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Publication Date

1978-04-01

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April 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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A DECOUPLED RIGID BENDER MODEL FOR THE
ANHARMONIC FORCE FIELD OF OCTAHEDRAL MOLECULES

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ABSTRACT

The molecular vibrational Hamiltonian for an octahedral molecule is derived to fourth order, subject to the constraint that the bond lengths are held constant. By assuming that the force field for the bending motions is a points-on-a-sphere potential, the location of the first difference bands for the pure bending motions is calculated; mode couplings are neglected. With these results, systematic trends in the anharmonic shifts can be predicted for the complete family of metal-hexafluorides. The effects of mode couplings and the importance of these calculations for understanding the initial process in the multiphoton dissociation of SF_6 are briefly discussed.

I. INTRODUCTION

In the last decade, the theory of molecular vibrations has received renewed attention.^{1,2,11} Development of successful approaches to the practical problem of solving the vibration-rotation Hamiltonian for a single electronic surface has allowed the molecular spectroscopist to derive quantitatively accurate potential energy surfaces for three atom systems.² Understanding the consequences of finite vibrational displacements (large amplitude motion) has been the cornerstone to all successful applications to date. In this paper, the effect of finite atomic displacements on the difference and combination bands for the uncoupled bending motions of octahedral molecules is investigated. A slightly different approach than the standard one developed by Hoy, Mills, and Strey,^{1a} and Bunker and coworkers^{2c-2f} is introduced.

In brief, the molecular Hamiltonian is expressed and *solved* in curvilinear coordinates, in contrast to a normal coordinate system. The major advantage is a simplification of the potential energy function. As noted by other authors,^{1b} the minimal energy path for a bending motion can be approximated to a high degree of accuracy by assuming the bond lengths are held fixed at some averaged value, so that the atoms move along arcs. (Bunker and coworkers have generalized this approximation by letting the bond lengths have a functional dependence upon the angles, chosen to minimize the bend-stretch interaction terms.) The disadvantage of this approach is that the simplification of the potential energy surface introduces terms in the kinetic energy

operator analogous to the way in which the hydrogen atom Laplacian operator becomes "coordinate" dependent when expressed in a spherical versus a Cartesian coordinate system. The disadvantage is only a practical one, since the prescription for expressing the molecular Hamiltonian in a generalized, non-orthogonal, curvilinear coordinate system has been theoretically derived.³ In practice, the major difficulty reduces to inverting the classical velocities to their conjugate momenta. For motions of more than three dimensions, this can be a tedious procedure.

A novel means of effecting this transformation is introduced which allows the conjugate momenta to be expressed to any arbitrary order in the displacement coordinates. In practice, the kinetic energy can be derived to the same order as the potential energy, without approximations. It appears that the final limitation on treating molecular vibrations is the ability to numerically solve the resulting Schrödinger equation.

For the octahedral bending motions, trends in the location of the difference bands for the three lowest groups of energy levels are shown here. It is also argued that the spectral range of combination and difference bands are not suitably distinct to allow us to make unambiguous use of the results calculated here in an actual molecular system. The extension to include the effects of combination bands is discussed, but not derived. Various approximations to the kinetic energy are compared and related to the apparent effects these approximations have on the spectrum. Finally, the application of these calculations to multiphoton dissociation and to simpler molecules is discussed and future work outlined.

II. POTENTIAL ENERGY FUNCTION AND COORDINATE SYSTEM

The bending potential function for an octahedral molecule is a function of three sets of triply degenerate symmetry coordinates. The qualitative form of these coordinates are shown in Fig. 1 and their associated (but not equivalent) normal coordinate definition given in Table 1. The potential energy can be decomposed into terms which depend on only one kind of symmetry coordinate (V_1, V_2, V_3) and terms which couple two or more symmetry coordinates (V_4, V_5, V_6, V_7).

$$\begin{aligned} V_{\text{BEND}} = & V_1(T_{1u}) + V_2(T_{2g}) + V_3(T_{2u}) + V_4(T_{1u}, T_{2g}) \\ & + V_5(T_{1u}, T_{2u}) + V_6(T_{2g}, T_{2u}) + V_7(T_{1u}, T_{2u}, T_{2g}) \end{aligned} \quad (1)$$

The individual members of the above terms, expressed in terms of the symmetry coordinates to fourth order are:

$$\begin{aligned} V_1(T_{1u}) = & \frac{1}{2} F_{44} (S_{4a}^2 + S_{4b}^2 + S_{4c}^2) + F_{4444} (S_{4a}^2 + S_{4b}^2 + S_{4c}^2)^2 \\ & + F_{444'4'} (S_{4a}^2 S_{4b}^2 + S_{4a}^2 S_{4c}^2 + S_{4b}^2 S_{4c}^2) \end{aligned} \quad (2)$$

$$\begin{aligned} V_2(T_{2g}) = & \frac{1}{2} F_{55} (S_{5a}^2 + S_{5b}^2 + S_{5c}^2) + F_{55'5''} (S_{5a} S_{5b} S_{5c}) \\ & + F_{5555} (S_{5a}^2 + S_{5b}^2 + S_{5c}^2)^2 + F_{555'5'} (S_{5a}^2 S_{5b}^2 + S_{5a}^2 S_{5c}^2 + S_{5b}^2 S_{5c}^2) \end{aligned} \quad (3)$$

$$\begin{aligned} V_3(T_{2u}) = & \frac{1}{2} F_{66} (S_{6a}^2 + S_{6b}^2 + S_{6c}^2) + F_{6666} (S_{6a}^2 + S_{6b}^2 + S_{6c}^2)^2 \\ & + F_{666'6'} (S_{6a}^2 S_{6b}^2 + S_{6a}^2 S_{6c}^2 + S_{6b}^2 S_{6c}^2) \end{aligned} \quad (4)$$

$$\begin{aligned}
 V_4(T_{1u}, T_{2g}) &= F_{44'5} (S_{4a} S_{4b} S_{5c} + S_{4a} S_{4c} S_{5b} + S_{4b} S_{4c} S_{5a}) \\
 &+ F_{4455} (S_{4a}^2 + S_{4b}^2 + S_{4c}^2) (S_{5a}^2 + S_{5b}^2 + S_{5c}^2) \\
 &+ F_{44'55'} (S_{4a} S_{4b} S_{5a} S_{5b} + S_{4a} S_{4c} S_{5a} S_{5c} + S_{4b} S_{4c} S_{5b} S_{5c})
 \end{aligned} \tag{5}$$

$$\begin{aligned}
 V_5(T_{1u}, T_{2u}) &= F_{4466} (S_{4a}^2 + S_{4b}^2 + S_{4c}^2) (S_{6a}^2 + S_{6b}^2 + S_{6c}^2) \\
 &+ (F_{444'6} + F_{666'4}) \left((S_{4a}^2 - S_{6a}^2) (S_{4c} S_{6c} - S_{4b} S_{6b}) \right. \\
 &+ (S_{4b}^2 - S_{6b}^2) (S_{4a} S_{6a} - S_{4c} S_{6c}) + (S_{4c}^2 - S_{6c}^2) \\
 &\left. + (S_{4b} S_{6b} - S_{4a} S_{6a}) \right) + F_{44'66'} (S_{4a} S_{4b} S_{6a} S_{6b} \\
 &+ S_{4b} S_{4c} S_{6b} S_{6c} + S_{4a} S_{4c} S_{6a} S_{6c})
 \end{aligned} \tag{6}$$

