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Anharmonic Potential Functions of Simple Molecules. II. Direct Numerical Diagonalization of Vibratinal Hamiltonian Matrix and Its Application to CO_2 and CS_2

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A general formalism is presented for the calculation of the vibration-rotation energy levels of linear symmetrical XY_2 type molecules through direct numerical diagonalization of the vibrational hamiltonian matrix. This method is applied to the CO_2 and CS_2 molecules, of which the general quartic force fields have been known accurately. The results are compared with those obtained by an ordinary perturbation treatment, and the truncation effects of the matrix sizes as well as of the expansions of the potential functions are discussed. Special attention is paid to the peculiarities in the potential function of CO_2 for which very strong mixings of the basis harmonic oscillator wave functions are observed. The general formula for evaluating the matrix elements of the transition moment are also discussed and its applicability to the problems of vibrational intensities and the dipole moment functions is discussed.

In Part I,[1)] a method was presented in which the vibration or vibration-rotation energy levels of a diatomic molecule are calculated from the harmonic and anharmonic force constants by solving the vibrational hamiltonian numerically. This method has an advantage over the conventional contact transformation approach,[2)] since a true (perturbed) orthonormal wave function is readily obtained for a given vibrational level through numerical diagonalization. Two basic physical properties of a molecule, *i.e.* the potential and dipole moment functions may be handled simultaneously by this method.[3)]

As pointed out in I, the numerical diagonalization method is very attractive in handling the polyatomic molecules, since no special treatment is required for the anharmonic resonances. Efforts have been made to extend this method to a linear symmetrical triatomic molecule. This extension is not altogether simple, since the vibration-rotation hamiltonians of polyatomic molecules are complex and possess extra terms which are not present in diatomic molecules. The basic algorithms to compute vibration and vibration-rotation energy levels have been established for this type of molecule, and they are applied to the cases of the CO_2 and CS_2 molecules. The results are reported in the present paper.

Hamiltonian

The general form of vibration-rotation hamiltonian of a polyatomic molecule is given by Goldsmith, Amat, and Nielsen.[4)] The form is greatly simplified in the specific case of a linear symmetrical molecule XY_2.[5)] The vibration-rotation hamiltonian may be expressed as the sum of vibrational, rotational, and Coriolis hamiltonians. With replacement of a degenerate pair of bending coordinates q_{2x} and q_{2y} by cylindrical coordinates r_2 and χ_2, it has the following form.[6)]

$$\mathbf{H} = \mathbf{H}_{\mathrm{vib}} + \mathbf{H}_{\mathrm{rot}} + \mathbf{H}_{\mathrm{Cor}}, \tag{1}$$

$$\begin{aligned}\mathbf{H}_{\mathrm{vib}} = {} & (1/2) \sum_{s=1,3} \omega_s(q_s^2+p_s^2) + (\omega_2/2)(r_2^2+p_{r_2}^2) \\ & + (k_{111}q_1^2+k_{122}r_2^2+k_{133}q_3^2)q_1 \\ & + k_{1111}q_1^4+k_{1133}q_1^2q_3^2+k_{3333}q_3^4 \\ & + (k_{1122}q_1^2+k_{2222}r_2^2+k_{2233}q_3^2)r_2^2 \\ & + \mathbf{H}_{\mathrm{vib}'},\end{aligned} \tag{2}$$

$$\mathbf{H}_{\mathrm{vib}'} = B_e(j_x^2+j_y^2) \sum_{k=0} R_k q_1^k, \tag{3}$$

$$\mathbf{H}_{\mathrm{rot}} = B_e(J_x^2+J_y^2) \sum_{k=0} R_k q_1^k, \tag{4}$$

$$\mathbf{H}_{\mathrm{Cor}} = -2B_e(j_xJ_x+j_yJ_y) \sum_{k=0} R_k q_1^k, \tag{5}$$

where $R_k=(-1)^k(k+1)\gamma_1^{(k/2)}$, $\gamma_1=(2B_e/\omega_1)$, j_x and j_y are the dimensionless vibrational angular momenta ($j_x=p_x/\hbar$ and $j_y=p_y/\hbar$). The totally symmetric q_1 normal coordinate plays essentially the same role as q in diatomic molecules, and each hamiltonian is expressed as a power series expansion of q_1. This is suited for numerical treatment and the hamiltonians may be truncated at a desired order of approximation. The normal coordinates q_{2x}, q_{2y}, and q_3 do not appear in the expressions in Eqs. (3)—(5). The molecular vibrations affect the moments of inertia through the shift of the average nuclear positions as well as by the anisotropy of the mean square amplitude of vibration. The former effect is linear in normal coordinates and vanishes unless $\langle \bar{q}_r \rangle \neq 0$, which holds only for $r=1$ in linear XY_2. The latter effect is quadratic in normal coordinates, and there are, indeed, non-vanishing terms for q_{2x}^2, q_{2y}^2, and q_3^2, but they are all cancelled out when the Eckart condition is imposed to separate vibration and rotation. This problem has been discussed by Oka[6a)] in greater detail.

The term designated $\mathbf{H}_{\mathrm{vib}}'$ arises from the squared vibrational angular momentum and contributes only to the vibrational energies of a molecule, it is treated as a part of vibrational hamiltonian. The general quartic potential function is used in Eq. (2). If higher-order force constants are included, another term,

$$(B_e/2) \sum_{k=1} \gamma^{(k/2)} q_1^k, \tag{6}$$

which is originated from pseudo-potential $U(q's)$[2,7)] must also be considered in $\mathbf{H}_{\mathrm{vib}}'$.

