiv \pi - \gamma$. The components of the vectors $\mathbf{a}_i(\rho)$ and \mathbf{d}_i are always taken in the molecule-fixed xyz -axis system and the components of \mathbf{r}_i and \mathbf{R} are always taken in the laboratory-fixed XYZ -axis system. Figure 2 illustrates the relationship between the XYZ - and xyz -axis systems, and between the configurations \mathbf{r}_i , $\mathbf{a}_i(\rho)$, and $\mathbf{a}_i(\rho) + \mathbf{d}_i$, for the DCN molecule.

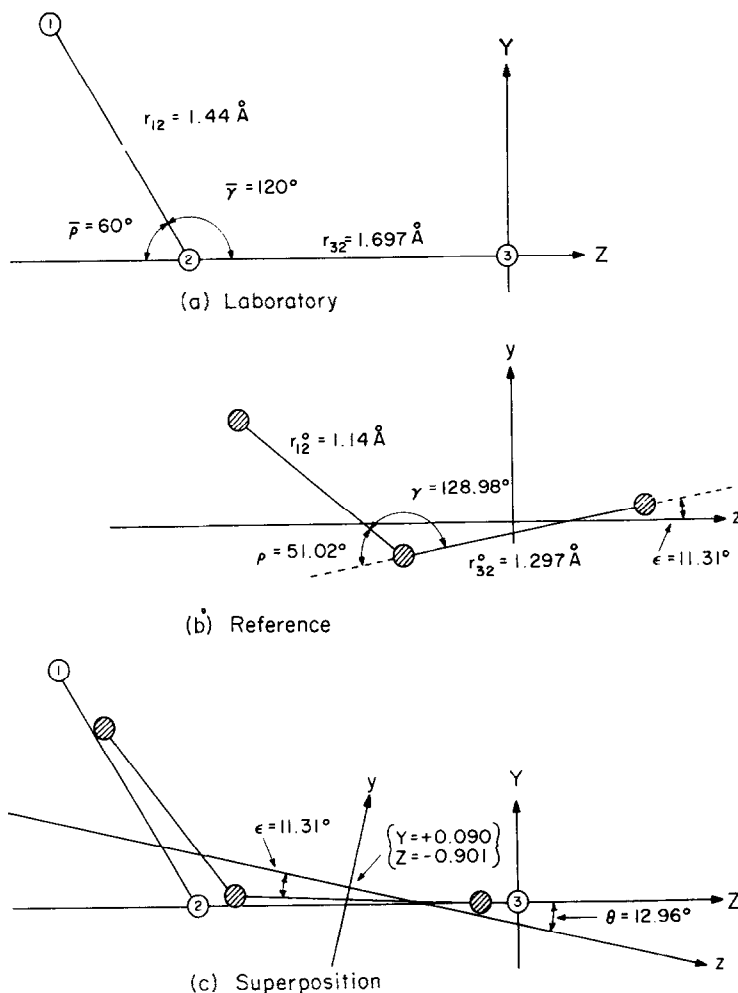


FIG. 2. The relation between an arbitrary laboratory-fixed configuration and its reference configuration for the DCN molecule: (a) an arbitrary configuration of the D, C, and N atoms (numbered 1, 2, and 3, respectively) in space; (b) the reference configuration calculated from (a), using Eqs. (2), (4), and (8) in the text; (c) the superposition of (a) and (b), with the molecule-fixed axis system both rotated and translated with respect to the laboratory-fixed axis system. For further explanation see the text following Eq. (8.)

The reference configuration considered here for triatomic molecules, defined by $\mathbf{a}_i(\rho)$, is characterized by fixed bond lengths r_{12}^0 and r_{32}^0 and by a variable valence angle $\gamma \equiv \pi - \rho$. The location of a given reference configuration in the molecule-fixed axis system is chosen so that: (i) all atoms lie in the yz plane, (ii) the center of mass is at the origin, and (iii) the z -axis makes an angle ϵ with r_{32}^0 (see Fig. 2b). The components of the vectors $\mathbf{a}_i(\rho)$ in this molecule-fixed axis system are thus given by

$$\begin{aligned}
 a_{1x} &= a_{2x} = a_{3x} = 0, \\
 a_{1y} &= \frac{m_2 + m_3}{m} r_{12}^0 \sin(\rho - \epsilon) - \frac{m_3}{m} r_{32}^0 \sin \epsilon, \\
 a_{2y} &= -\frac{m_1}{m} r_{12}^0 \sin(\rho - \epsilon) - \frac{m_3}{m} r_{32}^0 \sin \epsilon, \\
 a_{3y} &= -\frac{m_1}{m} r_{12}^0 \sin(\rho - \epsilon) + \frac{m_1 + m_2}{m} r_{32}^0 \sin \epsilon, \\
 a_{1z} &= -\frac{m_2 + m_3}{m} r_{12}^0 \cos(\rho - \epsilon) - \frac{m_3}{m} r_{32}^0 \cos \epsilon, \\
 a_{2z} &= \frac{m_1}{m} r_{12}^0 \cos(\rho - \epsilon) - \frac{m_3}{m} r_{32}^0 \cos \epsilon, \\
 a_{3z} &= \frac{m_1}{m} r_{12}^0 \cos(\rho - \epsilon) + \frac{m_1 + m_2}{m} r_{32}^0 \cos \epsilon,
 \end{aligned} \tag{2}$$

where m_1, m_2, m_3 are the masses of the three atoms of the triatomic molecule and m is their sum. The angle ϵ is chosen by requiring that the angular momentum of the reference configuration vanish in the molecule-fixed axis system [see p. 145 Ref. (11) for a similar discussion], i.e.,

$$\sum_i m_i \mathbf{a}_i(\rho) \times \left(\frac{d\mathbf{a}_i}{d\rho} \right) = 0. \tag{3}$$

Using Eqs. (2) and (3) we determine $d\epsilon/d\rho$ [see Eq. (38)] which can be integrated to give,

$$\epsilon(\rho) = (\frac{1}{2})\rho + \frac{u_1 - u_3}{[(u_1 + u_3)^2 - 4u_{13}^2]^{1/2}} \arctan \left[\left(\frac{u_1 + u_3 - 2u_{13}}{u_1 + u_3 + 2u_{13}} \right)^{1/2} \tan(\rho/2) \right], \tag{4}$$

where

$$\begin{aligned}
 u_1 &= m_1(m_2 + m_3)(r_{12}^0)^2, \\
 u_3 &= m_3(m_2 + m_1)(r_{32}^0)^2, \\
 u_{13} &= m_1 m_3 r_{12}^0 r_{32}^0,
 \end{aligned} \tag{5}$$

and where the constant of integration has been chosen such that $\epsilon = 0$ when $\rho = 0$. This choice of ϵ prevents the y and z axes from being principal axes of the reference configuration except when $\rho = 0$,¹ i.e., for $\rho \neq 0$,

$$I_{yz}^0 = -\sum_i m_i a_{iy} a_{iz} \neq 0. \quad (6)$$

The small displacements \mathbf{d}_i occurring in Eq. (1) are subject to 7 constraint equations.

$$\begin{aligned} \sum_i m_i \mathbf{d}_i &= \mathbf{0}, \\ \sum_i m_i \mathbf{a}_i(\rho) \times \mathbf{d}_i &= \mathbf{0}, \\ \sum_i m_i (d\mathbf{a}_i/d\rho) \cdot \mathbf{d}_i &= 0. \end{aligned} \quad (7)$$

These equations must be introduced in order to reduce the number of degrees of freedom on the right-hand side of Eq. (1) from $3N + 7$ to $3N$, bringing it into agreement with the number of degrees of freedom on the left-hand side. (There are $3N$ components of the \mathbf{r}_i on the left-hand side, and without constraints there are 3 components of \mathbf{R} plus 3 Eulerian angles $\chi\theta\phi$ plus one bending angle ρ plus $3N$ components of the \mathbf{d}_i on the right-hand side.) As a consequence of introducing the 7 constraints in Eqs. (7), values of \mathbf{R} , $\chi\theta\phi$, and ρ can now be calculated from any set of laboratory-fixed coordinates for the three nuclei. If Eq. (1) is rearranged to express \mathbf{d}_i as a function of all the other quantities, then the 7 constraint equations, together with the properties of the $\mathbf{a}_i(\rho)$ mentioned above, lead to the following 7 equations.

$$\begin{aligned} \mathbf{0} &= \sum_i m_i (\mathbf{r}_i - \mathbf{R}) \\ \mathbf{0} &= \sum_i m_i \mathbf{a}_i(\rho) \times [S(\chi\theta\phi) \cdot (\mathbf{r}_i - \mathbf{R})] \\ 0 &= \sum_i m_i (d\mathbf{a}_i/d\rho) \cdot [S(\chi\theta\phi) \cdot (\mathbf{r}_i - \mathbf{R}) - \mathbf{a}_i]. \end{aligned} \quad (8)$$

The first vector equation allows one to calculate \mathbf{R} as a function of the \mathbf{r}_i . The components of \mathbf{R} are just the laboratory-fixed coordinates of the center of mass of the nuclei. When the given values of \mathbf{r}_i , the calculated values of \mathbf{R} , and the expressions for the components of $S(\chi\theta\phi)$, $\mathbf{a}_i(\rho)$, and $d\mathbf{a}_i/d\rho$ are substituted in the second vector equation and in the last equation, we obtain four equations in the four unknowns χ , θ , ϕ , and ρ . These equations determine the values of these latter quantities.

¹ In the usual treatment of molecular vibrations, the reference configuration is chosen to be the equilibrium configuration of the molecule and is not allowed to vary. In addition, the x , y , z Cartesian axes are chosen to be the principal axes of the equilibrium configuration.

It is in this way that the diagram presented in Fig. 2 was constructed. Figure 2a shows an arbitrary configuration of the atoms D, C, and N in space. The CD bond length is 1.44 Å, the CN bond length is 1.697 Å, and the bending angle $\bar{\gamma}$ is 120°. The N atom lies at the origin of the laboratory-fixed axis system (*XYZ*), the C atom lies on the negative *Z*-axis, and the D atom lies in the *YZ* plane. This configuration corresponds to laboratory-fixed coordinates \mathbf{r}_i for the D, C, and N atoms of (0, 1.247, -2.417), (0, 0, -1.697), and (0, 0, 0), respectively (in Å units).

Figure 2b shows the reference configuration calculated from these laboratory-fixed coordinates using Eqs. (2), (4), and (8) in the text. The CD and CN bond lengths of the reference configuration were taken to be 1.14 and 1.297 Å, respectively. After some algebra, the calculations associated with Fig. 2 reduce to: (i) solving numerically two simultaneous transcendental equations, in the variables ρ and $\theta - \epsilon$, which arise from Eqs. (8); and (ii) calculating ϵ from ρ using Eq. (4). These calculations are somewhat simpler than those of the most general case, because the arbitrary configuration was chosen to lie in the *YZ* plane. The reference configuration always lies in the *yz* plane. Hence, the angles χ and ϕ of $S(\chi \theta \phi)$ could be given the relatively convenient values $\chi = +\pi/2$ and $\phi = -\pi/2$. The bending angle $\gamma \equiv \pi - \rho$ of the reference configuration was then calculated to be 128.98°, the angle ϵ between the CN bond of the reference configuration and the *z*-axis of the molecule-fixed axis system (*xyz*) was calculated to be 11.31°, and the angle θ between the *z*-axis and the *Z*-axis was calculated to be 12.96°. The angles ρ , ϵ , and θ determined from this calculation were all positive. Considerable care is needed to interpret correctly the sense of the rotation corresponding to positive and negative values of each of these angles.

Figure 2c shows the superposition of Figs. 2a and 2b, with the molecule-fixed axis system both rotated (through an angle θ) and translated with respect to the laboratory-fixed axis system. The origin of the molecule-fixed axis system is at (0, +0.090, -0.901) in the laboratory-fixed axis system, i.e., at the center of mass of the configuration in Fig. 2a. Vectors drawn from the reference configuration atoms to the arbitrary-configuration atoms in Fig. 2c would be the displacement vectors \mathbf{d}_i . Components of the vectors \mathbf{d}_i in the molecule-fixed axis system satisfy the constraint equations (7).

It is worthwhile pointing out that there are many sets of 7 equations which fulfill the mathematical requirements of removing 7 degrees of freedom from the right-hand side of Eq. (1). Some of these sets of constraints are more desirable than others, however, because they eliminate troublesome terms from the quantum mechanical kinetic energy operator. The set of constraints we have chosen, i.e., Eqs. (7), is one such desirable set.

In the derivation of the kinetic energy expression given in the next section, use will be made of the time derivatives of Eqs. (7). These can be obtained easily, but it should be noted that $(d\mathbf{a}_i/dt) = \dot{\rho}(d\mathbf{a}_i/d\rho)$ and $(d/dt)(d\mathbf{a}_i/d\rho) = \dot{\rho}(d^2\mathbf{a}_i/d\rho^2)$, where $\dot{\rho} = d\rho/dt$.

The prescription on the right-hand side of Eq. (1) for calculating the laboratory-fixed coordinates \mathbf{r}_i of each atom, when the other coordinates ($\mathbf{R}; \chi, \theta, \phi; \rho; \mathbf{d}_i$) are given, can be understood as follows. Take the reference configuration $\mathbf{a}_i(\rho)$. Add to each reference position the displacement \mathbf{d}_i to obtain a configuration representing the actual shape of the molecule. Transform the components of the vectors $\mathbf{a}_i + \mathbf{d}_i$ from molecule-fixed axes to laboratory-fixed axes by means of the rotation matrix $S^{-1}(\chi\theta\phi)$. Add to this the laboratory-fixed coordinates of the center of mass of the molecule. The final result is the laboratory-fixed coordinates of each atom.