$$\begin{aligned}
 V_6(T_{2g}, T_{2u}) &= F_{566'} (S_{5a} S_{6b} S_{6c} + S_{5b} S_{6a} S_{6c} + S_{5c} S_{6a} S_{6b}) \\
 &+ F_{5566} (S_{5a}^2 + S_{5b}^2 + S_{5c}^2) (S_{6a}^2 + S_{6b}^2 + S_{6c}^2) \\
 &+ F_{55'66'} (S_{5a} S_{5b} S_{6a} S_{6b} + S_{5a} S_{5c} S_{6a} S_{6c} + S_{5b} S_{5c} S_{6b} S_{6c})
 \end{aligned} \tag{7}$$

$$\begin{aligned}
 V_7(T_{1u}, T_{2g}, T_{2u}) = & F_{456} (S_{4a} S_{5c} S_{6b} - S_{4b} S_{5c} S_{6a} + S_{4b} S_{5c} S_{6a} \\
 & - S_{4c} S_{5a} S_{6b} + S_{4c} S_{5b} S_{6a} - S_{4a} S_{5b} S_{6c}) \\
 & + F_{455',6} (S_{4a} S_{5a} S_{5b} S_{6b} - S_{4a} S_{5a} S_{5c} S_{6c} + S_{4b} S_{5a} S_{5b} S_{6a} \\
 & - S_{4b} S_{5b} S_{5c} S_{6a} - S_{4c} S_{5a} S_{5c} S_{6a} + S_{4c} S_{5b} S_{5c} S_{6b}) \quad (8)
 \end{aligned}$$

These symmetry-allowed terms were generated by considering the transformation properties of product functions of the polynomial representations of the symmetry coordinates (see Table 1). These coefficients are related to the derivatives of the potential surface by the expressions in Table 2.

It is assumed that the bending potential can also be expressed as a points-on-a-sphere (POS) potential

$$V_{\text{POS}} = k \sum_{i,j} \left(\frac{1}{q_{ij}} \right)^n \quad k, n > 0 \quad (9)$$

where k and n are parameters and q_{ij} is the internuclear distance between ligands i and j .

Previously, Bartell and Plato⁴ used the POS model to investigate the energetics of axial-equatorial interchange in trigonal bipyramids. They found that the POS model reproduced the experimentally observed ordering of force constants in PF_5 . This suggests that for fluoride systems, the POS model might also predict the anharmonic force constants quite well.

An alternative potential force field initially considered was an exponential overlap repulsion model, (EOR). Here

$$V_{\text{BEND}} = A \left(\sum_{i>j} e^{-\alpha r \theta_{ij}} \right) \quad A, \alpha > 0 \quad (10)$$

where θ_{ij} is the angle between the ligand central atom bonds i and j , and

α, A are parameters. For the T_{2g} motion, a physically reasonable expansion of Eq. (2) could be found. For the T_{1u}, T_{2u} motions, linear potential terms in the symmetry coordinates were produced by the EOR potential. As noted by Klemperer,⁵ for bending motions expanded about an end point of the domain of the angles, such non-quadratic terms in the potential are possible. Since a central force field (such as the POS model) does not have linear terms in the angles, the (EOR) model was not pursued further. For comparison, the T_{2g} (EOR) anharmonic constants scaled to the POS quadratic force constants are displayed in Table 3.

In the POS model, the interligand distances, q_{ij} , can be expressed as trigonometric functions of the symmetry coordinates.

$$q_{ij} = q_{ij}(S_4, S_5, S_6) \quad (11)$$

The POS potential can then be expanded as a Taylor series in the symmetry coordinates. The coefficients of this expansion are functions only of the parameter n .

To find the functional relation connecting the q_{ij} with the symmetry coordinates, the Eckart conditions were introduced. In the Cartesian coordinate system with origin at the center of mass, these conditions are given by:

$$\begin{aligned} y_1 + y_4 &= x_2 + y_3 \\ y_6 + z_2 &= z_4 + y_5 \\ x_5 + z_3 &= z_1 + x_6 \end{aligned} \quad (12)$$

In these equations, the atom numbering and axis orientation are shown in Fig. 1 with the equilibrium positions of the atoms defined by replacing a, b, c by zero in the expressions in Table 4. We notice that for each

atom, only two of the three Cartesian components of the center of mass system are involved in the Eckart conditions. This means that we are free to choose the functional dependence of the third component without effecting the Eckart conditions. To ensure that the atoms always move at a fixed distance from the central atom, the third component was chosen to be of the form

$$x_i \approx \sqrt{r_o^2 - (y_o - y_i)^2 - (z_o - z_i)^2} + x_o \quad (13)$$

where (x_o, y_o, z_o) labels the position of the central atom. The actual functional forms of the center of mass coordinates for all three motions are listed in Table 4. For the T_{1u} mode, the central atom moves. In this case the X-M-X unit (see Fig. 1) along the direction of the M atom motion was displaced as a "single atom." This is the physical origin of the constant β in the T_{1u} motion. For all three modes, it is trivial to verify that the center of mass, fixed bond length, and Eckart conditions are satisfied by this parameterization.

With these parameterizations, only the uncoupled bending force constants could be found. For the general case of simultaneous displacements in any of the nine bending modes, the Eckart conditions used above are not applicable. The trajectories executed by the atoms for a general "bend" are not the same as those given above. It is unclear whether the anharmonic constants for a pure symmetry mode would be changed given the Eckart conditions for a general bend, but the differences are expected to be small.

The potential constants for the pure symmetry modes are given below in units of $\left(\frac{2k}{r^n}\right)$:

$$F_{44} = \frac{(1+\beta)^2}{8} 2^{-n/2} [n(n+4) + n \cdot 2^{-n/2}]$$

$$F_{55} = 2^{-n/2} \left(\frac{n^2}{8} + \frac{n}{4} \right)$$

$$F_{66} = 2^{-n/2} \left(\frac{n^2}{8} + 2^{-n/2} \frac{n}{8} \right)$$

$$F_{555} = \frac{3}{8} 2^{-n/2} \left(\frac{n^2}{8} + \frac{n}{4} \right)$$

$$\begin{aligned} F_{4444} &= \frac{(1+\beta)^2}{96} 2^{-n/2} \left[-\frac{n(n+4)}{4} + (1+\beta)^2 \frac{n(n+2)}{64} (n^2 + 10n + 48) \right. \\ &\quad \left. + 2^{-n/2} \frac{n}{16} (3n+2)(1+\beta)^2 \right] \end{aligned} \quad (14)$$

$$F_{5555} = \frac{2^{-n/2}}{96} \left[-\frac{n(n+2)}{2} + \frac{(n+6)(n+4)(n+2)n}{32} \right]$$