Energy Levels

Vibrational Energy Levels. As diatomic molecules, the vibrational hamiltonian matrix elements may be evaluated from the harmonic oscillator basis functions,

$$\langle n|\mathbf{H}_{\mathrm{vib}}|n'\rangle$$

where $|n\rangle$ represents $|n_1, n_2, l_2, n_3\rangle$.[8] The vibrational energy levels are calculated by diagonalizing the vibrational hamiltonian matrix numerically. For a given vibrational level v, the corresponding wave function is evaluated as a linear combination of the basis harmonic oscillator wave functions, and may be expressed as

$$|v\rangle = \sum_n a_{vn}|n\rangle, \tag{7}$$

where the coefficients a_{vn}'s are the corresponding elements of eigen vectors. The basis functions may be arranged according to their symmetry so that the resultant vibrational hamiltonian matrix is divided into symmetry blocks, each of which may be treated separately. Therefore, Eq. (7) holds in each symmetry block. It is readily seen that the wave functions $|v\rangle$ also form an orthonormal set.

Vibration-Rotation Energy Levels. The rotational energy levels in a given vibrational state v are given as

$$E_v(J) = B_v[J(J+1)-l_2^2]-D_v[J(J+1)-l_2^2]^2 \tag{8}$$

Both $\mathbf{H}_{\text{rot}}$ and $\mathbf{H}_{\text{Cor}}$ must be considered to obtain the rotational constants B_v. The contribution from $\mathbf{H}_{\text{rot}}$ is simpler to evaluate, and the procedure is essentially similar to the evaluation of B_v in diatomic molecules. By applying the first order perturbation treatment, the contribution from $\mathbf{H}_{\text{rot}}$ to $E_v(J)$ is given as

$$\begin{aligned} E_v(J)^r &= \langle v,J|\mathbf{H}_{\text{rot}}|v,J\rangle \\ &= B_e[J(J+1)-l_2^2]\sum_{k=0} R_k\langle v|q_1^k|v\rangle, \end{aligned} \tag{9}$$

which is further reduced to

$$\begin{aligned} E_v(J)^r &= B_e[J(J+1)-l_2^2]\sum_{k=0}\sum_n\sum_{n'} a_{vn}a_{vn'}R_k\langle n|q_1^k|n'\rangle \\ &= B_e[J(J+1)-l_2^2] \\ &\quad\times[1+\sum_{k=1}\sum_n\sum_{n'} a_{vn}a_{vn'}R_k\langle n|q_1^k|n'\rangle]. \end{aligned} \tag{10}$$

TABLE 1. NON-VANISHING MATRIX ELEMENTS FOR J_+, J_-, j_+, AND j_-

(a) J_+ and J_-

$$\langle J, l_2|J_+|J, l_2+1\rangle = \langle J, l_2+1|J_-|J, l_2\rangle = [J(J+1)-l_2(l_2+1)]^{1/2}$$

$$\langle J, l_2|J_-|J, l_2-1\rangle = \langle J, l_2-1|J_+|J, l_2\rangle = [J(J+1)-l_2(l_2-1)]^{1/2}$$

(b) j_+ and j_-

$\langle n_2, l_2, n_3|j_+|n_2', l_2', n_3'\rangle = \langle n_2', l_2', n_3'|j_-|n_2, l_2, n_3\rangle$

	n_2'	l_2'	n_3'	Matrix element
j_+	n_2-1	l_2-1	n_3+1	$\Omega_{23}[(n_2+l_2)(n_3+1)]^{1/2}$
	n_2+1	l_2-1	n_3-1	$\Omega_{23}[(n_2-l_2+2)n_3]^{1/2}$
	n_2-1	l_2-1	n_3-1	$\Phi_{23}[(n_2+l_2)n_3]^{1/2}$
	n_2+1	l_2-1	n_3+1	$\Phi_{23}[(n_2-l_2+2)(n_3+1)]^{1/2}$
j_-	n_2+1	l_2+1	n_3-1	$\Omega_{23}[(n_2+l_2+2)n_3]^{1/2}$
	n_2-1	l_2+1	n_3+1	$\Omega_{23}[(n_2-l_2)(n_3+1)]^{1/2}$
	n_2+1	l_2+1	n_3+1	$\Phi_{23}[(n_2+l_2+2)(n_3+1)]^{1/2}$
	n_2-1	l_2+1	n_3-1	$\Phi_{23}[(n_2-l_2)n_3]^{1/2}$

$\Omega_{23}=(1/2)[(\omega_2/\omega_3)^{1/2}+(\omega_3/\omega_2)^{1/2}]$
$\Phi_{23}=[(\omega_2/\omega_3)^{1/2}-(\omega_3/\omega_2)^{1/2}]$

R_k, a_{vn}, and the matrix element $\langle n|q_1^k|n'\rangle$ are all known. The contribution from $\mathbf{H}_{\text{Cor}}$ to the rotational energy is more complex. Obviously, the diagonal matrix element $\langle v, J|\mathbf{H}_{\text{Cor}}|v, J\rangle$ vanishes, and the second-order contribution must be considered,

$$E_v(J)^C = \sum H_{vv'}{}^{(1)}H_{v'v}{}^{(1)}/(E_v{}^\circ-E_{v'}{}^\circ) \tag{11}$$

$\mathbf{H}_{\text{Cor}}$ may be expressed in more convenient form by using ladder operators $J_\pm=J_x\pm iJ_y$ and $j_\pm=j_y\pm ij_x$,

$$\mathbf{H}_{\text{Cor}} = -B_e(j_+J_-+j_-J_+)\sum_{k=0} R_kq_1^k. \tag{12}$$

The relevant non-vanishing matrix elements are listed in Table 1. Again, $|v\rangle$ and $|v'\rangle$ may be expressed in terms of the harmonic oscillator wave functions, $|v\rangle=\sum_n a_{vn}|n\rangle$ and $|v'\rangle=\sum_m a_{v'm}|m\rangle$. As expected from the nature of Coriolis force, $H_{vv'}$ vanishes unless the direct product of v and v' contains the π_g representation to which the rotations around the x- and y- axes (R_x, R_y) belong. For example, if v belongs to the $\sigma_g{}^+$ species, v' should be the π_g state, and if v belongs to the π_u state, v' should be either in the $\sigma_u{}^+$ or Δ_u state. $H_{vv'}{}^{(1)}$ is given as

$$\begin{aligned} H_{vv'}{}^{(1)} &= \sum_n\sum_m a_{vn}a_{v'm}\langle n,J|\mathbf{H}_{\text{Cor}}|m,J\rangle \\ &= -B_e[J(J+1)-l_2(l_2-1)]^{1/2}\sum_n\sum_m a_{vn}a_{v'm}\langle n|j_+|m\rangle \\ &\quad -B_e[J(J+1)-l_2(l_2+1)]^{1/2}\sum_n\sum_m a_{vn}a_{v'm}\langle n|j_-|m\rangle. \end{aligned} \tag{13}$$