III. THE HAMILTONIAN

Starting from Eq. 11-1-(3) of Ref. (4) we make use of the various restrictions on the \mathbf{d}_i given in Eqs. (7) to obtain the following expression for the classical rotation-vibration kinetic energy (in matrix notation):

$$T = \frac{1}{2}\omega^{\text{tr}}I\omega + \frac{1}{2}\dot{\rho}^2[(d\mathbf{a}/d\rho)^{\text{tr}}M(d\mathbf{a}/d\rho) - 2(d^2\mathbf{a}/d\rho^2)^{\text{tr}}M\mathbf{d}] + \frac{1}{2}\dot{\mathbf{d}}^{\text{tr}}M\dot{\mathbf{d}} - 2\dot{\rho}\sum_{\alpha}\omega_{\alpha}(d\mathbf{a}/d\rho)^{\text{tr}}MM^{\alpha}\mathbf{d} + \sum_{\alpha}\omega_{\alpha}\mathbf{d}^{\text{tr}}MM^{\alpha}\mathbf{d}. \quad (9)$$

The quantities occurring in Eq. (9) are defined as follows: ω is a 3-component column vector containing the molecule-fixed components of the angular velocity vector of the molecule-fixed axis system in the laboratory-fixed axis system and ω^{tr} is its transpose; I is the 3×3 moment of inertia tensor; \mathbf{a} is a 9-component column vector containing the coordinates of the three atoms in their reference configuration and \mathbf{a}^{tr} is its transpose; $d\mathbf{a}/d\rho$ is the derivative with respect to ρ of the column vector \mathbf{a} and $(d\mathbf{a}/d\rho)^{\text{tr}}$ is its transpose; M is a diagonal 9×9 matrix of the atomic masses; \mathbf{d} is a 9-component column vector containing the molecule-fixed components of the displacement vectors and \mathbf{d}^{tr} is its transpose; $\dot{\mathbf{d}}$ is the time derivative (in the xyz -axis system) of the column matrix \mathbf{d} , and $\dot{\mathbf{d}}^{\text{tr}}$ is its transpose; the M^{α} are 9×9 Mead and Polo ($I\mathcal{Q}$) matrices which form vector cross products; and $\alpha = x, y, z$. If we set $d\mathbf{a}/d\rho = d^2\mathbf{a}/d\rho^2 = 0$ in Eq. (9), then that expression reduces to an expression equivalent to Eq. 11-1-(8) of Ref. (4).

It is now appropriate to use the ideas and notation of Wilson's FG matrix formalism (4), and to do this we introduce the following linear transformations:

$$\begin{bmatrix} S \\ \sigma \end{bmatrix} = \begin{bmatrix} B \\ \beta \end{bmatrix} \begin{bmatrix} \mathbf{d} \end{bmatrix}, \quad (10a)$$

$$\begin{bmatrix} \mathbf{d} \end{bmatrix} = \begin{bmatrix} A & | & \alpha \end{bmatrix} \begin{bmatrix} S \\ \sigma \end{bmatrix}. \quad (10b)$$

The various matrices and portions of partitioned matrices occurring in Eqs. (10) are defined as follows. The column matrix \mathbf{d} contains the 9 components of the 3 displacement vectors \mathbf{d}_i , which for the moment do not necessarily obey the constraint equations. The column matrix S contains the 2 vibrational coordinates (linearized internal stretching coordinates) S_1 and S_3 , which are defined more pre-

cisely following Eq. (14). The 2×9 matrix B allows one to calculate the value of each vibrational coordinate S_k from a given set of displacement vectors \mathbf{d}_i . The elements of the B matrix are here considered to be functions of the large amplitude coordinate ρ ; for ordinary molecules these elements are constants. The column matrix σ contains seven "constraint coordinates." The 7×9 matrix β allows one to calculate the value of each constraint coordinate from a given set of displacement vectors \mathbf{d}_i . The elements of β are chosen such that the equations represented by

$$\sigma = \beta \mathbf{d} = 0 \quad (11)$$

are completely equivalent to the 7 constraint equations given in Eqs. (7) above. Some elements of the β matrix here are functions of ρ ; for ordinary molecules they are all constants. The partitioned 9×9 matrix containing A and α is the inverse of the 9×9 matrix containing B and β . This inverse will exist if the two vibrational coordinates and the seven constraint coordinates are all linearly independent.

An examination of the traditional FG matrix formalism (4) indicates that the G matrix and its inverse must have the following properties

$$\begin{aligned} G &= BM^{-1}B^{\text{tr}}, \\ G^{-1} &= A^{\text{tr}}MA. \end{aligned} \quad (12)$$

These two equations can be shown to be consistent with each other if and only if

$$A^{\text{tr}}M\alpha\beta M^{-1}B^{\text{tr}} = 0. \quad (13)$$

If we set up, in the usual way, the B matrix for the problem under investigation here, we obtain the results given in Table I. It can be shown that this B matrix satisfies

$$\beta M^{-1}B^{\text{tr}} = 0, \quad (14)$$

so that Eq. (13) is also fulfilled and the traditional FG matrix formalism can be used.

Equation (14) implies that the rows of the β matrix and the rows of the B matrix are orthogonal with an inverse-mass weight factor. Thus, once either the β matrix or the B matrix is fixed, the other matrix must be carefully selected. In the present work we choose to work with a B matrix whose rows are defined in the usual way for the stretching vibrations of a triatomic molecule (see Table I). This choice of the B matrix, together with Eq. (14), requires that the two bond lengths of the reference configuration do not vary with ρ . If, on the other hand, we had chosen to use a reference configuration in which the bond lengths did vary with ρ (e.g., assumed their equilibrium values for each ρ), then a different B matrix would have to be used.

TABLE I
THE B MATRIX

	d_{1x}	d_{1y}	d_{1z}	d_{2x}	d_{2y}	d_{2z}	d_{3x}	d_{3y}	d_{3z}
S_1	0	$+\sin(\rho - \epsilon)$	$-\cos(\rho - \epsilon)$	0	$-\sin(\rho - \epsilon)$	$\cos(\rho - \epsilon)$	0	0	0
S_3	0	0	0	0	$-\sin \epsilon$	$-\cos \epsilon$	0	$\sin \epsilon$	$\cos \epsilon$

The A matrix for this problem, for the coordinates

$$\begin{aligned} s &= (S_1 + S_3)/2^{1/2}, \\ a &= (S_1 - S_3)/2^{1/2}, \end{aligned} \quad (15)$$

is given² in Table I of Thorson and Nakagawa (13) for $m_1 = m_3 \rightarrow M$, $m_2 \rightarrow m$, $\epsilon = 1/2\rho \rightarrow \alpha$, $x \leftrightarrow y$, and $z \leftrightarrow -z$.

Using the expressions

$$\begin{aligned} \mathbf{d} &= AS, \\ \dot{\mathbf{d}} &= \dot{\rho}\alpha S + A\dot{S}, \end{aligned} \quad (16)$$

where $\alpha \equiv dA/d\rho$, and changing notation somewhat, we can rewrite Eq. (9) as

$$T = 1/2\omega^{\text{tr}}I\omega + \sum_{\alpha} \omega_{\alpha}S^{\text{tr}}A^{\text{tr}}MM^{\alpha}A\dot{S} + \omega_{\rho}S^{\text{tr}}\alpha^{\text{tr}}MA\dot{S} + 1/2\dot{S}^{\text{tr}}G^{-1}\dot{S}, \quad (17)$$

where $\alpha = x, y, z$. We now have

$$\omega^{\text{tr}} = [\omega_x, \omega_y, \omega_z, \omega_{\rho}], \quad (18)$$

where

$$\omega_{\rho} = \dot{\rho},$$

and we have enlarged the I matrix to be

$$I = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} & I_{x\rho} \\ I_{yx} & I_{yy} & I_{yz} & I_{y\rho} \\ I_{zx} & I_{zy} & I_{zz} & I_{z\rho} \\ I_{\rho x} & I_{\rho y} & I_{\rho z} & I_{\rho\rho} \end{bmatrix}, \quad (19)$$

where

$$I_{\alpha\beta} = \sum_i m_i [\delta_{\alpha\beta} (\mathbf{a}_i + \mathbf{d}_i) \cdot (\mathbf{a}_i + \mathbf{d}_i) - (\mathbf{a}_i + \mathbf{d}_i)_{\alpha} (\mathbf{a}_i + \mathbf{d}_i)_{\beta}], \quad (20)$$

$$I_{\alpha\rho} = I_{\rho\alpha} = -2(d\mathbf{a}/d\rho)^{\text{tr}}MM^{\alpha}AS + S^{\text{tr}}A^{\text{tr}}MM^{\alpha}\alpha S,$$

and

$$I_{\rho\rho} = (d\mathbf{a}/d\rho)^{\text{tr}}M(d\mathbf{a}/d\rho) - 2(d^2\mathbf{a}/d\rho^2)^{\text{tr}}MAS + S^{\text{tr}}\alpha^{\text{tr}}M\alpha S,$$

for $\alpha, \beta = x, y, z$.

² The signs of the elements $z_1^a = z_3^a$ in Table I of (13) are incorrect.

We have so far considered only the kinetic energy expression. We must also consider the potential energy expression V , which can be expanded for each value of ρ as a Taylor series in S_1 and S_3 :

$$\begin{aligned} V &= V_0(\rho) + \sum_i K_i(\rho)S_i + \frac{1}{2} \sum_{ij} F_{ij}(\rho)S_iS_j + \dots \\ &= V_0(\rho) + K^{\text{tr}}S + \frac{1}{2}S^{\text{tr}}FS + \dots \end{aligned} \quad (21)$$

In this equation $V_0(\rho)$ is the bending potential function of the reference configuration ($S_1 = S_3 = 0$). Furthermore, the coefficients $K_i(\rho)$ are *not* in general zero for all values of ρ , since the reference configuration is not the equilibrium configuration for all values of ρ [see comments following Eq. (14) and also see Eq. (55)]. The terms linear in the S_i , and cubic and higher-order terms can be considered as perturbations in the following discussion of normal coordinates.

Following Ref. (4) we introduce normal coordinates by writing

$$S = LQ, \quad (22)$$

where the matrix L is chosen such that $L^{-1}GFL$ is diagonal [the F matrix contains the $F_{ij}(\rho)$]. Differentiating Eq. (22) with respect to time yields

$$\dot{S} = \dot{\rho}\mathcal{L}Q + L\dot{Q}, \quad (23)$$

where $\mathcal{L} \equiv dL/d\rho$. We now rewrite Eq. (17) as

$$T = \frac{1}{2}\omega^{\text{tr}}I\omega + \sum_{\alpha} \omega_{\alpha}Q^{\text{tr}}\zeta^{\alpha}\dot{Q} + \frac{1}{2}\dot{Q}^{\text{tr}}\dot{Q}, \quad (24)$$

where α ranges over the *four* quantities x, y, z, ρ . The ζ 's are defined by

$$\begin{aligned} \zeta^{\alpha} &= L^{\text{tr}}A^{\text{tr}}MM^{\alpha}AL, \quad \text{for } \alpha = x, y, z, \\ \zeta^{\rho} &= L^{\text{tr}}\mathcal{Q}^{\text{tr}}MAL + \mathcal{L}^{\text{tr}}G^{-1}L. \end{aligned} \quad (25)$$

The components of I not involving the subscript ρ are still defined by Eq. (20). The other components are redefined to be

$$\begin{aligned} I_{\rho\alpha} &= I_{\alpha\rho} = -2(d\mathbf{a}/d\rho)^{\text{tr}}MM^{\alpha}ALQ + Q^{\text{tr}}L^{\text{tr}}A^{\text{tr}}MM^{\alpha}(\mathcal{Q}L + A\mathcal{L})Q, \\ I_{\rho\rho} &= (d\mathbf{a}/d\rho)^{\text{tr}}M(d\mathbf{a}/d\rho) - 2(d^2\mathbf{a}/d\rho^2)^{\text{tr}}MALQ \\ &\quad + Q^{\text{tr}}[L^{\text{tr}}\mathcal{Q}^{\text{tr}}M\mathcal{Q}L + \mathcal{L}^{\text{tr}}A^{\text{tr}}MA\mathcal{L} + 2L^{\text{tr}}\mathcal{Q}^{\text{tr}}MA\mathcal{L}]Q. \end{aligned} \quad (26)$$

We have obtained in Eq. (24) the classical kinetic energy expression, expressed in terms of the coordinates and velocities. If we set $\omega_{\rho} \equiv \dot{\rho} = 0$, Eq. (24) reduces to an expression like Eq. 11-1-(14) of Ref. (4).

We can derive the quantum mechanical kinetic energy operator by following, almost exactly, the arguments of Sects. 2, 3, and 4 of Chap. 11 of Ref. (4). There is one final choice to make, however, and that concerns the volume element to be used for integration [see Eq. 11-3-(4) of Ref. (4)]. Here we choose the volume element

$$d\tau = dQ_1 dQ_3 d\rho \sin \theta d\theta d\phi d\chi. \quad (27)$$

This is consistent with a kinetic energy operator of the following form:

$$T = \frac{1}{2}\mu^{1/4} \sum_{\alpha,\beta} (J_\alpha - p_\alpha)\mu_{\alpha\beta}\mu^{-1/2} (J_\beta - p_\beta)\mu^{1/4} + \frac{1}{2}\mu^{1/4} \sum_k P_k\mu^{-1/2}P_k\mu^{1/4}, \quad (28)$$

where $\alpha, \beta = x, y, z$ or ρ and $k = 1$ or 3 . The momenta in Eq. (28) are given classically by

$$\begin{aligned} J_\alpha &= (\partial T / \partial \omega_\alpha), \\ p_\alpha &= Q^{\text{tr}} \zeta^\alpha P, \end{aligned} \quad (29)$$

and

$$P_k = (\partial T / \partial \dot{Q}_k).$$

The quantum mechanical operators corresponding to J_x, J_y and J_z , i.e., to the three molecule-fixed components of the total angular momentum, are given in Eqs. 11-4-(6) of Ref. (4), where p_x, p_θ and p_ϕ represent $-i\hbar(\partial/\partial\chi)$, $-i\hbar(\partial/\partial\theta)$, and $-i\hbar(\partial/\partial\phi)$, respectively. The quantum mechanical operators corresponding to J_ρ and P_k are $-i\hbar(\partial/\partial\rho)$ and $-i\hbar(\partial/\partial Q_k)$, respectively. The μ matrix is the inverse of the I' matrix where

$$I'_{\alpha\beta} = [I_{\alpha\beta} - Q^{\text{tr}} \zeta^\alpha (\zeta^\beta)^{\text{tr}} Q]. \quad (30)$$

Using Eq. (22) the potential energy expression in Eq. (21) becomes

$$V = V_0(\rho) + K^{\text{tr}} L Q + \frac{1}{2} Q^{\text{tr}} \Lambda(\rho) Q + \dots, \quad (31)$$

where the 2×2 diagonal matrix $\Lambda(\rho)$ is $L^{\text{tr}} F L$.