$$F_{6666} = \frac{2^{-n/2}}{96} \left[\left(\frac{n}{2} + \frac{(n+6)(n+4)(n+2)n}{64} + \frac{n(2+n)}{8} \right) + 2^{-n/2} \frac{(n(3n+2))}{16} \right]$$

$$\begin{aligned} F_{444'4'} &= \frac{2^{-n/2}}{96} (1+\beta)^2 \left[n + \frac{n(n+2)}{4} (2 - 9(1+\beta)^2) + \frac{3(1+\beta)^2}{8} n(n+2)(n+4) \right. \\ &\quad \left. + (1+\beta)^2 \frac{n(n+2)(n+4)(n+6)}{64} + 2^{-n/2} \frac{(8n - 3n(n+2)(1+\beta)^2)}{16} \right] \end{aligned}$$

$$F_{555'5'} = \frac{2^{-n/2}}{96} \left[\frac{23n(n+2)}{32} - \frac{(n+6)(n+4)(n+2)n}{16} \right]$$

$$F_{666'6'} = \frac{2^{-n/2}}{96} \left[-n - \frac{3n(n+2)(n+4)}{8} + \frac{(n+6)(n+4)(n+2)n}{64} - \frac{7n(n+2)}{4} \right. \\ \left. + 2^{-n/2} \left(\frac{n(2-3n)}{16} \right) \right]$$

The numerical values for the force constants are listed in Table 3. For the quadratic force constants, the relative ordering $F_{44} > F_{55} > F_{66}$ is independent of n . This is the same ordering that is observed for most of the fifteen octahedral hexafluorides.⁶ In MoF_6 and WF_6 , $F_{55} > F_{44}$, while F_{66} is still the smallest force constant. While the POS model agrees well with the relative ordering of the quadratic constants it was found that in most cases a single value of the potential parameter, n , could not be determined which simultaneously reproduced all three experimental force constant ratios (F_{44}/F_{55} , F_{44}/F_{66} , F_{55}/F_{66}).

The results of Bartell and coworkers^{4,7} suggest that the range $4 \leq n \leq 7$ is appropriate for polyatomic fluorides. This is near the range found when comparing the quadratic POS-free constants for octahedral hexafluorides in the present work.

The total number of anharmonic potential coefficients for the general bending surface expanded to fourth order in the symmetry coordinates is eighteen. Without any reasonable way of choosing the sign and magnitude of these constants it would be virtually impossible to conclude anything meaningful about their effect on the bending eigenvalues. The POS model provides a means of picking a restricted path through this eighteen dimensional

parameter space. Encouraged by the results predicted for the quadratic force field, it is reasonable to assume that the anharmonic potential space is spanned in a physically meaningful manner. A single value of the repulsive exponent, n , probably does not give an accurate representation of the entire bending surface. It is suggested that for the range of n considered in the calculations to follow, that the probable behavior of the bending eigenvalues has been spanned.

III. KINETIC ENERGY

The classical kinetic energy in the center of mass Cartesian coordinate system has the form,³

$$\begin{aligned}
 T = & \frac{I_{xx}(\bar{r})}{2} \omega_x^2 + \frac{I_{yy}(\bar{r})}{2} \omega_y^2 + \frac{I_{zz}(\bar{r})}{2} \omega_z^2 - I_{xy}(\bar{r}) \omega_x \omega_y - I_{xz}(\bar{r}) \omega_x \omega_z \\
 & - I_{yz}(\bar{r}) \omega_y \omega_z + \omega_x \sum_k X_k(\bar{r}) \dot{r}_k + \omega_y \sum_k Y_k(\bar{r}) \dot{r}_k + \omega_z \sum_k Z_k(\bar{r}) \dot{r}_k \\
 & + \sum_k \frac{M_k(\bar{r})}{2} \dot{r}_k^2
 \end{aligned} \tag{15}$$

In this equation, $\bar{r}$ indicates that the quantity depends on the atomic coordinates. I_{ij} is the i - j th component of the moment of inertia; $\omega_x, \omega_y, \omega_z$ are the three components of the angular velocity; $X_k(\bar{r}), Y_k(\bar{r}), Z_k(\bar{r})$ are the Coriolis coupling constants. By replacing the Cartesian components with their functional dependence upon the symmetry coordinates, an analogous kinetic energy will be obtained with the r_k 's interpreted as the curvilinear symmetry coordinates. In this case, the last term in Eq. (15) must be

rewritten as

$$\sum_{i,j} \frac{M_{ij}(\bar{r})}{2} \dot{r}_i \dot{r}_j$$

to emphasize that cross terms in the velocities are possible.

By taking partial derivatives of Eq. (15) with respect to the classical velocities, a matrix is obtained relating the momenta, (P_i, J_i) to the velocities, $(\dot{r}_i, \dot{\omega}_i)$. Here J_i is the i^{th} component of the total angular momentum vector. Inverting this matrix and substitution of the resulting expressions (relating the velocities to the momenta) into the kinetic energy will convert the kinetic energy into the variables appropriate for a Hamiltonian. For each uncoupled bending mode, there are six classical velocities. Since, in general, none of the entries can be assumed to vanish, this inversion would involve an unmanageable number of terms once the explicit functional dependence of the coefficients in Eq. (15) are substituted. The method used to effect this inversion was to expand each terms as a power series in the coordinates, truncating after a given order. This order is two less than the order of the coordinates in the potential energy, since the kinetic energy is already quadratic in the momenta. The truncated matrix was inverted consistently to the same order as the original matrix using the MACSYMA symbolic manipulation program.⁸ By substituting the resulting equations for the classical velocities, the Hamiltonian form of the classical kinetic energy was obtained exactly to a given order in the independent variables.

In this work, only the vibrational motions are analyzed. The existence of degeneracies means that vibrational angular momentum will introduce terms in the rotational and Coriolis energies that have a pure

vibrational coordinate dependence. It was decided to use the Hamiltonian which contained these terms. The eigenvalues calculated will be those for states where the total angular momentum is zero.

The wave mechanical kinetic energy operator was obtained by the Podolsky transformation.⁹ The final fourth order form of the kinetic energy operators are given by:

$$\begin{aligned} KE_{T_{2g}} \begin{matrix} (a=S_{5a}, \\ b=S_{5b}, \\ c=S_{5c}) \end{matrix} &= \frac{4}{mr^2} \left[\frac{p_a^2 + p_b^2 + p_c^2}{2} + \frac{(b^2 + c^2)}{128} p_a^2 + \frac{(a^2 + c^2)}{128} p_b^2 + \frac{(a^2 + b^2)}{128} p_c^2 \right. \\ &\quad \left. - \frac{3}{32} (ab p_a p_b + bc p_b p_c + ac p_a p_c) + \frac{3i\hbar}{32} (ap_a + bp_b + cp_c) - \frac{3\hbar^2}{128} \right] \end{aligned} \quad (16)$$