It is readily seen from Table 1 that $H_{vv'}{}^{(1)}=H_{v'v}{}^{(1)}$ holds and that either $\langle n|j_+|m\rangle$ or $\langle n|j_-|m\rangle$ vanishes.[9] In the latter case, the leading term of $E_v(J)^C$ is given as

$$\begin{aligned} E_v(J)^C &= B_e^2[J(J+1)-l_2(l_2-1)] \\ &\quad\times\sum_{v'}[\sum_n\sum_m a_{vn}a_{v'm}\langle n|j_+|m\rangle]^2/(E_v{}^\circ-E_{v'}{}^\circ)] \end{aligned} \tag{14}$$

The final expression for B_v is, therefore,

$$\begin{aligned} B_v &= B_e\sum_{k=0}[R_k\sum_n\sum_m a_{vn}a_{vn'}\langle n|q_1^k|n'\rangle \\ &\quad +B_eR_k\sum_{v'}\{\sum_n\sum_m a_{vn}a_{v'm}\langle n|q_1^k\cdot j_+|m\rangle\}^2/(E_v{}^\circ-E_{v'}{}^\circ)]. \end{aligned} \tag{15}$$

The higher-order term in $\mathbf{H}_{\text{Cor}}$ is included in Eq. (15). The wave functions designated with n and n' belong to the same symmetry species, while those with n and m do not. The last integral Eq. (15) may be rewritten as $\langle n|q_1^k\cdot j_+|m\rangle = \langle n_2, l_2, n_3|j_+|m_2, l_2', m_3\rangle\cdot\langle n_1|q_1^k|m_1\rangle$, since j_+ (or j_-) does not involve q_1. When the σ_g^+ or σ_u^+ state $(l_2=0)$ is considered, the Coriolis contributions from the $l_2=-1$ states as well as those from the $l_2=+1$ states must be considered, and this doubles the value given in Eq. (15). Since $E_v(J)^C$ is derived by the ordinary second-order perturbation method, it breaks down for a case of accidental degeneracy in which a (v,J) level locates close to another (v', J') level with proper symmetry. Such a case must be handled separately.

l-*Type Doubling in* XY_2. So far it is implicitly assumed that the levels with the positive and negative l_2 values have identical energy. This holds for rotationless case. There is also no vibration-rotation hamiltonian which directly connects, for example, the 01^10 and $01^{-1}0$ states. However, these levels couple with each other through the third states (001 or 02^01 in the above example) by $\mathbf{H}_{\mathrm{Cor}}$. For illustration, the 01^10, 001, and $01^{-1}0$ levels are chosen and the vibration-rotation hamiltonian matrix for a given J is expressed,

$$\begin{array}{l} \phi(01^1\,0,J) \\ \phi(00\;\;1,J) \\ \phi(01^{-1}0,J) \end{array} \begin{bmatrix} E_{vJ}{}^\circ & a & 0 \\ a & E_{v'J}{}^\circ & a \\ 0 & a & E_{vJ}{}^\circ \end{bmatrix}$$

with $a=[J(J+1)]^{1/2}\langle 1^10|j_+|01\rangle=[J(J+1)]^{1/2}\langle 01|j_-|1^{-1}0\rangle=\sqrt{2}\,\Omega_{23}[J(J+1)]^{1/2}$. By using the linear combinations ϕ_c and ϕ_d given below, the matrix is reduced to

$$\begin{array}{l} \phi_c=(1/\sqrt{2})[\phi(01^10,J)+\phi(01^{-1}0,J)] \\ \qquad\phi(001,J) \\ \phi_d=(1/\sqrt{2})[\phi(01^10,J)-\phi(01^{-1}0,J)] \end{array} \begin{bmatrix} E_{vJ}{}^\circ & \sqrt{2}a & 0 \\ \sqrt{2}a & E_{v'J}{}^\circ & 0 \\ 0 & 0 & E_{vJ}{}^\circ \end{bmatrix}$$

This indicates that in calculating the rotational constants of the c and 001 levels, the contributions from $H_{vv}{}^{(2)}$ must be doubled, while the d state is free from Coriolis type interaction. This causes the well-known l-type doubling: A given J level of the 010 state splits into two sub-levels with slightly different energies. Since ν_3 is larger than ν_2, the rotational constant of the c sub-level is expected to be smaller than that of the d sub-level. It must be noted, however, the Eq. (15) still holds for evaluating the average rotational constant of the c and d levels. In the present calculation this average rotational constant is usually computed, and calculation of the l-type doubling constants is installed as option.

Higher Order Force Constants. The present method is not limited to the treatment of the general quartic force field, and any higher order terms may be included without disturbing the general procedure. This is an advantage of the direct diagonalization method over the contact transformation approach, since the latter requires at least the twice transformed hamiltonians to go beyond the quartic force field. It has already been pointed out[10,11] that some third-order parameters λ_1, λ_2, λ_3, and δ, which appear in Fermi resonance off-diagonal matrix elements are necessary to elucidate the vibration and vibration-rotation levels of most linear triatomic molecules, particularily those in CO_2. In the present treatment this is equivalent to including the quintic force constants k_{11112}, k_{12222}, and k_{12233}, and this has been done very easily.