IV. THE ENERGY LEVELS ASSOCIATED WITH THE BENDING COORDINATE

An approximation to the energy levels for the rotation-bending-stretching motion of a triatomic molecule undergoing large amplitude excitation of the bending vibration can be obtained from the zeroth-order Hamiltonian H_{rbs}^0 . The zeroth-order kinetic energy is derived by setting $Q_1 = Q_3 = 0$ in the μ matrix (which then becomes the μ^0 matrix) in the exact kinetic energy given in Eq. (28) and by ignoring the vibrational angular momenta p_α . The zeroth-order potential energy is obtained from Eq. (31) by omitting the (small) term linear in Q , the

terms cubic and higher in Q , and by replacing the two elements of $\Lambda(\rho)$ by their mean values λ_1 and λ_3 .

The replacing of μ by μ^0 is analogous to the similar approximation made in deriving the vibration-rotation Hamiltonian in the normal treatment [see, for example, Eq. 11-5-(1) of Ref. (4)]. It is justifiable here since Q_1 and Q_3 are always of small amplitude, regardless of the displacement of the bending angle. This is a result of having removed ρ from the vibrational problem. In the normal formalism Q_1 and Q_3 are not of small amplitude when the displacement of the bending angle from equilibrium is large. Thus, even though the elements of the μ matrix for a linear molecule do not depend on Q_2 in the normal treatment [see Eq. (27) of Amat and Henry (14)], their power series representation in Q_1 and Q_3 is not rapidly convergent when large displacements in the bending angle occur.

The zeroth-order rotation-bending-stretching Hamiltonian obtained is

$$H_{\text{rbs}}^0 = H_{\text{rb}}^0 + H_s^0, \quad (32)$$

where

$$H_{\text{rb}}^0 = \frac{1}{2}(\mu^0)^{1/4} \sum_{\alpha, \beta} J_{\alpha} \mu_{\alpha\beta}^0 (\mu^0)^{-1/2} J_{\beta} (\mu^0)^{1/4} + V_0(\rho) \quad (33)$$

and

$$H_s^0 = \frac{1}{2}(P_1^2 + P_3^2 + \lambda_1 Q_1^2 + \lambda_3 Q_3^2). \quad (34)$$

Henceforth in this section we concentrate on H_{rb}^0 . Since the elements of the μ^0 matrix depend on ρ , they do not commute with J_{ρ} , and we are unable to remove the determinant μ^0 from H_{rb}^0 . However, we can simplify H_{rb}^0 somewhat by using the commutation relation given in Eq. (13) of Hougen (15), which leads to an expression for H_{rb}^0 analogous to that of Eq. (14) of Hougen (15); this expression is

$$\begin{aligned} H_{\text{rb}}^0 = & \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta}^0 J_{\alpha} J_{\beta} + \frac{1}{2} \sum_{\beta} (J_{\rho} \mu_{\rho\beta}^0) J_{\beta} \\ & + \frac{1}{2} (\mu^0)^{1/4} \{ J_{\rho} \mu_{\rho\rho}^0 (\mu^0)^{-1/2} [J_{\rho} (\mu^0)^{1/4}] \} + V_0(\rho), \end{aligned} \quad (35)$$

where, for example, in the second term J_{ρ} only acts on $\mu_{\rho\beta}^0$. If all the elements of the μ^0 matrix did commute with J_{ρ} , then the expression for H_{rb}^0 would simply be the first term in the above expression [analogous to the first term in Eq. 11-5-(3) of Ref. (4)].

With the choice of reference configuration axes as discussed in the previous section [see Eqs. (2) and (4)] the zeroth order rotation-bending Hamiltonian becomes

$$\begin{aligned} H_{\text{rb}}^0 = & \frac{1}{2} \mu_{xx}^0 J_x^2 + \frac{1}{2} \mu_{yy}^0 J_y^2 + \frac{1}{2} \mu_{zz}^0 J_z^2 + \frac{1}{2} \mu_{yz}^0 (J_y J_z + J_z J_y) + \frac{1}{2} \mu_{\rho\rho}^0 J_{\rho}^2 \\ & + \frac{1}{2} (J_{\rho} \mu_{\rho\rho}^0) J_{\rho} + \frac{1}{2} (\mu^0)^{1/4} \{ J_{\rho} \mu_{\rho\rho}^0 (\mu^0)^{-1/2} [J_{\rho} (\mu^0)^{1/4}] \} + V_0(\rho), \end{aligned} \quad (36)$$

where

$$\begin{aligned}
 \mu_{xx}^0 &= 1/I_{xx}^0, \\
 \mu_{yy}^0 &= I_{zz}^0 / (I_{yy}^0 I_{zz}^0 - I_{yz}^0 I_{yz}^0), \\
 \mu_{zz}^0 &= I_{yy}^0 / (I_{yy}^0 I_{zz}^0 - I_{yz}^0 I_{yz}^0), \\
 \mu_{yz}^0 &= -I_{yz}^0 / (I_{yy}^0 I_{zz}^0 - I_{yz}^0 I_{yz}^0), \\
 \mu_{\rho\rho}^0 &= 1/I_{\rho\rho}^0, \\
 \mu^0 &= [I_{xx}^0 I_{\rho\rho}^0 (I_{yy}^0 I_{zz}^0 - I_{yz}^0 I_{yz}^0)]^{-1}, \\
 I_{xx}^0 &= (u_1 + u_3 + 2u_{13} \cos \rho)/m, \\
 I_{yy}^0 &= [u_1 \cos^2 (\rho - \epsilon) + u_3 \cos^2 \epsilon + 2u_{13} \cos \epsilon \cos (\rho - \epsilon)]/m, \\
 I_{zz}^0 &= [u_1 \sin^2 (\rho - \epsilon) + u_3 \sin^2 \epsilon - 2u_{13} \sin \epsilon \sin (\rho - \epsilon)]/m, \\
 I_{yz}^0 &= [u_1 \sin 2(\rho - \epsilon) - u_3 \sin 2\epsilon + 2u_{13} \sin (\rho - 2\epsilon)]/2m, \\
 I_{\rho\rho}^0 &= [u_1(1 - \epsilon')^2 + u_3(\epsilon')^2 - 2u_{13}\epsilon'(1 - \epsilon') \cos \rho]/m,
 \end{aligned} \tag{37}$$

and

$$\epsilon' = \frac{d}{d\rho} \epsilon = \frac{u_1 + u_{13} \cos \rho}{u_1 + u_3 + 2u_{13} \cos \rho}. \tag{38}$$

By using Eq. (4), all the $\mu_{\alpha\beta}^0$ in Eq. (36) can be obtained as explicit functions of ρ . This Hamiltonian is that of a rigidly bending rigid rotor ($Q_1 = Q_3 = 0$) and is comparable to that for a rigid rotor (all $Q_i = 0$) in the standard treatment.

Because J is rigorously a good quantum number for the problem under consideration, it is convenient to consider separately bending vibrational levels characterized by different values of J . The simplest set of bending vibrational levels to treat theoretically is characterized by $J = 0$. In this section of the paper we consider only such levels.³ Thus, putting $J_x = J_y = J_z = 0$ and $J_\rho = -i\hbar(\partial/\partial\rho)$ in Eq. (36), we obtain

$$\begin{aligned}
 H_b^0 &= -\frac{\hbar^2}{2I_{\rho\rho}^0} \frac{\partial^2}{\partial\rho^2} - \frac{\hbar^2}{2} \left(\frac{\partial}{\partial\rho} \frac{1}{I_{\rho\rho}^0} \right) \frac{\partial}{\partial\rho} \\
 &\quad - \frac{\hbar^2}{2} (\mu^0)^{1/4} \left\{ \frac{\partial}{\partial\rho} \frac{1}{I_{\rho\rho}^0} (\mu^0)^{-1/2} \left[\frac{\partial}{\partial\rho} (\mu^0)^{1/4} \right] \right\} + V_0(\rho).
 \end{aligned} \tag{39}$$

The equation we wish to solve is therefore,

$$(H_b^0 - E)\psi_b(\rho) = 0. \tag{40}$$

³ Note that states with $J = 0$ occur for linear molecules only when $\ell = 0$, i.e., only when $v_2 = 0, 2, 4, \dots$. States with $J = 0$ occur for bent molecules when $K = 0$, i.e., for all values of v_2 .

Making the substitution⁴

$$\psi_b(\rho) = [I_{\rho\rho}^0]^{1/2} \phi_b(\rho) \quad (41)$$

removes the linear derivative term and Eq. (40) becomes

$$\frac{\partial^2}{\partial \rho^2} \phi_b(\rho) = \left\{ f_1(\rho) + \frac{2I_{\rho\rho}^0}{\hbar^2} [V_0(\rho) - E] \right\} \phi_b(\rho), \quad (42)$$

where

$$\begin{aligned} f_1(\rho) = & -I_{\rho\rho}^0(\mu^0)^{1/4} \left\{ \frac{\partial}{\partial \rho} \frac{1}{I_{\rho\rho}^0} (\mu^0)^{-1/2} \left[\frac{\partial}{\partial \rho} (\mu^0)^{1/4} \right] \right\} \\ & + \frac{3}{4(I_{\rho\rho}^0)^2} \left(\frac{\partial}{\partial \rho} I_{\rho\rho}^0 \right)^2 - \frac{1}{2I_{\rho\rho}^0} \left(\frac{\partial^2}{\partial \rho^2} I_{\rho\rho}^0 \right) \quad (43) \\ = & (\mu^0)^{1/4} (I_{\rho\rho}^0)^{1/2} \left\{ \frac{\partial^2}{\partial \rho^2} [(\mu^0)^{-1/4} (I_{\rho\rho}^0)^{-1/2}] \right\}. \end{aligned}$$

We can obtain $f_1(\rho)$ as an explicit function of ρ and we notice that

$$\lim_{\rho \rightarrow 0} f_1(\rho) = -\frac{1}{4\rho^2} + g(u_1, u_3, u_{13}), \quad (44)$$

where $g(u_1, u_3, u_{13})$ is a function of u_1, u_3 , and u_{13} , but not of ρ . Thus, if we put $V_0(\rho) = \frac{1}{2}k_2\rho^2 - (\hbar^2/2I_{\rho\rho}^0)g(u_1, u_3, u_{13})$ in Eq. (42), and take the linear limit ($\rho \rightarrow 0$), then (42) reduces to an equation describing the $\ell = 0$ levels of the two-dimensional isotropic harmonic-oscillator bending vibration in a linear triatomic molecule with masses m_1, m_2, m_3 and bond lengths r_{12}^0, r_{32}^0 . (Note that the volume element corresponding to Eq. (42) in the linear limit is $I_{\rho\rho}^0(\rho = 0) d\rho$, which can easily be replaced by $d\rho$. The volume element is not $\rho d\rho$.)

To solve Eq. (42) we must choose a potential function $V_0(\rho)$ and then we can numerically integrate to determine $\phi_b(\rho)$ and E . The numerical integration technique that we have used is the Numerov-Cooley method (16). Using the IBM 360/50 system at NRC each eigenvalue took less than 3 sec to obtain. Because of the singularity at $\rho = 0$, where $f_1(\rho) \rightarrow -\infty$, the numerical integration had to be started off by a series solution at $\rho = 0$.

To test the accuracy of this method of solving one-dimensional equations such as Eq. (42), we first used the method to determine the eigenvalues of an isotropic two-dimensional harmonic oscillator perturbed by a Lorentz hump. The eigenvalues of this have previously been determined by a method involving truncation of the infinite Hamiltonian matrix [see Johns (17)]. The eigenvalues obtained agreed, to within machine precision [the 8 significant figures of Ref. (17)], with those obtained in Ref. (17). As a further check two independent derivations of H_b^0 were made, one in γ and the other in $\rho \equiv \pi - \gamma$, and the eigenvalues of these

⁴ This is equivalent to making the transformation $(I_{\rho\rho}^0)^{-1/2} H_b^0 (I_{\rho\rho}^0)^{+1/2}$. By doing this the volume element is changed from $d\rho$ to $(I_{\rho\rho}^0) d\rho$.

two H_b^0 agreed to 14 significant figures. By varying the interval size in the numerical integration procedure, and the number of steps in the series solution, results at least as accurate as any experimental determination of the energy levels can be obtained.

It is important to realize that the speed and accuracy of this method is virtually independent of the potential function used, unlike the methods used by Johns (17) or Dixon (18). Only one statement in the program need be changed in order to change $V_0(\rho)$.

As examples of the application of this program we have chosen to study the energy levels of (a) the \tilde{A}^1A'' bent excited electronic states of HCN and DCN; (b) the bent ground states of H_2O , HDO, and D_2O ; and (c) the linear ground states of HCN and DCN.