$$\begin{aligned} KE_{T_{2u}} \begin{matrix} (a=S_{6a}, \\ b=S_{6b}, \\ c=S_{6c}) \end{matrix} &= \frac{2}{mr^2} \left[\frac{p_a^2 + p_b^2 + p_c^2}{2} + \frac{(b^2 + c^2)}{64} p_a^2 + \frac{(a^2 + c^2)}{64} p_b^2 + \frac{(a^2 + b^2)}{64} p_c^2 \right. \\ &\quad \left. - \frac{3}{16} (ab p_a p_b + bc p_b p_c + ac p_a p_c) - \frac{3\hbar^2}{64} \right] \end{aligned} \quad (17)$$

$$\begin{aligned} KE_{T_{1u}} \begin{matrix} (a=S_{4a}, \\ b=S_{4b}, \\ c=S_{4c}) \end{matrix} &= \frac{2}{M_1 r^2} \left[\frac{(p_a^2 + p_b^2 + p_c^2)}{2} + \frac{\delta}{2} (a^2 p_a^2 + b^2 p_b^2 + c^2 p_c^2) \right. \\ &\quad \left. + \frac{\epsilon}{2} [(b^2 + c^2) p_a^2 + (a^2 + c^2) p_b^2 + (a^2 + b^2) p_c^2] \right. \\ &\quad \left. - \gamma (ab p_a p_b + bc p_b p_c + ac p_a p_c) + i\hbar (\gamma - \delta) (ap_a + bp_b + cp_c) \right. \\ &\quad \left. - \frac{3\hbar^2 (2\epsilon + \delta)}{4} \right] \end{aligned} \quad (18)$$

where for $KE_{T_{1u}}$:

$$\begin{aligned}
 \epsilon &= \frac{M_4^2}{32MM_1} & M_1 &= \frac{M_x(6M_x + M_o)}{2M_x + M_o} \\
 \delta &= \frac{M_3 - M_2 - M_1}{8M_1} & M_2 &= \frac{2M_x(6M_x + M_o)}{(2M_x + M_o)^4} [(6M_x + M_o)^3 - (2M_x + M_o)^3] \\
 \gamma &= \frac{2M_4^2 + MM_3}{16M_1M} & M_3 &= M_1 \left(\frac{6M_x + M_o}{2M_x + M_o} \right)^3 \\
 & & M_4 &= M_1 \frac{(2M_x - M_o)}{(2M_x + M_o)}
 \end{aligned} \tag{19}$$

It should be emphasized that these operators were derived by inverting the complete matrix for the classical momenta. If only the vibrational block is inverted, neglecting the rotational and Coriolis terms in the classical kinetic energy, a different set of vibrational momenta is obtained.

IV. THE HAMILTONIAN AND CALCULATION OF EIGENVALUES

The decoupled bending Hamiltonians were cast into a dimensionless form by the transformations

$$S_a = \left(\frac{\hbar^2}{mk} \right)^{\frac{1}{4}} x ; \quad P_a = \left(\frac{mk}{\hbar^2} \right)^{\frac{1}{4}} P_x \tag{20}$$

with similar transformations for S_b, S_c, P_b, P_c . Defining the parameter

$$\alpha = \frac{5.805}{r(\text{\AA})} \left(\frac{1}{m(\text{amu})\omega(\text{cm}^{-1})} \right)^{\frac{1}{2}} \tag{21}$$

where ω is the harmonic frequency in wavenumbers for the mode, $m(\text{amu})$ the mass for that mode in the harmonic approximation in atomic mass units, and $r(\text{\AA})$ the M-X bond length in angstroms. The dimensionless Hamiltonians for the three modes are given by

$$\begin{aligned}
 H_D(T_{1u}, T_{2u}) = & - \frac{(P_x^2 + P_y^2 + P_z^2)}{2} + \frac{(x^2 + y^2 + z^2)}{2} + k_1(n) \alpha(xyz) \\
 & + k_2(n) \alpha^2(x^2y^2 + y^2z^2 + z^2x^2) + k_3(n) \alpha^2(x^2 + y^2 + z^2)^2 \\
 & - \frac{\alpha^2}{4N^2} [(x^2 + y^2)P_z^2 + (x^2 + z^2)P_y^2 + (y^2 + z^2)P_x^2] \\
 & + \frac{3\alpha^2}{N^2} (xyP_xP_y + yzP_yP_z + xzP_xP_z + xP_x + yP_y + zP_z) - \frac{3\alpha^2}{4N^2}
 \end{aligned} \quad (22)$$

$$\begin{aligned}
 H_D(T_{1u}) = & - \frac{(P_x^2 + P_y^2 + P_z^2)}{2} + \frac{(x^2 + y^2 + z^2)}{2} + k_2(n) \alpha^2(x^2y^2 + y^2z^2 + x^2z^2) \\
 & + k_3(n) \alpha^2(x^2 + y^2 + z^2)^2 - \frac{\delta\alpha^2}{2} (x^2P_x^2 + y^2P_y^2 + z^2P_z^2) \\
 & - \frac{\epsilon\alpha^2}{2} [(x^2 + y^2)P_z^2 + (x^2 + z^2)P_y^2 + (y^2 + z^2)P_x^2] \\
 & - \frac{3\alpha^2(2\epsilon + \delta)}{4} + \frac{\alpha^2(\gamma - \delta)}{2} (xP_x + yP_y + zP_z)
 \end{aligned} \quad (23)$$

where the anharmonic constants are defined by

	T_{1u}	T_{2u}	T_{2g}	
$k_1(n)$	0	0	$k_{55'5''}/k_{55}$	(24)
$k_2(n)$	$k_{444'4}/k_{44}$	$k_{666'6}/k_{66}$	$k_{555'5'}/k_{55}$	
$k_3(n)$	k_{4444}/k_{44}	k_{6666}/k_{66}	k_{5555}/k_{55}	
N^2	--	8	4	

For each molecule, the spectrum is parametrically dependent on the two parameters α, n . Alpha scales the calculated spectrum to the harmonic frequency while n governs the relative deviations of the potential surface from this quadratic curvature. The parameters α, β for the hexafluorides are bounded by the values for SF_6 and UF_6 . The results presented for these two molecules can then be extended to other hexafluoride systems.

The eigenvalues were computed for each symmetry by diagonalizing the dimensionless Hamiltonian in a triply-degenerate, harmonic oscillator representation. The number of basis functions was determined by two restrictions. First, the maximum value of the sum $(L+M+N)$ was specified where the integers L, M, N are the quantum labels of the individual harmonic oscillator functions. Secondly, partial symmetry blocking was introduced for each symmetry. The T_{1u} and T_{2u} blocks were divided into even and odd blocks under inversion. The T_{2g} Hamiltonian was split into an A+E block and a T block. The dimensions of the resulting Hamiltonians are in Table 5. The calculated eigenvalues are presented in Tables 6-13. The first difference band transitions are plotted in Figs. 2-8, relative to the harmonic frequency. The dotted lines in these figures are the fourth order results. The solid lines are those results assuming the kinetic energy is that of a three-dimensional isotropic harmonic oscillator. For the T_{2u} SF_6 transitions (Fig. 4) the curvilinear harmonic bending transitions are indicated by dots and the transition labels starred. These are for a harmonic bending potential with the correct fourth order kinetic energy, indicating that in a curvilinear coordinate system, the degenerate harmonic oscillator levels are split even when the potential is exactly harmonic. For the T_{1u} modes, the effect of the kinetic energy constant β , originating from the displacement of the

central atom, was tested for UF_6 , SF_6 by letting the U and S atoms become infinitely massive, or in the limit $\beta = 0$. For this limit, the kinetic energy corrections to the transition frequencies were calculated and are shown by the dotted lines in Figs. 6 and 7. Figure 8 displays the correct T_{1u} frequencies for both $^{32}\text{SF}_6$ and $^{238}\text{UF}_6$ to indicate the bounds on the transition frequencies within the family of octahedral hexafluorides.