Computational Methods

Most of numerical computations have been carried out on a MELCOM 7700 system in Educational Computer Centre in the University of Tokyo. A HITAC 8800/8700 system in Computer Centre in the University of Tokyo has also been used for eigenvalue problems of large matrices. Programs written in FORTRAN IV are compatible in both systems: only the sizes of a certain arrays are changed.

Generation of Basis Functions and Matrix Elements. In actual calculations, the harmonic oscillator basis functions are specified by a set of four integers corresponding to n_1, n_2, l_2, and n_3 ($l_2=n_2$, $n_2-2, \ldots,$ 1 or 0). A desired number of the basis functions are systematically generated with the condition of $n_1+n_2+n_3<n$, where n is a suitable interger. The following simple rule has been applied to identify the symmetry species of a given basis function:

(i) n_2+n_3 (even, odd) $\leftrightarrow$ (g, u)

(ii) l_2 $(0, 1, 2, 3, \cdots)$ $\leftrightarrow$ $(\sigma^+, \pi, \delta, \phi, \cdots)$

The matrix elements of the vibrational hamiltonian are generated by using the subroutines OPERQ and OPERR. The former was described in I, and the latter is written to evaluate the radial part matrix elements $\langle n,l|r^m|n',l'\rangle$. The diagonal part of vibrational hamiltonian matrix has a familiar form of

$$\begin{aligned}\langle n|\mathbf{H}_{\mathrm{vib}}|n\rangle &= \sum_i \omega_i(n_i+d_i/2) \\ &\quad+\sum_{i,j} x^*{}_{ij}(n_i+d_i/2)(n_j+d_j/2)+x^*{}_{l_2l_2}l_2{}^2 \end{aligned}\tag{16}$$

where $d_1=d_3=1$ and $d_2=2$. The asterisks indicate that they differ from the x_{ij}'s defined by Nielsen,[2] and if the general quartic force field is employed, $x^*{}_{ii}=(3/2)k_{iiii}$, $x^*{}_{l_2l_2}=k_{2222}/2$, and $x_{ij}{}^*=k_{iijj}$ with an exception of $x^*{}_{23}=k_{2233}+B_e[(\omega_2/\omega_3)+(\omega_3/\omega_2)]$. The last term in $x^*{}_{23}$ arises from $\mathbf{H}_{\mathrm{vib}}{}'$. The contributions from $\mathbf{H}_{\mathrm{vib}}{}'$ are also considered for the evaluation of off-diagonal matrix elements which involve $\langle n_2, l_2, n_3|n_2\pm2, l_2, n_3\rangle$, $\langle n_2, l_2, n_3|n_2, l_2, n_3\pm2\rangle$, $\langle n_2, l_2, n_3|n_2\pm2, l_2, n_3\pm2\rangle$, and $\langle n_2, l_2, n_3|n_2\pm2, l_2, n_3\mp2\rangle$. The resultant vibrational hamiltonian matrix is divided into symmetry blocks, which can be treated separately. The correction of the zero-point energy, however, should be done to each level.

Just as in the case of diatomic molecules, the vibrational hamiltonian matrix is obtained as the form of matrix sum:

$$\mathbf{H}_{\mathrm{vib}}=\sum k^{(i)}\mathbf{A}^{(i)}\tag{17}$$

The harmonic and anharmonic force constants are numbered consecutively; $i=1,2\ldots,f$. $\mathbf{A}^{(1)}$ represents the contribution of the i-th force constant to the vibrational hamiltonian matrix, the elements of which may be evaluated once for all if the set of basis functions has been determined. Non-vanishing matrix elements $a_{ij}^{(k)}$ may be stored in magnetic tapes or discs. The contribution from the $\mathbf{H}_{\mathrm{vib}}{}'$ term may also be included in Eq. (17) by formally setting $k^{(0)}\equiv1$. The elements of $\mathbf{A}^{(0)}$ are easily obtained from Eq. (3). Also time-consuming is the process to calculate the second term in Eq. (15). The computing time is considerably abridged, however, by storing the non-vanishing elements of $\langle n|q_1^k\cdot j_+|m\rangle$ and $\langle n|q_1^k\cdot j_-|m\rangle$ for $k=0$ to 4.

Eigenvalue Problems. In the present calculations it is necessary to solve real $n\times n$ symmetric matrices, where n ranges from 30 to 200. Usually 30 lowest eigenvalues and eigenvectors are obtained for each symmetry block. The Givens-Householder method for symmetric matrices[12] is satisfactory in most cases. In HITAC 8700/8800 system it takes eight seconds to solve 100×100 matrix (30 seconds for a 200×200 matrix). Double precision arithmetics are used to retain the desired accuracy.

As seen from Eq. (2), the present calculation is primarily based on the force constants in dimensionless normal coordinates. However, the force constants in curvilinear internal coordinates are more convenient for the systematic handling of various isotopic molecules, since the latters are independent to isotopic substitutions. Therefore, a subprogram is implemented which handles the transformation from the internal to the normal coordinate systems. Either the general valence force constants or the force constants in dimensionless normal coordinates are allowed as input.

Results and Discussion

Application to CO_2 and CS_2. The present method has been applied to two XY_2 type linear molecules, *i.e.* CO_2 and CS_2. They are probably only molecules of this type, of which the general quartic force fields have been studied extensively.[10,13–16] The force constants of CO_2 and CS_2 used in the present calculations have been taken from Refs. 10 and 16, respectively, they are listed in Table 2. It is clearly seen in Table 2 that the both sets of force constants show markedly similar trend. In terms of the Nielsen-Amat's perturbation scheme,[2,4] however, these molecules differ considerably in Fermi resonance of the $\nu_1 \simeq 2\nu_2$ type. It is known that the unperturbed ν_1° and $2\nu_2^\circ$ levels are almost coincident in CO_2, while they are apart by about 130 cm^{-1} in CS_2.[16] It is, therefore, interesting to see how they differ in the numerical diagonalization method.