(a) *The \tilde{A}^1A'' States of HCN and DCN*

In the ground state, $\tilde{X}^1\Sigma^+$, HCN has a linear equilibrium conformation whereas in the lowest known excited electronic state, \tilde{A}^1A'' , it has a bent conformation. As a consequence many vibrational levels involving the bending motion have been

TABLE II
COMPARISON OF OBSERVED AND CALCULATED VALUES OF $\Delta G_{v+1/2}$ (cm^{-1}) FOR
THE \tilde{A}^1A'' STATES OF HCN AND DCN^a

v	Obs (19)	Calc 1	O - C	Calc 2	O - C	Calc 3	O - C	Calc 4	O - C
(i) HCN Least-squares fit of observed data									
0	938.3	942.6	-4.3	936.0	+2.3	925.6	+12.7	937.1	+1.2
1	919.3	920.9	-1.6	919.2	+0.1	919.1	+0.2	919.4	-0.1
2	898.0	896.2	+1.8	898.7	-0.7	905.1	-7.1	898.3	-0.3
3	870.8	867.4	+3.4	872.1	-1.3	878.9	-8.1	871.5	-0.7
4	834.5	832.4	+2.1	834.1	+0.4	830.8	+3.7	834.1	+0.4
5	780.3	786.8	-6.5	778.7	+1.6	768.5	+11.8	779.6	+0.7
(ii) DCN Results predicted from parameters of (i)									
0		791.7		746.0		716.2		726.9	
1		777.5		736.2		714.0		716.9	
2	707.0	761.7	-54.7	724.8	-17.8	708.9	-1.4	705.7	+1.3
3	692.8	743.9	-51.1	711.3	-18.5	700.2	-7.4	692.9	-0.1
4	676.0	723.4	-47.4	694.8	-18.8	686.3	-10.3	677.6	+1.6
5		699.2		673.2		663.5		658.6	
(iii) Parameters obtained from (i)									
		Calc 1		Calc 2		Calc 3		Calc 4	
Barrier		7064.9 cm^{-1}		6272.4 cm^{-1}		5766.1 cm^{-1}		6353.0 cm^{-1}	
Shape		$k = 0.52036$		$k = 0.24699$		$C = 0.14113$		$k = 0.28620$	
factor		$\text{mdyn} \cdot \text{\AA}/\text{rad}^2$		$\text{mdyn} \cdot \text{\AA}/\text{rad}^2$				$\text{mdyn} \cdot \text{\AA}/\text{rad}^2$	
		($k = 0.52036$		($k = 0.24699$				($k = 0.28620$	
		$\times 10^{-18} \text{ N} \cdot \text{m}/\text{rad}^2)$		$\times 10^{-18} \text{ N} \cdot \text{m}/\text{rad}^2)$				$\times 10^{-18} \text{ N} \cdot \text{m}/\text{rad}^2)$	

^a We have taken $r_{12}^0 = r(\text{H}-\text{C}) = 1.140 \text{ \AA}$, $r_{32}^0 = r(\text{N}-\text{C}) = 1.297 \text{ \AA}$ and $\gamma^0 = 125^\circ$ (20).

observed in the \tilde{A}^1A'' state (19). The observed differences between successive levels with $K = 0$, $G(v+1) - G(v) \equiv \Delta G(v + \frac{1}{2})$, are listed for HCN and DCN in column 2 of Table II.

We have fitted the seven experimentally observed levels of the \tilde{A} state of HCN which have $K = 0$ in four separate least-squares calculations; in each calculation, the CH and CN reference configuration bond lengths and the HCN equilibrium angle were taken to be the equilibrium values given in Ref. (20).

The first two calculations (calculations 1 and 2 of Table II) were performed using the normal "infinitesimal amplitude" Hamiltonian for a rectilinear coordinate system (13, 18, 17). Thus, the Hamiltonian used consisted of a kinetic part $T_0(K = \ell = 0)$ and a potential part V_0 given by

$$\begin{aligned} T_0(r) &= -\frac{1}{2}\hbar^2 G_{22} \left(\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \right) \\ V_0(r) &= +\frac{1}{2}kr^2 + K_B/(c^2 + r^2), \end{aligned} \quad (45)$$

where r is the bending coordinate, G_{22} is the bending vibration G matrix element (shown on p. 304 of (4) as $G_{\phi\phi}^3$), k is a force constant (F_{22} in FG matrix notation), and K_B and c^2 are parameters.⁵ The first two calculations differ in the way in which the angular deformation, and hence the equilibrium angle, was related to the rectilinear bending coordinate. In the rectilinear formalism, the vibrational coordinate corresponding to the bending angle is linearly related to the Cartesian displacements of the atoms. Thus, the change in the true bending angle of the molecule is related to the change in the rectilinear bending coordinate in a relatively complicated way, as given, for example, by Plíva (10) in his Eqs. (7a)–(7c). In order to be completely consistent in a calculation using a rectilinear bending coordinate, it is necessary to calculate a value for r_{\min} from the equilibrium bond angle by means of Plíva's equations; this was done for calculation 1. A more naive determination of r_{\min} was used for calculation 2. To a good approximation, the rectilinear bending coordinate r of Eq. (45) is equal to the change in the bond angle of the linear molecule (measured in radians), provided that the deviation from linearity is not large. Thus, in calculation 2 we have not used Plíva's equations, but have simply set r_{\min} equal to the supplement of the equilibrium bond angle (measured in radians) of the bent \tilde{A} state of HCN. This is entirely equivalent to the approach previously used by Johns (17).

The third calculation (calculation 3 of Table II) was performed using Eq. (42) and a modified Plíva (21) potential:

$$V_0(\rho) = \frac{U(\rho)}{1+C} \left[1 + \frac{C \cdot U(\rho)}{B} \right], \quad (46)$$

⁵ In Ref. (17) a truncated matrix diagonalization technique was used for this problem, the $K = 0, 1, 2$, and 3 levels all being used in the least-squares fit. The results [Table I of Ref. (17)] are not quite the same as those obtained here since we only fit the $K = 0$ levels.

where B is the barrier height [$B = C_m \cos^2(\gamma_e/2)$ in ref. (21)], C is a shape parameter and $U(\rho)$ is given by

$$U(\rho) = \frac{2B}{\cos^2(\gamma_e/2)} \frac{\cos^2 \frac{1}{2}(\rho + \gamma_e)}{\cos(\rho/2)} \left[1 + \frac{\cos^2 \frac{1}{2}(\rho + \gamma_e)}{\cos^2 \frac{1}{2}(\rho - \gamma_e)} \right]^{-1}. \quad (47)$$

In (47), γ_e is the equilibrium value of the bond angle γ .

The fourth calculation (calculation 4 of Table II) was performed using Eq. (42) and a simple potential, analogous to that used in calculations 1 and 2, composed of a sum of quadratic and Lorentz terms

$$V_0(\rho) = +\frac{1}{2}k\rho^2 + K_B/(c^2 + \rho^2), \quad (48)$$

where k , K_B , and c^2 are parameters.

The results of the four least-squares calculations on the HCN data are given in part (i) of Table II. (Since we keep the equilibrium bond angle fixed, there are only two adjustable parameters in each of the four calculations.) Taken by themselves, these results are inconclusive, since calculations 3 and 4 are no better than calculations 1 and 2. This is perhaps not too surprising, since it is obviously possible to compensate for errors in the kinetic energy terms by changes in the potential energy terms.

The results predicted for DCN, which are given in part (ii) of Table II, are much more informative; in part (ii) we have used the potential function obtained from part (i) and simply changed the mass of hydrogen to that of deuterium in the kinetic energy expression (and in the expression relating γ_e to r_{\min} in calculation 1). Calculations 1 and 2 give poor fits to the levels of DCN, whereas calculations 3 and 4 give fits which are only slightly worse than the corresponding fits for HCN. In other words, when we use Eq. (42), the potentials are more nearly isotopically invariant (as indeed they should be). Thus, the function $f_1(\rho)$, arising from the dependence of $I_{\rho\rho}^0$ on ρ , is important.

It is perhaps surprising that the "completely consistent" approach to using the rectilinear coordinate system, as shown in calculation 1, leads to a considerably poorer fit to the experimental data than does the "naive" approach represented in calculation 2. It is the opinion of the authors, that T_0 in Eqs. (45) can thus be considered in two ways: either as representing the exact kinetic energy expression in rectilinear coordinates, or as representing an approximate kinetic energy expression in curvilinear coordinates. In the former case, the conversion from equilibrium bond angle to r_{\min} via Plíva's equations must be used; in the latter case, r_{\min} is just the supplement of the equilibrium angle. It is apparent that the curvilinear point of view leads to better agreement with experiment than the rectilinear point of view does. {We have already noted that the curvilinear kinetic energy expression reduces [see Eq. (44)] to the rectilinear kinetic energy expression as the displacement ρ from linearity becomes zero.}

Of the two potentials used in calculations 3 and 4, the one due to Plíva (21) is

intuitively the more desirable, despite the greater apparent complexity. In the Plíva potential both the barrier height and the equilibrium angle appear explicitly (the potential has a minimum at this equilibrium angle and a maximum, equal to B , when $\rho = 0$) and it also becomes infinite when $\rho = \pm\pi$. The much simpler expression of Eq. (48) does not have all the desirable attributes just mentioned, but it does serve to reproduce the experimental data much better.

The parameters obtained from the fits given in part (i) are given in part (iii) of Table II. Each of the three potential functions used has three parameters. For convenience, the programs were written so that these parameters were obtained as functions of the equilibrium angle γ_e , the barrier height, and a shape factor which was k in the first, second, and fourth calculations and C in the third calculation. Since we chose to keep γ_e fixed, only two parameters were varied in the least-squares fits. It is these two parameters, one of which is always the barrier, which are given in part (iii) of Table II.

We have found in trial calculations that the minimum value of the vibrational interval for the $K = 0$ levels occurs at an energy corresponding to the barrier height, as obtained for any K in the normal formalism (18). According to Ref. (17) the minimum interval in the \tilde{A} state of HCN is observed for the $K = 1$ levels to occur at an energy about 6800 cm^{-1} above the minimum in the potential energy. However, until we have determined the effect of allowing the molecule to rotate by diagonalizing the Hamiltonian of Eq. (36) we cannot say for certain if the minimum in a $K \neq 0$ curve does correspond to the barrier height. From the available $K = 0$ experimental results we deduce a barrier height⁶ of about 6350 cm^{-1} .

(b) *The \tilde{X}^1A_1 States of H_2O , HDO , and D_2O*

We have used Eq. (42) with the Plíva potential and the quadratic plus Lorentz potential in turn to fit the fundamental and first overtone of the bending vibration in H_2O . The equilibrium geometry of H_2O is well known so that each potential has two free parameters and the two frequencies can be fitted exactly. The resulting parameters were then used to calculate the second overtone in H_2O and the fundamentals and overtones of HDO and D_2O . The results, summarized in Table III, show that the two potentials fit the data almost equally well although the quadratic plus Lorentz potential serves to predict the second overtone of H_2O slightly better than does the Plíva potential. It is perhaps significant that the quadratic plus Lorentz potential gives a slightly higher barrier just as it did for the \tilde{A}^1A'' state of HCN.

⁶ This value for the barrier height depends upon the assumption that the equilibrium bond lengths do not change with bending angle; it could be slightly different from the true barrier height.

TABLE III
COMPARISON OF OBSERVED AND CALCULATED FUNDAMENTALS AND OVERTONES
(cm^{-1}) OF THE GROUND ELECTRONIC STATE BENDING VIBRATION OF H_2O ,
 HDO , AND D_2O^a

		Observation	Plüva potential	Quadratic + Lorentz potential
H_2O	ν_2	1594.8 (22)	1594.9	1595.0
	$2\nu_2$	3151.5 (23)	3151.4	3151.5
	$3\nu_2$	4666.3 (24)	4660.1	4662.6
HDO	ν_2	1402.2 (25)	1400.5	1400.5
	$2\nu_2$	2782.2 (26)	2773.0	2772.6
	$3\nu_2$	4145.6 (26)	4111.9	4112.3
D_2O	ν_2	1178.7 (25)	1171.5	1171.5
	$2\nu_2$		2324.8	2324.3
	$3\nu_2$		3457.1	3456.1
		Barrier	10155.4 cm^{-1}	10900.3 cm^{-1}
		Shape factor	$C = 0.020566$	$k = 0.51018 \text{ mdyn} \cdot \text{\AA} / \text{rad}^2$ ($k = 0.51018 \times 10^{-18} \text{ N} \cdot \text{m} / \text{rad}^2$)

^a We have taken $r_{12}^0 = r_{32}^0 = 0.957 \text{ \AA}$ and $\tau^0 = 104.5^\circ$ (20).

(c) *The $\tilde{X}^1\Sigma^+$ States of HCN and DCN*

In order to demonstrate that Eq. (42) can be applied equally well to linear molecules as to bent molecules we have fitted the first overtone of the bending vibration, $2\nu_2$, of the ground state of HCN. A simple potential, quadratic in ρ was used. It should be remembered that, for the moment at any rate, we only calculate the levels with $K \equiv \ell = 0$ so that levels such as ν_2 and $3\nu_2$ are not obtained but only $2\nu_2$, $4\nu_2$, $6\nu_2$, etc.⁷ The results obtained are compared with those obtained using the usual "infinitesimal-amplitude" harmonic oscillator approximation in Table IV. In contrast to the results of the usual harmonic oscillator formalism the present calculations predict a slightly anharmonic series of levels [i.e., not having a constant $\Delta G(v + \frac{1}{2})$] although this anharmonicity is rather less than that actually observed. The reason for the predicted anharmonicity is simply that we have allowed for the variation of $I_{\rho\rho}^0$ with the bending angle and therefore the term $f_1(\rho)$ is present as an effective anharmonicity.