All difference band transitions for the T_{1u}, T_{2u} modes are infrared active. The E_g, T_{2g} difference bands for the T_{2g} mode are Raman active. For the energy levels presented here, increasing the basis set changed the eigenvalues less than 1×10^{-7} in dimensionless units. For the SF_6 T_{1u} mode, this error is approximately $6 \times 10^{-4} \text{ cm}^{-1}$ in the difference band frequencies.

V. DISCUSSION

From Figs. 2 through 8 it can be seen that the relative ordering and trend of the eigenvalues is reasonably well approximated by neglecting the kinetic energy corrections to the anharmonic Hamiltonian. Except for the T_{2u} mode where the crossing of the A_g and E_g levels is shifted from $n=5$ to $n=8$, the anharmonic kinetic energy terms only change the magnitude of the frequency shifts, and this amounts to $\lesssim 0.00125 \omega_0$ for all modes, ω_0 being the harmonic frequency. (For SF_6 T_{1u} , ω_0 is 614 cm^{-1} so the correction is $\lesssim 0.7675 \text{ cm}^{-1}$.) The largest magnitude anharmonic shift with a "hard" potential, $n=14$, amounts to only $\sim 0.015 \omega_0$. (For SF_6 T_{1u} , this is 9.2 cm^{-1} .) For UF_6 and SF_6 the range of the shifted transition frequencies is given in Table 13 for the range of $n=4-7$. This covers the range of n found in work on other polyfluoride systems.^{3,7} These shifts are small enough that the neglected coupling terms between the modes could significantly

displace these frequencies. It is clear that the fundamental region will be severely crowded by these difference bands and the assignment of a room temperature spectrum virtually impossible until the coupling effects neglected above are taken into account.

Although the kinetic energy was found to be a minor correction for the octahedral bending modes, for systems like MX_5 , MX_4 , and MX_3 it could become significant. For octahedral molecules, the pure bending modes defined here are equivalent to their associated normal modes only when first order displacement terms are considered, except for the T_{1u} motion where the central atom motion is defined to preserve bond lengths. For MX_3 molecules of D_{3h} symmetry, there is no such equivalence between pure bending motions and normal coordinates to first order in angular displacements. This is a consequence of the center of bending and center of mass being unequal to first order in angular displacements. For this case, the rigid bender analysis will be expected to give a noticeably different fit to available data than an equivalent order expansion of the normal coordinate Hamiltonian. Work is continuing along these lines.

With an exactly solved model it is possible to estimate the amount of stretch-bend interaction by observing the deviation of the frequencies of a bending Hamiltonian to the experimentally derived ones. In particular, the question of the correlation of the N-H bond lengths as the NH_3 molecule inverts can be unambiguously answered.¹²

A final comment concerning the implications of this work on multi-photon dissociation of SF_6 is in order. By far the most complete study of the initial excitation process for SF_6 is the work of Cantrell, Overend,

et al.¹⁰ In their analysis it is assumed that the ν_3 mode can be approximated by a Morse oscillator in the bond stretches, and a curvilinear harmonic bender in the angular coordinates. By introducing the multi-dimensional, anharmonic ν_3 -ladder their analysis has given substantial evidence of the importance of anharmonic vibrational splittings in compensating for the rotational mismatch in energy between the laser field and the molecular levels. It is clear that the ν_3 -ladder is affected by the numerous high vibrational states of the lower frequency motions. Hence the magnitude and direction of the splitting of the $J=0$ vibrational levels cannot be accurately predicted by their model until the effect of these coupling interactions has been estimated. Also, from their work it is difficult to assess whether the parameters are truly related to the potential surface of SF_6 or whether they are contaminated by various averaged cross terms and kinetic energy effects. It is clear that an understanding of the potential surface for SF_6 needs more systematic calculations on well defined models which develop the Hamiltonians without approximation in a consistent manner. It is hoped that by understanding the pure bending surface, where it is tractable to explicitly derive the Hamiltonian in an exact power series, that insight may be gained to improve the form of the effective potentials used in modeling the initial excitation process in multi-photon dissociation. In future work the complete bending surface for SF_6 should indicate the importance of cross term coupling on the energy spectrum. The model presented here ought to offer a guideline on transferring the available spectroscopic data for SF_6 to UF_6 where the experimental difficulty of resolving a spectrum is great.

VI CONCLUSIONS

The foremost result of this work is the development of an exact, practical scheme for deriving classical Hamiltonians in a power series expansion of the coordinates about equilibrium. No special property of the coordinate system is necessary for this process and in this study a non-orthogonal, curvilinear coordinate system has been used. This enables one, through the Podolsky transformation to derive wave mechanical Hamiltonians to an arbitrarily high order without approximation. Consequently, one can parameterize molecular systems in a set of coordinates that approximate the physical motion and which are not necessarily algebraically simple.

Secondly, a reasonable model for the force field of the bending motions of an octahedral molecule has been used (the POS model) to predict the magnitude and position, relative to the fundamental transition, for pure bending mode difference bands. Using the resulting wavefunctions, it is possible to include the effect of intermode coupling terms via perturbation theory and to calculate the anharmonic frequency spectrum for the complete nine-dimensional bending surface. Even though the force field in this study is hypothetical, it does provide a formalism to transfer the anharmonic force field of one molecule to another within any family of MX_6 -type molecules. This approach is clearly advantageous in relating the available spectroscopic data for SF_6 to UF_6 since the large density of spectral lines and their low frequency in UF_6 prohibits a direct study of the UF_6 fundamental regions to predict a multiphoton dissociation process based on anharmonic splitting of the degenerate vibrational modes.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Larry Bernstein for suggesting this topic and in checking the results of some of the calculations. Professor William Klemperer has provided helpful guidance and support for this project in its early stages. Dr. Brian Howard and the faculty of the Physical Chemistry Laboratories, Oxford University are especially thanked for their hospitality towards the author during his stay at Oxford while on a Knox Fellowship. Professor Yuan Lee is thanked for providing financial assistance and suggesting the applicability of this work to multiphoton dissociation. Dr. Phil Bunker provided many helpful comments concerning this project and the theory of molecular vibrations.

This work was supported in part by the U.S. Department of Energy.

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TABLE 1. Octahedral symmetry coordinates and their polynomial representations.