Table 2. General quartic force constants of CO_2 and CS_2

	General valence[a)] representation			Dimensionless normal representation (cm^{-1})	
	CO_2[b)]	CS_2[c)]		CO_2	CS_2
K_{11}(md/Å)	8.0112	3.9383	ω_1	1354.31	672.57
K_{13}(md/Å)	1.2613	0.6441	ω_2	672.85	398.21
K_{22}(md·Å/rad^2)	0.3925	0.2846	ω_3	2396.32	1558.85
K_{111}(md/Å^2)	−18.989	−7.478	k_{111}	−45.78	−18.39
K_{113}(md/Å^2)	−1.955	−0.842	k_{122}	74.72	43.15
K_{122}(md/rad^2)	−0.609	−0.369	k_{133}	−249.14	−130.30
K_{1111}(md/Å^3)	26.251	8.697	k_{1111}	1.92	0.59
K_{1113}(md/Å^3)	3.676	0.643	k_{1122}	−11.15	−5.39
K_{1133}(md/Å^3)	3.022	0.479	k_{1133}	19.52	8.74
K_{1122}(md/Å·rad^2)	0.504	0.111	k_{2222}	2.45	1.70
K_{1223}(md/Å·rad^2)	1.870	0.461	k_{2233}	−27.56	−15.26
K_{2222}(md·Å/rad^4)	0.046	0.044	k_{3333}	6.30	3.83

a) $R_1 = \Delta r_{CX}$, $R_2 = \Delta\phi$, and $R_3 = \Delta r_{CX'}$. b) Set (iv) of Table 2 in Ref. 10. c) Set (i) of Table 2 in Ref. 1.

Truncation Effect. Presicion of the present calculations is determined, at least in part, from the number of basis functions taken for a symmetry block: the more basis functions are used, the more accurate results are usually expected. In the treatment of diatomic CO and HCl in I, 20 to 30 harmonic oscillator wave functions must be taken as basis to elucidate the vibrational levels up to $v=6$. As mentioned earlier, a set of three quantum numbers must be considered in XY_2,[17] and the sum of these quantum numbers $n=\sum n_s$ may be regarded as the measure corresponding to n in diatomic molecules. The value of n is in the ranges of 13—14 and 18—20 in the respective cases of 100 and 200 basis functions, the latter may be a practical limit in the present treatment. Therefore, the truncation effect of the matrix sizes has first been examined by varying the number of basis functions from 30 to 200 for each of eight symmetry blocks ($l_2=0$, 1, 2, 3). Parts of the results are given in Tables 3—6. In each table the results for the Σ_g^+, Σ_u^+, and Π_g blocks are given, the latter two blocks are chosen because relatively large number of corresponding experimental data is available. The calculated values for the 200×200 problem are given in the first column in each table and the differences from the 200×200 case are entered in the remaining columns. The entry of zero or small numbers indicates that the convergence is completed at that stage. For the lowest two or three levels 100 basis functions are sufficient, but 200 basis functions are needed to account for the lowest six to ten levels in a given symmetry block. The convergence in CS_2 is somewhat faster than that in CO_2, which is in accordance with our results in diatomic molecules (I). The off-diagonal matrix elements of CS_2 are relatively smaller than those of CO_2.

In order to calculate the rotational constants, the terms up to $k=4$ in Eqs. (4) and (5) have been retained just as in the case of diatomic molecules. Fewer terms may be used, since the values for $\gamma_1=(2B_e/\omega_1)$, which represent 'order of smallness', are 5.8×10^{-4} and 3.2×10^{-4} for CO_2 and CS_2, respectively, which are considerably smaller than the corresponding values of $(2B_e/\omega_e)$ in CO and HCl (1.7×10^{-3} and 7.0×10^{-3}) we have adopted the following values: $B_e=0.391600$ cm^{-1} for CO_2 and $B_e=0.108859$ cm^{-1} for CS_2.

Comparison with Contact Transformation Method. One of the primary purposes of the present study is to compare the results of the numerical diagonalization method with those in Refs. 10 and 18 which utilized the 2nd-order perturbation treatment with 3rd-order Fermi resonance corrections. The differences between the two calculated quantities are given in the columns designated as δ_{cal} in Tables 3—6. The differences are much larger than expected particularly for the higher levels of CO_2 which are involved in strong Fermi resonance. The general quartic force field is used in the both methods, the only difference is the inclusion of the third-order parameters λ's and δ in the treatment of Fermi resonances. These third-order parameters are rather complicated functions of force constants and geometrical parameters.[18] However, the contributions of force constants quadratic through quartic terms are considered to infinite order of approximation in the numerical diagonalization method, and the only extra terms which have to be considered are three quintic force constants, k_{11122}, k_{12222}, and k_{12233}. These quintic force constants may be evaluated from the values of the three λ's as well as those of the lower order force constants, but this requires the rather lengthy calculations. Fortunately, the sextic potential function of CO_2 has been explored by Cihla and Chedin[19] who reported the values of 0.665, −1.052, and 5.4 cm^{-1} respectively for k_{11122}, k_{12222}, and

Table 3. Calculated vibrational levels of CO_2 and their variations with the number of basis functions[a,b)]