⁷ The quantum number K , associated with the bent molecule, and the quantum number ℓ , associated with the linear molecule, represent the same physical quantity in a vibrating and rotating triatomic molecule, namely the projection of the total angular momentum along the molecule-fixed z -axis. These two symbols are thus equivalent, provided that precisely the same molecule-fixed z -axis (27) is used when defining K as is used when defining ℓ . The quantum number ν_2 associated with the bent molecule, and the quantum number ν_2 associated with the linear molecule, do not, however, represent the same quantity (see, for example, Fig. 1 of Ref. (17)).

TABLE IV
COMPARISON OF OBSERVED AND CALCULATED FUNDAMENTALS AND OVERTONES
(cm^{-1}) OF THE GROUND ELECTRONIC STATE BENDING VIBRATION OF HCN
AND DCN^a

Observed			Calculated	
			Traditional Kinetic Energy	Curvilinear Kinetic Energy
HCN	$2\nu_2$	1412.0 (25)	1412.0	1412.0
	$4\nu_2$	2799.2 (25)	2824.0	2816.3
DCN	$2\nu_2$	1130.0 (28)	1126.1	1123.7
			$k = 0.2450$ $\text{mdyn}\cdot\text{\AA}/\text{rad}^2$ $(k = 0.2450 \times 10^{-18}$ $\text{N}\cdot\text{m}/\text{rad}^2)$	$k = 0.2477$ $\text{mdyn}\cdot\text{\AA}/\text{rad}^2$ $(k = 0.2477 \times 10^{-18}$ $\text{N}\cdot\text{m}/\text{rad}^2)$

^a We have taken $r_{12}^0 = 1.066 \text{ \AA}$, $r_{32}^0 = 1.153 \text{ \AA}$, $\tau^0 = 180^\circ$ (20).

There is plainly much more that can be done with these data. The next step is to diagonalize the rigidly-bending rigid-rotor Hamiltonian of Eq. (36) and to fit levels with $J \neq 0$.

V. CUBIC STRETCH-BEND INTERACTION CONSTANTS IN THE POTENTIAL ENERGY FUNCTION

In Sect. IV we considered potential energy functions $V_0(\rho)$ which depended only upon the coordinate ρ of the bending vibration. Since such functions were used directly in numerical form it was unnecessary (and in some cases impractical) to try to represent them as power series expansions about some equilibrium point, and to introduce the traditional concepts of harmonic and anharmonic terms in the potential energy function.

For the considerations of Sects. VI and VII, however, it is necessary to consider potential functions which depend on the coordinate ρ of the bending vibration and also on the coordinates S_1 and S_3 of the two stretching vibrations. These functions, having more than one independent variable, cannot easily be handled numerically, so we revert now to the conventional power series representations of the potential energy. Power series representations are, of course, characterized by a number of harmonic and anharmonic force constants.

As mentioned in Sect. II, Plíva (9, 10) discussed the relation between potential constants for force fields expressed in terms of the true valence coordinates and force fields expressed in terms of the linearized valence coordinates. In this section we present part of a similar discussion for the coordinate system used here. This discussion is restricted to molecules with a linear equilibrium configuration. The three coordinate systems to be compared are represented as follows: The

first system consists of the true valence coordinates, i.e. the instantaneous difference of the angle $\bar{\rho}$ from 0° , and the two instantaneous differences Δr_{12} and Δr_{32} of the bond lengths from their reference configuration values. The second system consists of the usual rectilinear coordinates for a linear triatomic molecule, i.e. two coordinates \bar{S}_{2a} and \bar{S}_{2b} , associated with the degenerate bending vibration, and two coordinates \bar{S}_1 and \bar{S}_3 associated with the stretching vibrations. The third system, that is introduced in this paper, consists of a bending angle ρ and two stretching coordinates S_1 and S_3 .

The expressions for the first set of coordinates in terms of the second were given by Plíva [Eqs. (7) and (8) of Ref. (10)]. The expressions for the first set of coordinates in terms of the third set are obtained by writing

$$\begin{aligned} r_{12} &= |\mathbf{r}_{12}| = |\mathbf{a}_1 + \mathbf{d}_1 - \mathbf{a}_2 - \mathbf{d}_2|, \\ r_{32} &= |\mathbf{r}_{32}| = |\mathbf{a}_3 + \mathbf{d}_3 - \mathbf{a}_2 - \mathbf{d}_2|, \end{aligned} \quad (49)$$

and

$$\sin \bar{\rho} = (|\mathbf{r}_{12} \times \mathbf{r}_{32}|) / (r_{12} \cdot r_{32}),$$

where we use Eqs. (2) for the \mathbf{a}_i and use the A matrix together with the first of Eqs. (16) to express the \mathbf{d}_i in terms of S_1 , S_3 , and ρ . The results obtained are

$$\begin{aligned} r_{12} &= (P^2 + X^2 \sin^2 \rho)^{1/2}, \\ r_{32} &= (Q^2 + Y^2 \sin^2 \rho)^{1/2}, \end{aligned} \quad (50)$$

and $\sin \bar{\rho} = \sin \rho [PQ + (PY + QX) \cos \rho - XY \sin^2 \rho] / (r_{12} \cdot r_{32})$, where we have used the symbols

$$\begin{aligned} P &= r_{12}^0 + S_1, \\ Q &= r_{32}^0 + S_3, \end{aligned} \quad (51)$$

$$\begin{aligned} X &= (m_2 m + m_1 m_3 \sin^2 \rho)^{-1} [m_1 m_3 (\cos \rho) S_1 + m_3 (m_1 + m_2) S_3], \\ \text{and } Y &= (m_2 m + m_1 m_3 \sin^2 \rho)^{-1} [m_1 m_3 (\cos \rho) S_3 + m_1 (m_3 + m_2) S_1]. \end{aligned}$$

As an example of the effect of these coordinate changes on the anharmonic force constants we consider the following force field which is harmonic in the first set of coordinates:

$$V = \frac{1}{2} F_{11} (\Delta r_{12})^2 + F_{13} (\Delta r_{12}) (\Delta r_{32}) + \frac{1}{2} F_{33} (\Delta r_{32})^2 + \frac{1}{2} F_{22} \bar{\rho}^2. \quad (52)$$

This force field is no longer purely harmonic when expressed in terms of the second set of coordinates. It has the form

$$\begin{aligned} V &= \frac{1}{2} F_{11} \bar{S}_1^2 + F_{13} \bar{S}_1 \bar{S}_3 + \frac{1}{2} F_{33} \bar{S}_3^2 + \frac{1}{2} F_{22} (\bar{S}_{2a}^2 + \bar{S}_{2b}^2) \\ &+ \bar{K}_{122} \bar{S}_1 (\bar{S}_{2a}^2 + \bar{S}_{2b}^2) + \bar{K}_{322} \bar{S}_3 (\bar{S}_{2a}^2 + \bar{S}_{2b}^2) + \dots, \end{aligned} \quad (53)$$

where \bar{K}_{122} and \bar{K}_{322} are given by⁸ [compare Eq. (10) of Ref. (10)],

$$\begin{aligned}\bar{K}_{122} &= \frac{1}{2}[F_{11}r_{12}^0(u_1 + u_{13})^2 + F_{13}r_{32}^0(u_1 + u_{13})^2]/(u_1 + u_3 + 2u_{13})^2 \\ &\quad - F_{22}(u_3 + u_{13})/[r_{12}^0(u_1 + u_3 + 2u_{13})], \\ \bar{K}_{322} &= \frac{1}{2}[F_{33}r_{32}^0(u_1 + u_{13})^2 + F_{13}r_{12}^0(u_3 + u_{13})^2]/(u_1 + u_3 + 2u_{13})^2 \\ &\quad - F_{22}(u_1 + u_{13})/[r_{32}^0(u_1 + u_3 + 2u_{13})],\end{aligned}\quad (54)$$

and where u_1 , u_3 , and u_{13} are defined in Eq. (5). This same force field is also anharmonic in the third set of coordinates. It has the form

$$\begin{aligned}V &= V_0(\rho) + \sum_i K_i(\rho)S_i + \frac{1}{2}\sum_{ij} F_{ij}(\rho)S_iS_j + \cdots \\ &= \frac{1}{2}F_{22}\rho^2 + (K_{122}\rho^2S_1 + K_{322}\rho^2S_3 + \cdots) \\ &\quad + (\frac{1}{2}F_{11}S_1^2 + F_{13}S_1S_3 + \frac{1}{2}F_{33}S_3^2 + \cdots) + \cdots,\end{aligned}\quad (55)$$

where K_{122} and K_{322} are given by

$$\begin{aligned}K_{122} &= F_{22}u_{13}(u_1 + u_{13})/[r_{12}^0(u_1u_3 - u_{13}^2)], \\ K_{322} &= F_{22}u_{13}(u_3 + u_{13})/[r_{32}^0(u_1u_3 - u_{13}^2)].\end{aligned}\quad (56)$$

We observe that one important difference between the cubic anharmonic constants \bar{K}_{122} and \bar{K}_{322} of the traditional rectilinear coordinate system and the cubic anharmonic constants K_{122} and K_{322} of the coordinate system used in this paper is the dependence of the former, but not the latter, on the quadratic constants F_{11} , F_{13} , F_{33} of the true valence coordinate system.

As an illustration of the above discussion we present⁹ in Table V the values of \bar{K}_{122} , \bar{K}_{322} , K_{122} , and K_{322} for two force fields for a molecule having the bond lengths and masses of CsOH. The bond lengths are (29) $r_{12}^0 = r(\text{O—H}) = 0.97 \text{ \AA}$ and $r_{32}^0 = r(\text{Cs—O}) = 2.40 \text{ \AA}$. The values $F_{11} = 7.66 \text{ mdyn/\AA}$ (766 N/m), $F_{13} = 0$, and $F_{33} = 1.1 \text{ mdyn/\AA}$ (110 N/m) were used in the calculations of Table V. The value of F_{11} is typical for an OH stretching force constant. Taking $F_{13} = 0$ corresponds to neglecting any interaction between the CsO stretch and the OH stretch in the potential energy expression. The value of F_{33} is in approximate agreement with the CsO stretching frequency found in matrix isolation

⁸ In this paper we consider anharmonic constants for three separate coordinate systems: for the coordinates Δr_{12} , Δr_{32} , ρ we use K' ; for the coordinates \bar{S}_1 , \bar{S}_{2a} , \bar{S}_{2b} , \bar{S}_3 we use \bar{K} ; and for the coordinates S_1 , S_3 , ρ we use K .

⁹ The vibrational labels used in this paper for CsOH do not agree with those used in Refs. 29, 30, and 37. In most triatomic monohydrides the hydrogen stretching motion is called ν_1 , and we have followed this convention. In the three references mentioned above the hydrogen stretching motion is called ν_3 . It is convenient for a second reason to give the *light* atom (the hydrogen atom) the numerical label 1: the angle ϵ , as defined here in Fig. 2, remains small at all times if it represents the angle between the molecule-fixed z -axis and the line joining the two *heavy* atoms of the triatomic molecule.

TABLE V
A COMPARISON OF THE VALUES OF TWO ANHARMONIC FORCE CONSTANTS, K_{122}
AND K_{322} , IN THREE DIFFERENT COORDINATE SYSTEMS, FOR TWO FORCE
FIELDS IN THE MOLECULE CsOH^a

Coordinate system	$F_{22} = 0.047 \text{ mdyn} \cdot \text{\AA}$ $= (0.047 \times 10^{-18} \text{ N} \cdot \text{m})$		$F_{22} = 0.47 \text{ mdyn} \cdot \text{\AA}$ $= (0.47 \times 10^{-18} \text{ N} \cdot \text{m})$	
	K_{122}	K_{322}	K_{122}	K_{322}
True internal (Eq. 52)	0	0	0	0
Traditional (Eq. 53)	+3.428	+0.001	+3.006	-0.005
This paper (Eq. 55)	+0.004	+0.047	+0.039	+0.468

^a See Eqs. (52)–(56) and the text for further details. Note that \bar{K}_{122} and \bar{K}_{322} of Eqs. (53) and (54) are given in the columns headed K_{122} and K_{322} , respectively. All values for K_{122} and K_{322} are in mdyn, i.e., in 10^{-8} N.

studies on CsOH (30). Two values for F_{22} were used in the calculations of Table V. The value $F_{22} = 0.047 \text{ mdyn} \cdot \text{\AA}$ ($0.047 \times 10^{-18} \text{ N} \cdot \text{m}$) is that derived from the matrix observations (30) on the bending vibration. The value $F_{22} = 0.47 \text{ mdyn} \cdot \text{\AA}$ ($0.47 \times 10^{-18} \text{ N} \cdot \text{m}$) represents a bending force constant deliberately increased tenfold from the observed value to give a hypothetically normal CsOH molecule (small-amplitude bending vibration).

Table V shows, as is well known, that a force field which is completely harmonic when written in terms of the true valence coordinates contains a large anharmonic interaction constant \bar{K}_{122} (involving for CsOH the bending vibration and the OH stretching vibration) when this force field is written in terms of the traditional rectilinear coordinate system. It was originally anticipated that any force field written in terms of the coordinate system used in this paper would contain very small cubic anharmonic terms if the force field written in terms of the true valence coordinates was completely harmonic. Table V shows that this is not necessarily the case. As can be seen algebraically from Eqs. (56), the coordinate system of this paper leads to a large anharmonic interaction constant K_{322} (involving for CsOH the bending vibration and the CsO stretching vibration) when F_{22} and m_3 are large. Nonetheless, Table V shows that a force field *which is purely harmonic when written in terms of the true valence coordinates*, leads to relatively small anharmonic constants when written in terms of the coordinates used in this paper, provided that F_{22} is small. (Small values of F_{22} correspond to large amplitudes for the bending vibration.)