Symmetry Coordinate ^a	Polynomial Representation
$S_{4a} \sim 1/\sqrt{8} (\Delta\beta_{15} + \Delta\beta_{25} + \Delta\beta_{35} + \Delta\beta_{45} - \Delta\beta_{16} - \Delta\beta_{26} - \Delta\beta_{36} - \Delta\beta_{46})$	z
$S_{4b} \sim 1/\sqrt{8} (\Delta\beta_{12} + \Delta\beta_{15} + \Delta\beta_{14} + \Delta\beta_{16} - \Delta\beta_{23} - \Delta\beta_{35} - \Delta\beta_{34} - \Delta\beta_{36})$	x
$S_{4c} \sim 1/\sqrt{8} (\Delta\beta_{12} + \Delta\beta_{23} + \Delta\beta_{25} + \Delta\beta_{26} - \Delta\beta_{14} - \Delta\beta_{34} - \Delta\beta_{45} - \Delta\beta_{46})$	y
$S_{5a} \sim 1/2 (-\Delta\beta_{12} + \Delta\beta_{23} - \Delta\beta_{34} + \Delta\beta_{14})$	xy
$S_{5b} \sim 1/2 (\Delta\beta_{26} - \Delta\beta_{25} + \Delta\beta_{45} - \Delta\beta_{46})$	yz
$S_{5c} \sim 1/2 (\Delta\beta_{16} - \Delta\beta_{36} + \Delta\beta_{35} - \Delta\beta_{15})$	xz
$S_{6a} \sim 1/\sqrt{8} (\Delta\beta_{15} - \Delta\beta_{16} + \Delta\beta_{26} - \Delta\beta_{25} + \Delta\beta_{35} - \Delta\beta_{36} + \Delta\beta_{46} - \Delta\beta_{45})$	$z(x^2 - y^2)$
$S_{6b} \sim 1/\sqrt{8} (\Delta\beta_{35} - \Delta\beta_{15} + \Delta\beta_{12} - \Delta\beta_{23} + \Delta\beta_{36} - \Delta\beta_{16} + \Delta\beta_{14} - \Delta\beta_{34})$	$x(y^2 - z^2)$
$S_{6c} \sim 1/\sqrt{8} (\Delta\beta_{14} - \Delta\beta_{12} + \Delta\beta_{26} - \Delta\beta_{46} + \Delta\beta_{34} - \Delta\beta_{23} + \Delta\beta_{25} - \Delta\beta_{45})$	$y(z^2 - x^2)$
^a $\Delta\beta_{ij}$ is the change in bond angle between atoms i and j. The numbering scheme is shown in Fig. 1 (S_{4a}).	

TABLE 2. Relation of potential constants to potential surface derivatives at equilibrium.

$F_{ii} = \frac{\partial^2 V}{\partial S_i^2}$	$F_{iiii} = \frac{1}{24} \frac{\partial^4 V}{\partial S_i^4}$
$F_{ii'i''} = \frac{\partial^3 V}{\partial S_i \partial S_{i'} \partial S_{i''}}$	$F_{iii'i'} = \frac{1}{4} \frac{\partial^4 V}{\partial S_i^2 \partial S_{i'}^2} - \frac{1}{12} \frac{\partial^4 V}{\partial S_i^4}$
$F_{ii'j} = \frac{\partial^3 V}{\partial S_i \partial S_{i'} \partial S_j}$	$F_{iiij} = \frac{1}{4} \frac{\partial^4 V}{\partial S_i^2 \partial S_j^2}$
	$F_{iii'j} = \frac{1}{2} \frac{\partial^4 V}{\partial S_i^2 \partial S_{i'} \partial S_j}$
	$F_{ii'jj'} = \frac{1}{24} \frac{\partial^4 V}{\partial S_i \partial S_{i'} \partial S_j \partial S_{j'}}$
$F_{ijk} = \frac{\partial^3 V}{\partial S_i \partial S_j \partial S_k}$	$F_{ijj'k} = \frac{1}{24} \frac{\partial^4 V}{\partial S_i \partial S_j \partial S_{j'} \partial S_k}$

* i,j,k are some particular symmetry coordinate. i',j',i'' are different coordinates from the same symmetry type as i,j, and (i,i') respectively.

TABLE 3. Force constants.^a

n	SF ₆ ($\beta = 1.0857$)			UF ₆ ($\beta = 0.27536$)									
	F ₄₄	F ₄₄₄₄	F _{444'4'}	F ₄₄	F ₄₄₄₄	F _{444'4'}	F ₅₅	F _{55'5''}	F ₅₅₅₅	F _{555'5'}	F ₆₆	F ₆₆₆₆	F _{666'6'}
1	2.19439	0.16561	0.250537	0.82049	0.09663	0.04117	0.265	0.099 0.026	0.013 0.002	-0.032 -0.002	0.151	0.020	-0.076
4	4.48609	0.62835	2.35483	1.67737	0.35905	0.39276	0.750	0.281 0.211	0.125 0.015	-0.268 -0.020	0.531	0.093	-0.231
7	3.73055	1.00069	4.59656	1.39487	0.56508	0.68565	0.696	0.261 0.186	0.230 0.013	-0.477 -0.016	0.548	0.141	-0.218
10	2.38431	0.97941	4.88707	0.89151	0.55055	0.70809	0.469	0.176 0.082	0.254 0.005	-0.519 -0.006	0.392	0.143	-0.140
14	1.07101	0.69163	3.53534	0.40045	0.38755	0.50489	0.219	0.082 0.018	0.196 0.001	-0.397 -0.001	0.192	0.105	-0.054

^aThe second set of force constants for S₅ symmetry motions are the EOR model constants. The remaining constants are for the POS model, in units of (2k/rⁿ).

TABLE 4. Center-of-mass atomic coordinates in symmetry coordinates.

T_{2g}	$r_1 = (\sqrt{1-a^2-c^2}, a, c)r_0$	
	$r_2 = (a, \sqrt{1-a^2-b^2}, b)r_0$	$a = \sin(S_{5a}/2)$
	$r_3 = (-\sqrt{1-a^2-c^2}, -a, -c)r_0$	
	$r_4 = (-a, -\sqrt{1-a^2-b^2}, -b)r_0$	$b = \sin(S_{5b}/2)$
	$r_5 = (c, b, \sqrt{1-b^2-c^2})r_0$	
	$r_6 = (-c, -b, -\sqrt{1-b^2-c^2})r_0$	$c = \sin(S_{5c}/2)$
	$r_m = (0, 0, 0)$	
T_{2u}	$r_1 = (\sqrt{1-a^2-c^2}, c, -a)r_0$	
	$r_2 = (-b, \sqrt{1-a^2-b^2}, a)r_0$	$a = \sin(S_{6a}/\sqrt{8})$
	$r_3 = (-\sqrt{1-a^2-c^2}, c, -a)r_0$	
	$r_4 = (-b, -\sqrt{1-b^2-a^2}, a)r_0$	$b = \sin(S_{6b}/\sqrt{8})$
	$r_5 = (b, -c, \sqrt{1-b^2-c^2})r_0$	
	$r_6 = (b, -c, -\sqrt{1-b^2-c^2})r_0$	$c = \sin(S_{6c}/\sqrt{8})$
	$r_m = (0, 0, 0)$	

continued . . .