Species	Level			$\nu_{calcd}(200)$	$\delta(150)$	$\delta(100)$	$\delta(50)$	$\delta(30)$	δ_{calcd}[c)]	δ'_{calcd}
	n_1	n_2	n_3							
Σ_g^+ ($l_2=0$)	0	2	0	1285.36	0	1	2	14	24	−44
	1	0	0	1386.84	0	1	3	19	117	95
Σ_u^+ ($l_2=0$)	0	0	1	2349.01	0	0	3	6	16	−179
	0	2	1	3615.49	1	7	24	162	−268	−207
	1	0	1	3708.80	1	11	38	250	582	−150
	0	4	1	4855.06	1	14	189	1505	−148	−293
	1	2	1	4977.27	7	34	637	2423	56	−242
	2	0	1	5084.90	2	31	378	2211	1452	161
	0	6	1	6071.02	4	38	927	2312	467	−630
	1	4	1	6228.21	28	136	2396	4131	−6	−313
	2	2	1	6337.93	41	197	3017	4982	1033	−312
	3	0	1	6479.10	10	119	1356	3736	2375	744
	0	0	3	6978.88	41	241	3684	4112	−616	−2276
Π_g ($l_2=1$)	0	1	1	3002.08	0	1	5	68	224	−84
	0	3	1	4247.76	0	7	24	136	26	−99
	1	1	1	4380.96	0	8	40	209	975	154
	0	5	1	5472.44	2	15	179	1593	—	—
	1	3	1	5625.28	7	39	539	2423	—	—
	2	1	1	5771.94	3	32	377	2362	—	—
	0	7	1	6676.55	5	37	1159	2554	1141	−722
	1	5	1	6854.70	34	134	2422	4294	956	219
	2	3	1	7004.07	46	201	3021	4932	2045	482
	3	1	1	7176.26	16	118	1556	4188	2765	1364
	0	1	3	7599.06	54	227	4146	4708	423	−2155

a) $\nu_{calcd}(n)$ in cm^{-1}: obtained by solving $n\times n$ secular equation. b) $\delta(n)=[\nu_{calcd}(n)-\nu_{calcd}(200)]\times 100$. c) $\delta_{calcd}=\nu_{calcd}-\nu_{calcd}(200)$, where ν_{calcd} was obtained by an ordinary perturbation method (Ref. 10 for CO_2 and Ref. 18 for CS_2).

Table 4. Calculated vibrational levels of CS_2 and their variations with the number of basis functions[a)]

Species	Level			$\nu_{calcd}(200)$	$\delta(150)$	$\delta(100)$	$\delta(50)$	$\delta(30)$	δ_{calcd}	δ'_{calcd}
	n_1	n_2	n_3							
Σ_g^+ ($l_2=0$)	1	0	0	657.90	0	1	2	9	9	−22
	0	2	0	800.97	0	0	0	9	81	55
	2	0	0	1313.64	0	1	26	330	−1	−62
	1	2	0	1443.58	0	1	9	235	339	62
	0	4	0	1617.79	0	1	8	198	197	153
Σ_u^+ ($l_2=0$)	0	0	1	1535.34	0	1	2	32	8	−87
	1	0	1	2186.65	0	4	14	708	−113	−201
	0	2	1	2321.87	0	2	5	88	265	58
	2	0	1	2835.98	2	17	281	1107	−275	−351
	1	2	1	2958.17	0	8	103	818	356	−13
	0	4	1	3124.11	0	4	32	697	586	364
	3	0	1	3483.17	14	48	1478	2291	−475	−539
	2	2	1	3592.81	9	30	1167	1654	420	−115
	1	4	1	3746.69	7	24	901	1260	1507	409
	0	5	1	3938.55	4	17	645	1451	962	829
Π_g ($l_2=1$)	0	1	1	1924.07	0	0	2	4	96	−43
	1	1	1	2567.12	0	4	12	96	34	−144
	0	3	1	2719.31	0	2	8	435	401	190
	2	1	1	3208.05	2	10	203	1108	−57	−279
	1	3	1	3348.55	1	8	103	934	661	172
	0	5	1	3528.15	1	7	40	829	754	576

a) See Footnotes to Table 3.

TABLE 5. CALCULATED ROTATIONAL CONSTANTS OF CO_2 AND THEIR VARIATIONS WITH THE NUMBER OF BASIS FUNCTIONS[a,b)]

Species	Level			$B(200)$	$\delta(150)$	$\delta(100)$	$\delta(50)$	$\delta(30)$	δ_{calcd}[c)]	δ'_{calcd}
	n_1	n_2	n_3							
Σ_g^+ $(l_2=0)$	0	2	0	3.19	0	1	2	24	59	13
	1	0	0	−0.66	0	0	1	22	−76	−65
Σ_u^+ $(l_2=0)$	0	0	1	−30.22	0	0	3	9	37	49
	0	2	1	−25.98	0	3	37	191	137	29
	1	0	1	−32.44	1	3	41	181	−98	115
	0	4	1	−17.70	3	9	256	438	285	291
	1	2	1	−37.09	6	24	486	612	6	−401
	2	0	1	−28.79	2	17	240	248	−189	15
	0	6	1	−8.25	5	50	501	1599	521	300
	1	4	1	−31.80	24	100	733	2413	377	788
	2	2	1	−41.71	17	103	639	1963	−444	267
	3	0	1	−23.03	13	64	273	2377	−131	−66
	0	0	3	−88.84	20	205	855	1746	386	848
Π_g $(l_2=1)$	0	1	1	−23.56	0	0	12	17	36	−133
	0	3	1	−19.36	0	5	46	192	64	227
	1	1	1	−25.40	1	4	71	225	−139	130
	0	5	1	−11.70	3	20	124	712	—	—
	1	3	1	−27.82	8	47	490	949	—	—
	2	1	1	−23.33	6	35	387	1068	—	—
	0	7	1	−2.36	9	77	660	2797	621	251
	1	5	1	−40.37	574	684	2701	4604	−1550	135
	2	3	1	−31.35	45	165	1105	3190	−271	574
	3	1	1	−16.70	40	268	441	7705	−266	−236
	0	1	3	−83.45	52	259	1737	3441	−115	855

a) $B(n)=[B_v^{\text{calcd}}(n)-B_{000}^{\text{calcd}}(n)]\times 10^4\ \text{cm}^{-1}$, where $B_v^{\text{calcd}}(n)$ is obtained from the eigen vectors of the $n\times n$ problem. b) $\delta(n)=[B(200)-B(n)]\times 100$; Note that the definition is reversed to make most of $\delta(n)$ positive. c) $\delta_{\text{calcd}}=B(200)-B_{\text{calcd}}$, where B_{calcd} is obtained by an ordinary perturbation method (Ref. 10 for CO_2 and Ref. 18 for CS_2).