VI. THE ROTATIONAL CONSTANT B AS A FUNCTION OF v_2 AND ℓ

The rotational constants, and their variation with vibrational and rotational state, are usually the most important results of a microwave study. Such information, if there is enough of it, can be used to determine the potential function of the molecule. It is thus of interest to determine the expression giving the dependence

of the rotational constant B on the bending vibrational quantum numbers v_2 and ℓ in a linear triatomic molecule carrying out a large amplitude bending vibration (the quantum number v_2 used here is that appropriate to a linear molecule⁷). The dependence of B on the two quantum numbers v_2 and ℓ cannot be determined by considering the bending vibration alone; both stretching vibrations must be considered as well. This unfortunate circumstance complicates both the algebra and the physical interpretation of this problem. In this section we obtain expressions for B and the ℓ -type doubling constant q_2 as functions of v_2 and ℓ .

The dependence of the rotational constant B on the two quantum numbers v_2 and ℓ can be calculated, of course, either by using the usual rectilinear coordinate system and Hamiltonian or by using the curvilinear coordinate system and Hamiltonian developed here. If the potential function is known and if both calculations are done exactly, the same final result must be obtained. However, different intermediate results (e.g., the second-order results usually quoted for the constant α_2) might conceivably occur. Such differences at a certain order of approximation are possible because the coordinates Q_1 and Q_3 used here are of small amplitude for large-amplitude bending motions, whereas in the usual treatment this is not so. We determine, below, algebraic expressions for the coefficients of $(v_2 + 1)$, $(v_2 + 1)^2$ and ℓ^2 in the series expansion of B , as well as the constant term and the term in $(v_2 + 1)$ in the series expansion of q_2 . The results for two of these five quantities can be compared with those obtained from the usual formalism, and, somewhat unexpectedly, little difference was found in several sample calculations.

Since the considerations of this section are particularly concerned with linear molecules undergoing a large amplitude bending vibration, it is convenient to use, instead of the volume element given in Eq. (27) above, the following volume element

$$d\tau = dQ_1 dQ_3 \rho d\rho \sin \theta d\theta d\phi d\chi. \quad (57)$$

The corresponding kinetic energy operator can be obtained by subjecting T in Eq. (28) to the transformation $\rho^{-1/2} T \rho^{1/2}$. The result of this transformation can be obtained formally from Eq. (28) by writing $\rho^{-1} J_\rho$ wherever J_ρ occurs and $\rho^{-1} p_\rho$ wherever p_ρ occurs, and be redefining the μ matrix to be the inverse of an I' matrix with elements given by

$$I'_{\alpha\beta} = [I_{\alpha\beta} - Q^{\text{tr}} \zeta^\alpha (\zeta^\beta)^{\text{tr}} Q] \rho^{-(\delta_{\rho\alpha} + \delta_{\rho\beta})}, \quad (58)$$

where $\alpha, \beta = x, y, z, \text{ or } \rho$. In this modified expression J_ρ and p_ρ are as defined in Eq. (29), and J_ρ is still to be replaced by $-i\hbar(\partial/\partial\rho)$ upon changing from the classical to the quantum mechanical operator.

The use of $\rho d\rho$, rather than $d\rho$, in the volume element of Eq. (57) leads to the occurrence of the factors ρ^{-1} as discussed after Eq. (57). This choice of a more complicated volume element and Hamiltonian has two slight advantages for lin-

TABLE VI
NONVANISHING DERIVATIVES $J_{\alpha\beta}^{(i)}$ OF THE $\alpha\beta$ COMPONENT OF THE MOMENT OF
INERTIA TENSOR I FOR A TRIATOMIC MOLECULE, TAKEN WITH RESPECT
TO THE SYMMETRY COORDINATE S_i^a

$J_{xx}^{(1)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] (u_1 + u_{13} \cos \rho)/r_{12}^0$
$J_{xx}^{(3)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] (u_3 + u_{13} \cos \rho)/r_{32}^0$
$J_{yy}^{(1)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_1 \cos^2 (\rho - \epsilon) + u_{13} \cos \rho \cos^2 \rho]/r_{12}^0$
$J_{yy}^{(3)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_3 \cos^2 \epsilon + u_{13} \cos \rho \cos^2 (\rho - \epsilon)]/r_{32}^0$
$J_{zz}^{(1)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_1 \sin^2 (\rho - \epsilon) + u_{13} \cos \rho \sin^2 \epsilon]/r_{12}^0$
$J_{zz}^{(3)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_3 \sin^2 \epsilon + u_{13} \cos \rho \sin^2 (\rho - \epsilon)]/r_{32}^0$
$J_{\rho\rho}^{(1)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_1(1 - \epsilon')^2 + u_{13}(\epsilon')^2 \cos \rho]/r_{12}^0$
$J_{\rho\rho}^{(3)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_3(\epsilon')^2 + u_{13}(1 - \epsilon')^2 \cos \rho]/r_{32}^0$
$J_{yz}^{(1)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_1 \sin 2(\rho - \epsilon) - u_{13} \cos \rho \sin 2\epsilon]/2r_{12}^0$
$J_{yz}^{(3)}$	$= -[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_3 \sin 2\epsilon - u_{13} \cos \rho \sin 2(\rho - \epsilon)]/2r_{32}^0$
$J_{x\rho}^{(1)}$	$= +[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_1(1 - \epsilon') - u_{13} \epsilon' \cos \rho]/r_{12}^0$
$J_{x\rho}^{(3)}$	$= -[2m_2/(m_2m + m_1m_3 \sin^2 \rho)] [u_3 \epsilon' - u_{13}(1 - \epsilon') \cos \rho]/r_{32}^0$

^a The derivatives are evaluated at $S_1 = S_3 = 0$, and are shown as functions of the angle ρ . The moment of inertia tensor is defined in Eqs. (20) and (26); the symmetry coordinates are defined by the B matrix in Table I.

ear molecules. First, the factor $\rho d\rho d\chi$ is analogous to the volume element in polar coordinates for the doubly degenerate bending vibration in a linear molecule. Second, this choice of volume element leads to a determinant of the I' matrix which is not zero when the molecule is linear, and consequently to a value for μ which is not infinite when the molecule is linear. Neither of these linear-molecule advantages seemed worth the extra complication for the work presented in Sect. IV.

The first step in investigating the behavior of B as a function of the bending vibrational quantum numbers is to determine the elements of the μ matrix as a function of the coordinates Q_1 , Q_3 , and ρ . Following Kivelson and Wilson (31), we write the I matrix, defined in Eqs. (20) and (26) above,¹⁰ in the form

$$I = I^0 + \sum_{i=1,3} J^{(i)} S_i \quad (59)$$

where we have omitted terms quadratic in the symmetry coordinates S_1, S_3 on the right-hand side, and where the 4×4 matrices I^0 and $J^{(i)}$ are considered to be functions of the angle ρ . The elements $I_{\alpha\beta}^0$ are given in Eq. (37) above. The elements $J_{\alpha\beta}^{(i)}$ are given in Table VI. The μ matrix is the inverse of the I' matrix given in Eq. (58). To first order in the symmetry coordinates S_i , we write, following Ref. (31),

$$\mu = (WI^0W)^{-1} - \sum_{i=1,3} W^{-1}(I^0)^{-1}(J^{(i)})(I^0)^{-1}W^{-1}S_i, \quad (60)$$

¹⁰ Note that the I' matrices defined by Eqs. (20) and (26) are identical if terms quadratic in the vibrational coordinates S_1, S_3 (or Q_1, Q_3) are omitted.

where W is a 4×4 diagonal matrix with elements 1, 1, 1, and ρ^{-1} in the xx , yy , zz , and $\rho\rho$ positions, respectively, which introduces the additional ρ -dependence required by Eq. (58).

It is convenient for the equations which follow to introduce the following coefficients¹¹ in the power series expansion of the elements of μ :

$$\mu_{\alpha\beta} = \rho^n \{ \mu_{\alpha\beta}^0 + \mu_{\alpha\beta}^{22} \rho^2 + \mu_{\alpha\beta}^{2222} \rho^4 + \cdots + \sum_i [\mu_{\alpha\beta}^i S_i + \mu_{\alpha\beta}^{i22} S_i \rho^2 + \cdots] + \cdots \}, \quad (61)$$

where $n = 0$ for μ_{xx} and μ_{yy} , $n = -2$ for μ_{zz} , $n = +2$ for $\mu_{\rho\rho}$, $n = +1$ for $\mu_{x\rho} = \mu_{\rho x}$, and $n = -1$ for $\mu_{yz} = \mu_{zy}$. These coefficients will not be tabulated here explicitly. The expression for $\mu_{\alpha\beta}$ can be transformed into a function of the normal coordinates Q_1 and Q_3 by setting $S = LQ$ in Eq. (61).

The second step in investigating the behavior of B as a function of the bending vibrational quantum numbers is to determine which terms of the exact Hamiltonian contribute significantly to this behavior. We use an approximate Hamiltonian given by [see Eq. (14) of Ref. (15)]

$$\begin{aligned} H'_{\text{rbs}} = & \frac{1}{2} \mu_{xx} J_x^2 + \frac{1}{2} \mu_{yy} J_y^2 \\ & + \frac{1}{2} \mu_{yz} (J_y J_z + J_z J_y) + \mu_{\rho x} \rho^{-1} J_\rho J_x + \frac{1}{2} [\rho^{-1} J_\rho \mu_{\rho x}] J_x \\ & + \frac{1}{2} (P_1^2 + \lambda_1 Q_1^2 + P_3^2 + \lambda_3 Q_3^2) \\ & + \frac{1}{2} \{ \rho^2 \mu_{\rho\rho}^0 \rho^{-1} J_\rho \rho^{-1} J_\rho + [\rho^{-1} J_\rho \rho^2 \mu_{\rho\rho}^0] \rho^{-1} J_\rho + \rho^{-2} \mu_{zz}^0 J_z^2 + F_{22} \rho^2 \} \\ & + \frac{1}{2} \{ (\mu_{\rho\rho} - \rho^2 \mu_{\rho\rho}^0) \rho^{-1} J_\rho \rho^{-1} J_\rho + [\rho^{-1} J_\rho (\mu_{\rho\rho} - \rho^2 \mu_{\rho\rho}^0)] \rho^{-1} J_\rho \\ & + (\mu_{zz} - \rho^{-2} \mu_{zz}^0) J_z^2 \} \\ & + V(\rho; Q_1, Q_3). \end{aligned} \quad (62)$$

Numerous terms occurring in the exact kinetic energy expression of Eq. (28) have been omitted from Eq. (62). Some of these terms are analogous to terms which Watson (32) has shown can be rigorously eliminated from the exact Hamiltonian in the ordinary formalism. Other terms represent interactions involving the two vibrational angular momenta p_x and p_ρ , both of which vanish when the molecule is linear. (Note that these vibrational angular momenta must be generated by the two stretching vibrations alone, since the bending motion is not considered to be a "vibration" in this formalism.) It is believed, after some investigation into the omitted terms, that they give only negligible contributions to the dependence of B on v_2 and ℓ , though some of them do contribute to the dependence of B on v_1 and v_3 , or on cross terms containing two or more vibrational quantum numbers. An algebraic approach, similar to that of Watson (32), which rigorously eliminates the majority of these worrisome terms is clearly needed here.

For the present purposes it is sufficient to include in the anharmonic potential $V(\rho; Q_1, Q_3)$ terms in $Q_1 \rho^2$, $Q_3 \rho^2$, ρ^4 , $Q_1 \rho^4$, and $Q_3 \rho^4$ only.

¹¹ Note that $\mu_{\alpha\beta}^0$ in this section is not equal to $\mu_{\alpha\beta}^0$ of Sect. IV (!).

The Hamiltonian in Eq. (62) can be divided into three parts: a part quadratic in J_x and J_y , a part linear in J_x and J_y , and a part independent of J_x and J_y . This division is convenient for an investigation of the dependence of B on the bending vibrational quantum numbers, because the B value is experimentally defined as the coefficient of $J(J+1)$ in the observed rotational energy level expression. We consider here energy expressions in $J(J+1)$ which arise: (i) from first-order contributions of terms quadratic in J_x and J_y , (ii) from second-order contributions of terms linear in J_x and J_y , and (iii) from second-order contributions involving one term quadratic in J_x and J_y and one term independent J_x and J_y .

As a basis set for the perturbation calculations, we use products of symmetric top wave functions and eigenfunctions of the third and of the fourth lines of Eq. (62). The third line of Eq. (62) yields the ordinary one-dimensional harmonic oscillator wave functions $|v_1\rangle$ and $|v_3\rangle$. The fourth line of Eq. (62) yields *part* of the ordinary two-dimensional isotropic harmonic oscillator wave functions $|v_2, \ell\rangle$, namely that part which depends on the amplitude of the bending motion. The part which depends on the phase of the motion is $e^{i\ell\chi}$; it is considered here as part of the symmetric top rotational wave function.

Matrix elements of Q_1 and Q_3 in a harmonic oscillator basis set and matrix elements of J_x , J_y , J_z in a symmetric top basis set can be found in many places (e.g., Refs. (4) and (33), respectively). Matrix elements of functions of ρ were evaluated here by relating all such functions to various combinations of the ladder operators $F, F^\dagger, G, G^\dagger$ given by Moffitt and Liehr (34). Considerable care must be taken in making such identifications, because of the separation in the Hamiltonian of the two polar coordinates ρ and χ for the two dimensional harmonic oscillator, and because of the dual role (rotational variable and vibrational variable) played by χ .

The expression we obtain for B is the sum of four contributions, $B^{(1)}, B^{(2)}, B^{(3)}$, and $B^{(4)}$, given below in Eqs. (64), (65), (66), and (67). Only terms involving (v_2+1) , $(v_2+1)^2$ and ℓ^2 are given; terms involving $(v_2+1/2)$, $(v_2+1/2)^2$ and terms cubic and higher in the bending vibrational quantum numbers have not been calculated.