TABLE 4 (continued)

T_{1u}	$r_1 = (-\beta a + \sqrt{1-(1+\beta)^2(b^2+c^2)}, b, c)r_0$	$\beta = \frac{4M_X}{2M_X + M_m}$ $a = \sin(S_{4a}/\sqrt{8})$ $b = \sin(S_{4b}/\sqrt{8})$ $c = \sin(S_{4c}/\sqrt{8})$
	$r_2 = (a, -\beta b + \sqrt{1-(1+\beta)^2(a^2+b^2)}, c)r_0$	
	$r_3 = (-\beta a - \sqrt{1-(1+\beta)^2(b^2+c^2)}, b, c)r_0$	
	$r_4 = (a, -\beta b - \sqrt{1-(1+\beta)^2(a^2+c^2)}, c)r_0$	
	$r_5 = (a, b, -\beta c + \sqrt{1-(1+\beta)^2(a^2+b^2)})r_0$	
	$r_6 = (a, b, -\beta c - \sqrt{1-(1+\beta)^2(a^2+b^2)})r_0$	
	$r_m = (-a, -b, -c)\beta r_0$	

TABLE 5. Composition of the Hamiltonian matrix.

Symmetry species	$(L + M + N)_{\max}$	Symmetry block	Dimension of Hamiltonian
T_{1u}	8	even	95
T_{1u}	7	odd	70
T_{2g}	9	A+E	55
T_{2g}	7	T	90
T_{2u}	8	even	95
T_{2u}	7	odd	70

TABLE 6. T_{2g} eigenvalues for SF_6 .*

$V_{T_{2g}} = 0.5(x^2 + y^2 + z^2) + c(n)(xyz) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2y^2 + y^2z^2 + x^2z^2)$							
	n	1	4	7	10	14	H.O.
$T_{2g}(SF_6)$	a(n)	0.00027	0.00093	0.00184	0.00301	0.00497	0.0
$\alpha = 0.0745$	b(n)	-0.00068	-0.00198	-0.00380	-0.00614	-0.01007	0.0
	c(n)	0.02794	0.02794	0.02794	0.02794	0.02794	0.0
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.5000	1.5015	1.5035	1.5061	1.5104	1.4995
		1.5005	1.5020	1.5040	1.5066	1.5104	1.5000
1	T_{2g}	2.5006	2.5041	2.5088	2.5148	2.5247	2.4996
		2.5010	2.5045	2.5092	2.5152	2.5251	2.5000
2	T_{2g}	3.5007	3.5062	3.5136	3.5231	3.5386	3.4998
		3.5009	3.5064	3.5138	3.5233	3.5388	3.5000
2	A_{2g}	3.5006	3.5080	3.5181	3.5308	3.5517	3.4991
		3.5015	3.5089	3.5190	3.5317	3.5526	3.5000
2	E_g	3.5026	3.5100	3.5200	3.5328	3.5536	3.5000
		3.5026	3.5100	3.5200	3.5327	3.5536	3.5000

*Lower values for each pair of energies are those neglecting the anharmonic kinetic energy terms.

TABLE 7. T_{2g} eigenvalues for UF_6^*

$V_{T_{2g}} = 0.5(x^2 + y^2 + z^2) + c(n)(xyz) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2y^2 + y^2z^2 + z^2x^2)$							
$T_{2g}(UF_6)$	n	1	4	7	10	14	H.O.
$\alpha = 0.0938$	a(n)	0.00044	0.00147	0.00291	0.00477	0.00788	0.0
	b(n)	-0.00108	-0.00314	-0.00603	-0.00974	-0.01597	0.0
	c(n)	0.03518	0.03518	0.03518	0.03518	0.03518	0.0
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.5001	1.5024	1.5056	1.5096	1.5164	1.4993
		1.5008	1.5031	1.5063	1.5104	1.5171	1.5000
1	T_{2g}	2.5011	2.5064	2.5138	2.5233	2.5387	2.4994
		2.5016	2.5070	2.5144	2.5239	2.5393	2.5000
2	T_{2g}	3.5013	3.5098	3.5214	3.5362	3.5604	3.4997
		3.5016	3.5101	3.5217	3.5366	3.5607	3.5000
2	A_g	3.5011	3.5126	3.5283	3.5482	3.5805	3.4986
		3.5025	3.5140	3.5297	3.5497	3.5814	3.5000
2	E_g	3.5043	3.5157	3.5314	3.5513	3.5835	3.5000
		3.5042	3.5157	3.5314	3.5513	3.5834	3.5000

*Lower values for each pair of energies are those neglecting the anharmonic kinetic energy terms.

TABLE 8. T_{2u} eigenvalues for SF_6 .*

$V_{T_{2u}} = 0.5(x^2 + y^2 + z^2) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2y^2 + y^2z^2 + x^2z^2)$							
$T_{2u}(SF_6)$	n	1	4	7	10	14	H.O.
$\alpha = 0.0648$	A(n)	0.00056	0.00074	0.00109	0.00154	0.00231	0
	B(n)	-0.00211	-0.00183	-0.00167	-0.00150	-0.00117	0
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.4998	1.5007	1.5021	1.5039	1.5070	1.4993
		1.5005	1.5014	1.5028	1.5046	1.5077	1.5000
1	T_{2u}	2.5006	2.5027	2.5060	2.5102	2.5173	2.4994
		2.5012	2.5033	2.5066	2.5107	2.5179	2.5000
2	T_{2g}	3.5006	3.5045	3.5105	3.5181	3.5311	3.4947
		3.5009	3.5048	3.5108	3.5184	3.5314	3.5000
2	A_{2g}	3.5012	3.5056	3.5127	3.5216	3.5368	3.5987
		3.5026	3.5070	3.5141	3.5229	3.5381	3.5000
2	E_g	3.5041	3.5075	3.5133	3.5207	3.5331	3.5000
		3.5041	3.5075	3.5133	3.5206	3.5331	3.5000

* Lower values for each pair of energies are those neglecting the anharmonic kinetic energy terms.

TABLE 9. T_{2u} eigenvalues for UF_6 .*

$V_{T_{2u}} = 0.5(x^2 + y^2 + z^2) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2 y^2 + y^2 z^2 + x^2 z^2)$							
	n	1	4	7	10	14	H.O.
$T_{2u}(UF_6)$	A(n)	0.00084	0.00110	0.00161	0.00229	0.00344	0
$\alpha = 0.0791$	B(n)	-0.00314	-0.00272	-0.00249	-0.00224	-0.00175	0
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.4998	1.5010	1.5031	1.5058	1.5104	1.4990
		1.5008	1.5021	1.5041	1.5068	1.5114	1.5000
1	T_{2u}	2.5010	2.5040	2.5088	2.5151	2.5256	2.4992
		2.5018	2.5048	2.5096	2.5159	2.5264	2.5000
2	T_{2g}	3.5010	3.5066	3.5154	3.5268	3.5459	3.4996
		3.5014	3.5071	3.5159	3.5272	3.5463	3.5000
2	A_{2g}	3.5019	3.5083	3.5186	3.5319	3.5541	3.4980
		3.5039	3.5103	3.5206	3.5339	3.5562	3.5000
2	E_g	3.5062	3.5112	3.5196	3.5305	3.5488	3.5000
		3.5061	3.5111	3.5195	3.5305	3.5488	3.5000

*Lower values for each pair of energy levels are those neglecting the anharmonic kinetic energy terms.