TABLE 6. CALCULATED ROTATIONAL CONSTANTS OF CS_2 AND THEIR VARIATIONS WITH THE NUMBER OF BASIS FUNCTIONS[a)]

Species	Level			$B(200)$	$\delta(150)$	$\delta(100)$	$\delta(50)$	$\delta(30)$	δ_{calcd}	δ'_{calcd}
	n_1	n_2	n_3							
Σ_g^+ $(l_2=0)$	1	0	0	−1.62	0	0	0	6	−3	0
	0	2	0	3.79	0	0	0	0	9	1
	2	0	0	−3.11	0	1	15	15	−6	−4
	1	2	0	2.65	0	0	2	8	6	−6
	0	4	0	7.18	0	0	1	7	37	2
Σ_u^+ $(l_2=0)$	0	0	1	−7.07	0	0	0	13	6	22
	1	0	1	−8.63	0	0	7	41	6	31
	0	2	1	−3.53	0	0	3	9	−7	34
	2	0	1	−10.05	1	3	89	85	5	34
	1	2	1	−4.68	0	2	38	70	−13	39
	0	4	1	−0.36	0	1	18	126	2	47
	3	0	1	−11.26	3	12	105	136	9	36
	2	2	1	−5.76	2	10	84	122	−15	41
	1	4	1	−1.27	1	9	69	302	−2	53
	0	6	1	2.63	1	11	53	447	22	60
Π_g $(l_2=1)$	0	1	1	−5.07	0	0	1	1	−5	26
	1	1	1	−6.29	0	1	7	42	−10	26
	0	3	1	−1.81	0	1	6	60	−7	41
	2	1	1	−7.32	0	4	82	114	−23	22
	1	3	1	−2.79	0	5	41	164	−14	47
	0	5	1	1.25	0	5	25	311	11	55

a) See Footnotes of Table 5.

k_{12233}. Another calculation has been proceeded by including the matrix elements originated from these three quintic force constants. In the last columns designated as δ_{cal}' in Tables 3 and 5, the corresponding differences are entered. Significant changes (most of them are improvements) are observed upon the inclusion of the three quintic force constants.

As mentioned earlier, the numerical diagonalization method has an advantage that in that process anharmonic resonances are automatically taken care of. As shown in I, however, this method is not free from the truncation effects of the potential functions. This effect is magnified in the special case of CO_2 in which an ordinary separation of higher-order force constants from the general quartic force constants does not work properly. Since a number of smaller anharmonic resonances are considered in the present process, the discrepancies in calculated vibrational levels and rotational constants are still expected, and the fit to the experimental data may be improved by slightly adjusting the 15 force constants including the three quintic force constants.

The inclusion of other quintic as well as sextic force constants has also been tested, the changes of calculated vibrational levels and rotational constants are far smaller than those induced by the three quintic force constants above, but they are not negligible. This encourages us to proceed the least-squares fit of higher-order force constants to experimental data. This will be our project in near future.

l-Type Doubling Constants. The *l*-type doubling constants for a given pair of the $l_2=\pm 1$ states may be evaluated through the procedure given earlier. In harmonic approximation the separation of the levels is expressed as

$$\Delta\nu = q^{e}_{\text{harm}}(v_2+1)J(J+1), \tag{18}$$

where

$$q^{e}_{\text{harm}} = (B_e{}^2/\omega_2)[1+4\omega_2{}^2/(\omega_3{}^2-\omega_2{}^2)]. \tag{19}$$

From the harmonic frequencies listed in Table 1 as well as the equilibrium rotational constants, the following values are obtained: q^{e}_{harm} $(CO_2)=5.27\times 10^{-4}\,\text{cm}^{-1}$ and q^{e}_{harm} $(CS_2)=7.63\times 10^{-5}\,\text{cm}^{-1}$. Deviations from the above values may be regarded as anharmonic effects. For a few vibrational levels of CO_2 and CS_2 the *l*-type doubling constants have been measured accurately[20-22]. In Table 7 the observed *l*-type doubling constants are listed along with the corresponding calculated values. The isotopically consistent set of force constants is used to evaluate the constants of $^{13}CS_2$ species. The agreements between the calculated and observed values are quite satisfactory.

Vibrational Wave Functions and Their Application to Intensity Problem. Another useful feature in the numerical diagonalization method is its readiness to obtain an orthonormal set of perturbed vibrational wave functions, $|v\rangle=\sum_n a_{vn}|n\rangle$. The six lowest levels in the Σ_u^+-block are chosen as examples for both CO_2 and CS_2, and the coefficients which make major contributions to the above levels are listed in Table 8. The mixings of the basis harmonic oscillator wave functions are so complete in CO_2, it is senseless to label a certain level in terms of a single basis function. The mixings are not so strong in CS_2 for which the labeling is much simpler. There also exists a considerable mixing between the wave functions $|n_1, n_2, l_2, n_3\rangle$ and $|n_1\pm 1, n_2, l_2, n_3\rangle$ probably through the cubic force constant k_{111}.