A piece of information in addition to the B value for excited bending vibrational states of linear molecules which is frequently obtained from microwave studies is the ℓ -type doubling constant q_2 . This constant is defined experimentally by expressing the separation ΔE between rotational levels of the same J in the $\ell = 1$ states of vibrational levels characterized by odd values of v_2 as

$$\Delta E = q_2(v_2+1)J(J+1). \quad (63)$$

By methods similar to those used in determining the dependence of the B value on the quantum numbers of the bending vibration, we find that q_2 is given by the sum of four contributions $q_2^{(1)}, q_2^{(2)}, q_2^{(3)}$, and $q_2^{(4)}$, given in Eqs. (68), (69), (70), and (71).

The first-order contributions of interest to the B value from terms quadratic in J_x and J_y are given by

$$B^{(1)} = (\hbar^3/4a)(\mu_{xx}^{22} + \mu_{yy}^{22})(v_2 + 1) + (\hbar^4/8a^2)(\mu_{xx}^{2222} + \mu_{yy}^{2222})[3(v_2 + 1)^2 - \ell^2], \quad (64)$$

where $a = (F_{22}/\mu_{\rho\rho}^0)^{1/2}$.

The second-order contributions of interest from terms linear in J_x and J_y are given by

$$\begin{aligned} B^{(2)} = & -(\hbar^4/a\omega_2)(\mu_{yz}^{22})^2\ell^2 + \sum_j \{ (\hbar^3a/4)(\omega_2^2 - \omega_j^2)^{-1} \\ & \cdot \{ [\sum_i \mu_{yz}^i L_{ij}]^2 + (\hbar^2/4a^2)[\sum_i \mu_{yz}^{i22} L_{ij}]^2 + (\hbar^2/2a^2)[\sum_i \mu_{yz}^{i22} L_{ij}] \\ & \cdot [\sum_k \mu_{\rho x}^{k22} L_{kj}] \} (v_2 + 1) + (7\hbar^5/16a)(9\omega_2^2 - \omega_j^2)^{-1} [\sum_i \mu_{\rho x}^{i22} L_{ij}]^2 \\ & \cdot (v_2 + 1) + (\hbar^4/4)(\omega_2^2 - \omega_j^2)^{-1} [\sum_i \mu_{yz}^i L_{ij}] [\sum_k \mu_{\rho x}^{k22} L_{kj}] (v_2 + 1)^2 \\ & + (\hbar^4/2)(\omega_2^2 - \omega_j^2)^{-1} [\sum_i \mu_{yz}^i L_{ij}] [\sum_k (\mu_{yz}^{k22} - \frac{1}{2}\mu_{\rho x}^{k22}) L_{kj}] \ell^2 \}, \end{aligned} \quad (65)$$

where we have made use of $\mu_{yz}^0 = \mu_{\rho x}^0 = \mu_{\rho x}^{22} = 0$ and $\mu_{\rho x}^i = \mu_{yz}^i$, and where vibrational energies are given by $(v_2 + 1)\hbar\omega_2$ or $(v_j + \frac{1}{2})\hbar\omega_j$.

The remaining contributions of interest to the B value come from second-order perturbation expressions involving one term quadratic in either J_x or J_y and one term independent of J_x and J_y . These second-order contributions can be divided into two groups: one group depending only on the harmonic part of the vibra-

TABLE VII
SOME ADDITIONAL QUANTITIES OCCURRING IN THE SECOND-ORDER
CONTRIBUTIONS TO THE B VALUE

$\eta_1^1 = m(u_1 + u_3 + 2u_{13})u_{13}(u_1 + u_{13})/2r_{12}^0(u_1u_3 - u_{13}^2)^2$
$\eta_1^3 = m(u_1 + u_3 + 2u_{13})u_{13}(u_3 + u_{13})/2r_{32}^0(u_1u_3 - u_{13}^2)^2$
$\eta_2^1 = [1/6 + m_1m_3/m_2m + u_{13}/2(u_1 + u_{13})]\eta_1^1$
$\eta_2^3 = [1/6 + m_1m_3/m_2m + u_{13}/2(u_3 + u_{13})]\eta_1^3$
$\eta_3^1 = -m(u_3 + u_{13})/2r_{12}^0(u_1u_3 - u_{13}^2)$
$\eta_3^3 = -m(u_1 + u_{13})/2r_{32}^0(u_1u_3 - u_{13}^2)$
$\eta_4^1 = [m_1m_3/m_2m + u_{13}/2(u_3 + u_{13})]\eta_3^1$
$\eta_4^3 = [m_1m_3/m_2m + u_{13}/2(u_1 + u_{13})]\eta_3^3$
$\eta_5^1 = -[2/3 + m_1m_3/m_2m - u_{13}/2(u_3 + u_{13})]\eta_3^1 - m(u_1 + u_{13})/r_{12}^0(u_1 + u_3 + 2u_{13})^2$
$\eta_5^3 = -[2/3 + m_1m_3/m_2m - u_{13}/2(u_1 + u_{13})]\eta_3^3 - m(u_3 + u_{13})/r_{32}^0(u_1 + u_3 + 2u_{13})^2$
$\eta_6^1 = 4u_{13}(u_1 + u_{13})/r_{12}^0(u_1u_3 - u_{13}^2)$
$\eta_6^3 = 4u_{13}(u_3 + u_{13})/r_{32}^0(u_1u_3 - u_{13}^2)$

tional potential energy expression, the other group depending on the anharmonic part. The division of the potential energy expression into harmonic and anharmonic parts depends, however, on the precise coordinate system used to express the potential energy function. We choose to use a function expressed in terms of the true valence coordinates of the molecule, since this leads to isotopically invariant anharmonic force constants (9, 10).

The contributions of interest to the B value arising from second-order terms containing one term quadratic in J_x or J_y and one term independent of J_x and J_y , and depending only on the potential constants of the *harmonic* force field in the true valence coordinates are the following:

$$\begin{aligned}
 B^{(3)} = & + \sum_j \left\{ -(\hbar^3 a/2) \omega_j^{-2} \left[\sum_i (\mu_{xx}^i + \mu_{yy}^i) L_{ij} \right] \left[\sum_k \eta_3^k L_{kj} \right] \right. \\
 & + (\hbar^5/4a) \omega_j^{-2} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k (-3\mu_{\rho\rho}^{k22}/4 + \eta_2^k) L_{kj} \right] \\
 & - (3\hbar^5/2a)(4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k \eta_2^k L_{kj} \right] \left\{ (v_2 + 1) \right. \\
 & + \sum_j \left\{ +(\hbar^4/4) \omega_j^{-2} \left[\sum_i (\mu_{xx}^i + \mu_{yy}^i) L_{ij} \right] \left[\sum_k \eta_4^k L_{kj} \right] \right. \\
 & - (\hbar^4/2) \omega_j^{-2} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k \eta_3^k L_{kj} \right] \\
 & + (\hbar^4/4)(4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k (\eta_1^k - 1/4\mu_{\rho\rho}^k) L_{kj} \right] \left\{ \right. \\
 & \cdot (v_2 + 1)^2 + \sum_j \left\{ +(\hbar^4/4) \omega_j^{-2} \left[\sum_i (\mu_{xx}^i + \mu_{yy}^i) L_{ij} \right] \left[\sum_k \eta_5^k L_{kj} \right] \right. \\
 & \left. \left. - (\hbar^4/4)(4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k (\eta_1^k - 1/4\mu_{\rho\rho}^k) L_{kj} \right] \right\} \ell^2. \right.
 \end{aligned} \tag{66}$$

In deriving the expression given in (66) we have made use of $\mu_{\rho\rho}^i = \mu_{zz}^i$, and of an equation analogous to (56) giving the contribution to K_{i2222} from the harmonic bending force constant F_{22} for the true valence angle. F_{22} was then eliminated from (66), since $F_{22} = \omega_2^2/\mu_{\rho\rho}^0$. This elimination gives rise, after some rearrangement of terms, to the quantities η_i^k found in Table VII. Furthermore, in deriving (66) we have included terms through ρ^4 in line seven of the Hamiltonian given in (62), but have included only terms through ρ^2 in lines five and six of (62). This may at first seem inconsistent. Closer inspection of the algebraic results, however, indicates that contributions from $\mu_{\rho\rho}^i$ and K_{i22} occur together, and that contributions from $\mu_{\rho\rho}^{i22}$, μ_{zz}^{i22} and K_{i2222} occur together.

The contributions of interest to the B value arising from second-order terms containing one term quadratic in J_x or J_y and one term independent of J_x and J_y , and depending on the *anharmonic* potential constants of the force field in the

true valence coordinates are the following:

$$\begin{aligned}
 B^{(4)} = & + \sum_j \left\{ -(\hbar^3/4a) \omega_j^{-2} \left[\sum_i (\mu_{xx}^i + \mu_{yy}^i) L_{ij} \right] \left[\sum_m K_{m22} L_{mj} \right] \right. \\
 & - (\hbar^5/8a^3) \omega_j^{-2} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_m (K_{2222} \eta_6^m + K_{m2222}) L_{mj} \right] \\
 & + (3\hbar^5/4a^3) (4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \\
 & \cdot \left[\sum_m (K_{2222} \eta_6^m + K_{m2222}) L_{mj} \right] \} (v_2 + 1) + \sum_j \left\{ - (3\hbar^4/8a^2) \omega_j^{-2} \right. \\
 & \cdot \left[\sum_i (\mu_{xx}^i + \mu_{yy}^i) L_{ij} \right] \left[\sum_m (K_{2222} \eta_6^m + K_{m2222}) L_{mj} \right] - (\hbar^4/4a^2) \omega_j^{-2} \\
 & \cdot \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_m K_{m22} L_{mj} \right] + (\hbar^4/8a^2) (4\omega_2^2 - \omega_j^2)^{-1} \\
 & \cdot \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_m K_{m22} L_{mj} \right] \} (v_2 + 1)^2 \\
 & + \sum_j \left\{ + (\hbar^4/8a^2) \omega_j^{-2} \left[\sum_i (\mu_{xx}^i + \mu_{yy}^i) L_{ij} \right] \left[\sum_m (K_{2222} \eta_6^m + K_{m2222}) L_{mj} \right] \right. \\
 & - (\hbar^4/8a^2) (4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} + \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_m K_{m22} L_{mj} \right] \} \ell^2 \\
 & - (\hbar^4/4a^3 \omega_2) (\mu_{xx}^{22} + \mu_{yy}^{22}) K_{2222} [3(v_2 + 1)^2 - \ell^2],
 \end{aligned} \tag{67}$$

where K_{i22} , K_{2222} and K_{i2222} represent anharmonic force constants in the true valence coordinate system.

The first-order contribution to q_2 from terms quadratic in J_x and J_y is given by

$$q_2^{(1)} = -(\hbar^3/4a) (\mu_{xx}^{22} - \mu_{yy}^{22}) - (3\hbar^4/8a^2) (\mu_{xx}^{2222} - \mu_{yy}^{2222}) (v_2 + 1). \tag{68}$$

The second-order contribution from terms linear in J_x and J_y is given by

$$\begin{aligned}
 q_2^{(2)} = & \sum_j \left\{ -(\hbar^3 a/4) (\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i \mu_{yz}^i L_{ij} \right]^2 - (\hbar^5/16a) (\omega_2^2 - \omega_j^2)^{-1} \right. \\
 & \cdot \left[\sum_i (\mu_{yz}^{i22} - \mu_{\rho x}^{i22}) L_{ij} \right]^2 - (\hbar^5/4a) (9\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i \mu_{\rho x}^{i22} L_{ij} \right]^2 \} \\
 & - \sum_j (\hbar^4/4) (\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i \mu_{yz}^i L_{ij} \right] \left[\sum_k \mu_{\rho x}^{k22} L_{kj} \right] (v_2 + 1).
 \end{aligned} \tag{69}$$

The second-order contribution arising from one term quadratic in J_x or J_y and one term independent of J_x and J_y , and depending only on the harmonic part of

the force field (when that field is expressed in terms of the true valence coordinates) is given by

$$\begin{aligned}
 q_2^{(3)} = & \sum_j \left\{ + (\hbar^5/8a) \omega_j^{-2} \left[\sum_i (\mu_{xx}^{i22} - \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k (\mu_{zz}^{k22} + \mu_{\rho\rho}^{k22}) L_{kj} \right] \right. \\
 & + (\hbar^5/a) (4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} - \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k \eta_2^k L_{kj} \right] \} \\
 & + \sum_j \left\{ + (\hbar^4/2) \omega_j^{-2} \left[\sum_i (\mu_{xx}^{i22} - \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k \eta_3^k L_{kj} \right] \right. \\
 & + (\hbar^4/4) (4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} - \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_k (\frac{1}{4}\mu_{\rho\rho}^k - \eta_1^k) L_{kj} \right] \} \\
 & \cdot (v_2 + 1).
 \end{aligned} \tag{70}$$

The second-order contribution arising from one term quadratic in J_x or J_y and one term independent of J_x and J_y , and depending on the anharmonic force constants (when the field is expressed in terms of the true valence coordinates) is given by

$$\begin{aligned}
 q_2^{(4)} = & + (3\hbar^4/4a^3 \omega_2) (\mu_{xx}^{22} - \mu_{yy}^{22}) K_{2222} (v_2 + 1) - \sum_j (\hbar^5/2a^3) \\
 & \cdot (4\omega_2^2 - \omega_j^2)^{-1} \left[\sum_i (\mu_{xx}^{i22} - \mu_{yy}^{i22}) L_{ij} \right] \left[\sum_n (\eta_6^n K_{2222} + K_{n2222}) L_{nj} \right] \\
 & + \sum_j (\hbar^4/4a^2) [+ \omega_j^{-2} - (\frac{1}{2}) (4\omega_2^2 - \omega_j^2)^{-1}] \left[\sum_i (\mu_{xx}^{i22} - \mu_{yy}^{i22}) L_{ij} \right] \\
 & \cdot \left[\sum_n K_{n22} L_{nj} \right] (v_2 + 1).
 \end{aligned} \tag{71}$$

VII. THE CsOH AND CsOD MICROWAVE DATA

Microwave observations (29) have shown that the dependence of the B value on the bending vibrational quantum numbers is given in MHz by Eq. (72a) for CsOH and by (72b) for CsOD.

$$B_{0v_2\ell 0} = 5518.74 - 18.95(v_2 + 1) + 1.207(v_2 + 1)^2 - 1.615\ell^2, \tag{72a}$$

$$B_{0v_2\ell 0} = 4999.23 - 3.08(v_2 + 1) + 0.642(v_2 + 1)^2 - 0.830\ell^2. \tag{72b}$$

Furthermore, it was found in Ref. (29) that: (i) the contribution to $B_{0v_2\ell 0}$ of terms cubic and higher in $(v_2 + 1)$ and ℓ was negligible, and (ii) the contribution to $B_{v_1v_2\ell 0}$ of cross terms of the form $(v_1 + \frac{1}{2})(v_2 + 1)$, etc., was negligible. The vibrational data (30) on matrix-isolated CsOH and CsOD provide values for the CsO stretching frequency and the bending frequency, but the OH and OD stretching frequencies could not be unambiguously assigned. It is not known with certainty whether the molecule is linear or bent. The B value expressions [Eqs. (72)] are slightly anomalous for a linear molecule, insofar as: (i) the sign of the term linear in $(v_2 + 1)$ is not that expected for a triatomic molecule, and (ii)

the relative contributions of the quadratic term are much larger than expected.