TABLE 10. T_{1u} eigenvalues for $^{32}\text{SF}_6$.

$V(x,y,z) = 0.5(x^2 + y^2 + z^2) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2y^2 + y^2z^2 + x^2z^2)$						
$T_{1u}(\text{SF}_6)$	n	1	4	7	10	14
	a(n)	0.000195	0.000467	0.000851	0.001344	0.002176
$\alpha = 0.03374$	b(n)	0.000056	0.000634	0.001418	0.002340	0.003759
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.5008	1.5022	1.5042	1.5067	1.5108
1	T_{1u}	2.5014	2.5048	2.5095	2.5153	2.5247
2	E_g	3.5019	3.5075	3.5152	3.5248	3.5404
2	T_{2g}	3.5026	3.5090	3.5178	3.5287	3.5463
2	A_{1g}	3.5021	3.5043	3.5193	3.5316	3.5515

TABLE 11. T_{1u} eigenvalues for $^{238}\text{UF}_6$.

$V(x,y,z) = 0.5(x^2 + y^2 + z^2) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2y^2 + y^2z^2 + x^2z^2)$						
$T_{1u}(\text{UF}_6)$	n	1	4	7	10	14
$\alpha = 0.06111$	a(n)	0.000197	0.000526	0.000996	0.001600	0.002621
	b(n)	0.000166	0.000875	0.001837	0.002899	0.004709
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.5009	1.5026	1.5051	1.5081	1.5131
1	T_{1u}	2.5017	2.5058	2.5115	2.5185	2.5301
2	E_g	3.5028	3.5095	3.5189	3.5304	3.5496
2	T_{2g}	3.5031	3.5109	3.5217	3.5347	3.5564
2	A_{1g}	3.5023	3.5110	3.5232	3.5379	3.5624

TABLE 12. Modified T_{1u} eigenvalues $^{\infty}\text{SF}_6$ *

$V(x,y,z) = 0.5(x^2 + y^2 + z^2) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2y^2 + y^2z^2 + x^2z^2)$							
$T_{1u}(\text{SF}_6)$	n	1	4	7	10	14	H.O.
$M_0 = \infty$	a(n)	0.000060	0.000215	0.00037	0.000606	0.00100	0
$\alpha = 0.0487$	b(n)	0.000100	0.000379	0.000755	0.001196	0.001875	0
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.4999 1.5003	1.5007 1.5011	1.5016 1.5019	1.5028 1.5032	1.5047 1.5051	1.4996 1.5000
1	T_{1u}	2.5004 2.5007	2.5022 2.5025	2.5042 2.5045	2.5070 2.5073	2.5116 2.5119	2.4997 2.5000
2	E_g	3.5012 3.5015	3.5042 3.5054	3.5075 3.5097	3.5122 3.5157	3.5197 3.5254	3.5000 3.5000
2	T_{2g}	3.5016 3.5012	3.5046 3.5042	3.5084 3.5074	3.5137 3.5121	3.5223 3.5297	3.4998 3.5000
2	A_{2g}	3.5007 3.5013	3.5047 3.5048	3.5090 3.5086	3.5149 3.5139	3.5246 3.5125	3.4992 3.5000

*Lower values for each pair of energies are those neglecting the anharmonic kinetic energy terms.

TABLE 13. Modified T_{1u} eigenvalues $^{\infty}UF_6$.*

$V(x,y,z) = 0.5(x^2 + y^2 + z^2) + a(n)(x^2 + y^2 + z^2)^2 + b(n)(x^2y^2 + y^2z^2 + x^2z^2)$							
$T_{1u}(UF_6)$	n	1	4	7	10	14	H.O.
$M_0 = \infty$	a(n)	0.000121	0.000432	0.000748	0.001220	0.002020	0
$\alpha = 0.0691$	b(n)	0.000207	0.000763	0.001519	0.002406	0.003774	0
H.O. Level	Symmetry	Energy	Energy	Energy	Energy	Energy	Energy
0	A_{1g}	1.4998	1.5014	1.5031	1.5055	1.5095	1.4992
		1.5006	1.5022	1.5039	1.5063	1.5103	1.5000
1	T_{1u}	2.5008	2.5045	2.5085	2.5141	2.5231	2.4994
		2.5014	2.5051	2.5091	2.5147	2.5238	2.5000
2	E_g	3.5024	3.5085	3.5151	3.5243	3.5394	3.5000
		3.5024	3.5085	3.5151	3.5243	3.5394	3.5000
2	T_{2g}	3.5023	3.5093	3.5170	3.5274	3.5444	3.4997
		3.5027	3.5096	3.5173	3.5278	3.5448	3.5000
2	A_{2g}	3.5015	3.5094	3.5180	3.5298	3.5490	3.4985
		3.5030	3.5109	3.5195	3.5313	3.5506	3.5000

* Lower values for each pair of energies are those neglecting the anharmonic kinetic energy terms.

TABLE 14. Calculated SF₆ and UF₆ difference bands.

Transition	Symmetry	SF ₆ (cm ⁻¹)	UF ₆ (cm ⁻¹)
<i>T_{1u}</i>			
0 → 1	A _{1g} → T _{1u}	614	186
1 → 2	T _{1u} → E _g	614.1 - 614.2	186.1 - 180.2
1 → 2	T _{1u} → T _{2g}	614.9 - 615.8	186.3 - 186.7
1 → 2	T _{1u} → A _{1g}	615 - 616.8	186.3 - 187.0
<i>T_{2g}</i>			
0 → 1	A _{1g} → T _{2g}	525	202
1 → 2	T _{2g} → T _{2g}	524.6	201.8
1 → 2	T _{2g} → A _{1g}	525.7 - 527	202.5 - 203.3
1 → 2	T _{2g} → E _g	526.8 - 528.2	203.1 - 203.9
<i>T_{2u}</i>			
0 → 1	A _{1g} → T ₂	347	147
1 → 2	T _{2u} → T _{2g}	346.9 - 347.3	146.9 - 147.1
1 → 2	T _{2u} → A _{2g}	347.3 - 347.9	147.2 - 147.6
1 → 2	T _{2u} → E _g	347.9 - 348	147.6 - 147.7

FIGURE CAPTIONS

Fig. 1. Octahedral bending symmetry coordinates.

Fig. 2. T_{2g} SF_6 $1 \rightarrow 2$ transitions.

Fig. 3. T_{2g} UF_6 $1 \rightarrow 2$ transitions.

Fig. 4. T_{2u} SF_6 $1 \rightarrow 2$ transitions.

Fig. 5. T_{2u} UF_6 $1 \rightarrow 2$ transitions.

Fig. 6. T_{1u} SF_6 $1 \rightarrow 2$ transitions with infinitely heavy S atoms.

Fig. 7. T_{1u} UF_6 $1 \rightarrow 2$ transitions with infinitely heavy U atom.

Fig. 8. T_{1u} SF_6 , UF_6 $1 \rightarrow 2$ transitions.

XBL 783-7859

Fig. 1

Fig. 2

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Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

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Fig. 8

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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