The usefulness of the coefficient a_{vn} may be demonstrated in its application to the calculation of the transition moment from v to v' states, $R_v{}^{v'}$, the square of which is related to the total integrated intensity of the band:

$$R_v{}^{v'} = \langle v'|M|v\rangle, \tag{20}$$

where M is the dipole moment function $M=M(q_1, q_2, q_3)$, which may be expressed as the sum of the $M_{/\!/}$ and $M_{\perp}$ components for linear symmetrical XY_2 molecule. The former is parallel to the molecular axis (z-axis) and has the same symmetry property as $T_z(\sigma_u^+)$, whereas the latter is perpendicular to the z-axis and has the Π_u symmetry to which T_x and T_y belong. The both components are expanded as

$$M_{/\!/} = \mu_3 q_3 + \mu_{13} q_1 q_3 + \sum_{i=1}^{3} \mu_{ii3} q_i{}^2 q_3 + \cdots \tag{21}$$

and

$$M_{\perp} = \mu_2 q_2 + \mu_{12} q_1 q_2 + \sum_{i=1}^{3} \mu_{ii2} q_i{}^2 q_2 + \cdots \tag{22}$$

For simplicity q_2 is used instead of r_2. The zeroth order term vanishes because of the molecular symmetry ($D_{\infty h}$). If $v\times v' \ni \sigma_u^+$, Eq. (20) is rewritten as

$$\begin{aligned} R_v{}^{v'} = \langle v'|M|v\rangle &= \mu_3 \sum_n\sum_m a_{vn}a_{v'm}\langle n|q_3|m\rangle \\ &+ \mu_{13}\sum_n\sum_m a_{vn}a_{v'm}\langle n|q_1q_3|m\rangle + \cdots \end{aligned} \tag{23}$$

Similar expression may be written for the case of $v\times v' \ni \Pi_u$. In Eq. (23), the first term vanishes unless $m_1=n_1$, $m_2=n_2$ $(l'_2=l_2)$ and $m_3=n_3\pm 1$, while the second term vanishes unless $m_1=n_1\pm 1$, $m_2=n_2(l'_2=l_2)$, and $m_3=n_3\pm 1$. Such requirements considerably simplify the practical calculations.

TABLE 7. OBSERVED AND CALCULATED *l*-TYPE DOUBLING CONSTANTS FOR CO_2 AND CS_2

i) $^{12}C^{16}O_2$			ii) $^{12}C^{32}S_2$			iii) $^{13}C^{32}S_2$		
Level	q_{obsd}[a)]	q_{calcd}	Level	q_{obsd}[b)]	q_{calcd}	Level	q_{obsd}[c)]	q_{calcd}
$0\ 1^1\ 0$	6.10	6.16	$0\ 1^1\ 0$	7.82	7.65	$0\ 1^1\ 0$	8.52	7.92
$1\ 1^1\ 0$	9.64	9.61	$1\ 1^1\ 0$	9.05	8.63	$0\ 1^1\ 1$	8.68	7.83
$0\ 3^1\ 0$	9.19	9.12	$0\ 3^1\ 1$	14.65	14.38	$1\ 1^1\ 1$	9.75	9.05
$1\ 1^1\ 1$	8.59	9.39	$1\ 3^1\ 1$	15.78	15.57	$0\ 3^1\ 1$	15.19	14.59
						$2\ 1^1\ 1$	11.60	10.57

a) Ref. 20; unit $10^{-4}\,\text{cm}^{-1}$. b) Ref. 21; unit $10^{-5}\,\text{cm}^{-1}$. c) Ref. 22; unit $10^{-5}\,\text{cm}^{-1}$.

Table 8. Some examples of eigenvector coefficients a_{vn}'s in CO_2 and CS_2[a]

Level	CO_2 $\sum_u^+$-block				$\sum a^2_{vn}$
2349.01	0.980 (001)	0.188 (101)			0.996
3615.49	0.724 (021)	0.639 (101)	0.201 (201)		0.973
3708.80	0.675 (021)	0.671*(101)	0.227*(201)		0.957
4855.06	0.711 (121)	0.565 (041)	0.333 (201)		0.936
4977.27	0.699 (201)	0.553*(041)	0.335 (301)	0.256*(101)	0.972
5084.90	0.648 (121)	0.601*(041)	0.330*(201)		0.890
Level	**CS_2 $\sum_u^+$-block**				**$\sum a^2_{vn}$**
1535.34	0.980 (001)	0.184 (101)			0.994
2186.65	0.912 (101)	0.282 (201)	0.211 (021)		0.956
2321.87	0.969 (021)	0.190*(101)			0.975
2835.98	0.821 (201)	0.359 (301)	0.305 (121)		0.896
2958.17	0.861 (121)	0.347 (041)	0.254*(201)		0.895
3124.11	0.929 (041)	0.332*(121)			0.973

a) Asterisks indicate negative coefficients.

It is emphasized here that Eq. (23) is valid for any transitions satisfying the relation $v \times v' \ni \sigma_u^+$. This contrasts with the expressions derived from the perturbation method[23] or those derived from the contact transformation method as has been applied to the intensity problem of the bent XY_2 molecules.[24] Actually the numerical diagonalization method was used by Foord and Whiffen[25] for the treatment of the dipole moment function of OCS. They obtained the vibrational wave functions by solving a 30×30 vibrational hamiltonian matrix.

Conclusions. In the present paper it has been shown that the direct diagonalization method is applicable to the treatment of vibration and vibration-rotation problem of linear symmetrical XY_2 molecules. This method has a certain merits over the conventional perturbation method: Exact solutions are usually secured if the number of basis functions is taken large enough, the quintic and higher-order force constants are easily accomodated and the method may be extended to handle with the general sextic potential function. A set of orthonormal vibrational wave functions may be obtained regardless of the potential functions employed. Eq. (23) holds whatever potential functions may be used. The obvious demerit of the present method is that it involves the eigenvalue problem for large martices to avoid the truncation effect of the vibrational hamiltonian matrix. In addition, the calculation of vibration-rotation constants is not simple and rather time consuming. However, the rapid progress of existing computers as well as of computational technique has made the above calculations quite manageable, and its application to the determination of more precise force field or to the intensity problem through dipole moment functions seems very promising.

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9) In the preceding example of $v \ni \pi_u$, $\langle v|j_+|v'\rangle = 0$ if $v' \ni \Delta_u$ and $\langle v|j_-|v'\rangle = 0$ if $v' \ni \sigma_u^+$.

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