Before attempting to extract information from the experimental data for CsOH and CsOD by means of the formalism presented here, it is of interest to compare the value of α_2 obtained from the present formalism with the value obtained from the traditional formalism when both are taken to second order, and further to compare the three kinds of contributions to α_2 in the two formalisms. We write

$$\alpha_2 = \alpha_2^{\langle J^2 \rangle} + \alpha_2^{\langle J^1 \rangle \langle J^1 \rangle} + \alpha_2^{\langle J^2 \rangle \langle J^0 \rangle}, \quad (73)$$

where α_2 , as well as γ_{22} and $\gamma_{\ell\ell}$ are defined by the following expression

$$B(v_2, \ell) = B_e - \alpha_2(v_2 + 1) + \gamma_{22}(v_2 + 1)^2 + \gamma_{\ell\ell}\ell^2. \quad (74)$$

The three quantities on the right of Eq. (73) represent respectively: the first-order contribution from terms quadratic in J_x and J_y , the second-order contribution from terms linear in J_x and J_y , and the second-order contribution from products of a term quadratic in J_x and J_y and a term independent of J_x and J_y . In the traditional formalism (35), these three contributions correspond to: α_2^{harm} , α_2^{Cor} , and α_2^{anh} , respectively.

Table VIII gives the results of second-order calculations of α_2 performed with the traditional formalism and with the formalism of this paper, for the molecular structure and the two force fields for CsOH used in Table V. We note immediately that the same value for α_2 is obtained from each formalism taken to second order. This is not too surprising for the force field characterized by $F_{22} = 0.47 \text{ mdyn} \cdot \text{\AA}$ ($0.47 \times 10^{-18} \text{ N} \cdot \text{m}$), since such a force field corresponds to a relatively small amplitude bending vibration (root-mean-square zero-point amplitude = 11.6°). It is more surprising however, for the force field characterized by $F_{22} = 0.047 \text{ mdyn} \cdot \text{\AA}$ ($0.047 \times 10^{-18} \text{ N} \cdot \text{m}$), with its larger root-mean-square zero-point amplitude of 20.6° . We conclude from Table VIII (somewhat unhappily from the point of view of this work), that the traditional formalism for calculating α_2 does not break down in second order when the amplitude of the bending vibration becomes quite large, even though the assumptions implicitly contained in the traditional formalism concerning the smallness of the vibrational amplitudes are no longer fulfilled. We note also that even though the final value of α_2 is almost identical for the two formalisms, the three contributions to the sum are quite different. In particular, the bulk of the contribution to α_2 from a completely harmonic force field in the true valence coordinates comes from second-order cross-term contributions to the energy in the traditional formalism, but from first-order contributions in the present formalism. In short, this new formalism gives a better answer to first order, but no better answer to second order, when compared with the traditional formalism.

We begin our consideration of the microwave data on CsOH and CsOD given in Eqs. (72) by calculating the coefficients in the B value expression [Eq. (74)] for a completely harmonic force field of the form (52). For various reasons, in-

TABLE VIII

THE THREE CONTRIBUTIONS TO α_2 , CALCULATED FROM THE TRADITIONAL FORMALISM AND FROM THE FORMALISM IN THIS PAPER, USING THE STRUCTURE AND THE TWO FORCE FIELDS FOR CsOH DESCRIBED FOLLOWING EQ. (56)

	$F_{22} = 0.047 \text{ mdyn} \cdot \text{\AA}$ $= 0.047 \times 10^{-18} \text{ N} \cdot \text{m}$		$F_{22} = 0.47 \text{ mdyn} \cdot \text{\AA}$ $= 0.47 \times 10^{-18} \text{ N} \cdot \text{m}$		
	Traditional formalism	This paper	Traditional formalism	This paper	
$\alpha_2 \langle J^2 \rangle$	0	-19.44	0	-6.15	MHz
$\alpha_2 \langle J^1 \rangle \langle J^1 \rangle$	+3.76	+0.49	+1.30	+0.26	MHz
$\alpha_2 \langle J^2 \rangle \langle J^0 \rangle$	-22.09	+0.65	-5.18	+2.01	MHz
α_2 (total)	-18.33	-18.30	-3.88	-3.88	MHz

TABLE IX

CALCULATED COEFFICIENTS IN THE B VALUE EXPRESSION [EQ. (74)] FOR CsOH FOR FOUR DIFFERENT HARMONIC FORCE FIELDS IN THE TRUE VALENCE COORDINATES ($1.00 \text{ mdyn/\AA} = 100 \text{ N/m}$)

	Force field				
	(i)	(ii)	(iii)	(iv)	
F_{11}	7.15	7.234	7.66	7.66	mdyn/ \AA
F_{33}	1.1527	1.0	1.1	1.1	mdyn/ \AA
F_{13}	1.1	0	-1.1	0	mdyn/ \AA
F_{22}	0.047	0.0465	0.047	0.047	mdyn/ \AA
ω_1	3548.5	3599.7	3738.1	3704.2	cm^{-1}
ω_2	307.7	306.1	307.7	307.7	cm^{-1}
ω_3	335.5	335.5	322.6	351.8	cm^{-1}
α_2	-21.53	-18.14	-13.98	-18.30	MHz
γ_{22}	-0.07	-0.03	+0.01	-0.03	MHz
γ_{tt}	-0.63	-0.77	-0.96	-0.74	MHz

cluding the absence of an experimental value for the OH stretching frequency, the harmonic force field of CsOH is not well characterized. Table IX presents four possible force fields⁹ and the resultant coefficients in the B value expression [Eq. (74)]. The first force field in Table IX is that favored by Abramowitz (36) as best describing the observed values for the CsO stretching frequency of CsOH and CsOD. The second force field⁹ is one used by Lide and Matsumura (37) in their discussion of the dependence of B on ν_2 and ℓ for CsOH/CsOD and RbOH/RbOD. The third field illustrates the effect of a large negative value for the stretch-stretch interaction constant. The fourth force field illustrates the fact that changes in the stretch-stretch interaction constant strongly affect α_2 , whereas changes in the two stretching force constants themselves do not. We conclude

from Table IX that uncertainties in the harmonic force field, i.e., in F_{13} , lead to large uncertainties in the harmonic contribution to α_2 .

In an effort to evaluate the effect on B of various anharmonic force constants [when the force field is expressed in the true valence coordinates of Eq. (52)],^{8,9} calculations were carried out in which each of the five force constants K'_{122} , K'_{322} , K'_{222} , K'_{1222} , and K'_{3222} were set equal to 0.1 mdyn (0.1×10^{-8} N) in turn ($0.1 \text{ mdyn} \cdot \text{\AA}$ (0.1×10^{-18} N·m) for K'_{2222}) while the other four were set equal to zero. The harmonic force field used in these calculations is given in column (i) of Table IX. The results of these calculations are presented in Table X. Table X shows that the two anharmonic constants K'_{122} and K'_{322} affect α_2 much more than they do γ_{22} and γ_{44} , whereas the three constants K'_{222} , K'_{1222} , and K'_{3222} affect γ_{22} and γ_{44} much more than they do α_2 . This is not surprising, if we recall that $\langle \rho^2 \rangle \propto (v_2 + 1)$ and $\langle \rho^4 \rangle \propto [3(v_2 + 1)^2 - \ell^2]$.

Because the three constants K'_{222} , K'_{1222} , and K'_{3222} have very little effect on α_2 , it seems appropriate, as a first approximation, to set them equal to zero and then determine the value of K'_{122} and K'_{322} consistent with the experimentally observed values of α_2 for CsOH and CsOD. For the harmonic force field given in column (i) of Table IX α_2 in MHz can be written in the form

$$\begin{aligned}\alpha_2(\text{CsOH}) &= -21.5 + 82.1 K'_{122} - 578 K'_{322}, \\ \alpha_2(\text{CsOD}) &= -24.5 + 49.6 K'_{122} - 376 K'_{322}.\end{aligned}\quad (75)$$

For the force field given in column (ii) of Table IX Lide and Matsumura⁹ have shown that⁹

$$\begin{aligned}\alpha_2(\text{CsOH}) &= -18.4 - 6.8 K'_{122} - 584 K'_{322}, \\ \alpha_2(\text{CsOD}) &= -22.9 - 8.3 K'_{122} - 387 K'_{322}.\end{aligned}\quad (76)$$

TABLE X
CALCULATED COEFFICIENTS IN THE B VALUE EXPRESSION [Eq. (74)] FOR CsOH
FOR VARIOUS ANHARMONIC FORCE FIELDS ($0.1 \text{ mdyn} = 0.1 \times 10^{-8}$ N;
 $0.1 \text{ mdyn} \cdot \text{\AA} = 0.1 \times 10^{-18}$ N·m)^a

	Force field						
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	
K'_{122}	0	+0.1	0	0	0	0	mdyn
K'_{322}	0	0	+0.1	0	0	0	mdyn
K'_{222}	0	0	0	+0.1	0	0	mdyn·Å
K'_{1222}	0	0	0	0	+0.1	0	mdyn
K'_{3222}	0	0	0	0	0	+0.1	mdyn
α_2	-21.53	-13.32	-79.32	-21.61	-21.52	-21.55	MHz
γ_{22}	-0.07	-0.09	-0.23	+28.10	-1.68	+11.20	MHz
γ_{44}	-0.63	-0.61	-0.68	-10.02	-0.10	-4.39	MHz

^a The harmonic part of the force field is given in column (i) of Table IX.

[Our calculations using the force field of column (ii) agree closely with the results given in Eqs. (76).] The observed values for α_2 for both CsOH and CsOD are given in Eqs. (72) above, i.e., $\alpha_2(\text{CsOH}) = +19.0$ MHz and $\alpha_2(\text{CsOD}) = +3.1$ MHz. Values for K'_{122} and K'_{322} can be obtained from these values of α_2 by solving simultaneously the pair of equations given in (75) or (76). From Eq. (75) we obtain

$$\begin{aligned} K'_{122} &= -0.329 \text{ mdyn} = -0.329 \times 10^{-8} \text{ N}, \\ K'_{322} &= -0.117 \text{ mdyn} = -0.117 \times 10^{-8} \text{ N}. \end{aligned} \quad (77)$$

From Eq. (76) we obtain

$$\begin{aligned} K'_{122} &= -0.321 \text{ mdyn} = -0.321 \times 10^{-8} \text{ N} \\ K'_{322} &= -0.060 \text{ mdyn} = -0.060 \times 10^{-8} \text{ N}. \end{aligned} \quad (78)$$

Lide and Matsumura (37) prefer to set $K'_{122} = 0$ in Eq. (76), from which they obtain

$$\begin{aligned} K'_{122} &= 0, \\ K'_{322} &= -0.064 \quad \text{or} \quad -0.067 \text{ mdyn}. \end{aligned} \quad (79)$$

The conclusion to be reached here seems to be that our lack of knowledge concerning the harmonic force field for CsOH and CsOD precludes any quantitative determination of K'_{122} or K'_{322} .

A final unresolved question concerns whether the microwave data on CsOH and CsOD require or exclude a linear equilibrium configuration for these two molecules. Because of our lack of knowledge concerning the harmonic force field, it is not possible to answer this question with complete certainty. However, it is clear that the rather unusual expressions obtained for the dependence of the B value of CsOH and CsOD on the bending vibrational quantum numbers can be fitted by suitable choices for the harmonic and anharmonic force constants in the formalism presented in Sect. VI. That formalism, as specialized in Eqs. (64)–(67), rests upon the assumption of oscillations (large or small) in an angular bending coordinate about a linear equilibrium configuration. If more spectral data are obtained and the bending vibrational energy levels are determined, then the theory developed in Sect. IV can be used to determine the bending potential surface and bending vibrational wave functions. Alternatively the solution of the rigidly-bending rigid-rotor Hamiltonian in Eq. (36) may lead to a determination of $V_0(\rho)$ from the microwave data on the vibrational levels in the excited states of the bending vibration.

ACKNOWLEDGMENTS

We would like to thank Mr. R. L. Ferch for much computational assistance in obtaining the results of Tables II, III, and IV. We thank Dr. D. R. Lide for bringing the microwave

results on CsOH to our attention and for criticizing the manuscript, and Dr. J. Plíva for some useful discussions and for criticizing the manuscript. Many other colleagues have also contributed suggestions for which we thank them.

RECEIVED: October 9, 1969

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