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Anharmonic Potential Functions and Intrinsic Reaction Coordinates of Polyatomic Molecules

Katsunosuke MACHIDA
Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606
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A general method has been developed to describe the atomic motion along a given intrinsic reaction coordinate (IRC) in the vicinity of the potential minimum of a polyatomic molecule whose anharmonic force constants are known experimentally or theoretically. The components of the position vector of a configuration point on an IRC in the normal coordinate space are expanded as power series of the path length from the origin measured along the IRC. Explicit expressions of the expansion coefficients up to the third order have been given in terms of the normal frequencies and the anharmonic force constants with respect to the normal coordinates. The atomic loci along the IRC are given by transformation from the normal coordinates to the Cartesian displacements. Through application to formaldehyde and water, the method has proved to be useful to check if a given normal coordinate can be connected to any dissociation path on large distortion of the molecule.

The intrinsic reaction coordinate, hereafter abbreviated as IRC, has been introduced by Fukui in 1970 as a concept of fundamental importance in reaction dynamics of polyatomic molecules.[1] An IRC describes how a molecule is distorted when the atomic displacement associated with a chemical reaction proceeds with an infinitesimal rate. Determination of the IRC is an indispensable step in understanding the reaction mechanism. An IRC should coincide with one of the normal coordinates if the potential function which regulates the molecular vibrations around the equilibrium configuration is rigorously harmonic.[1,2] In actual molecules, however, presence of anharmonic terms in the potential leads to deviation of any IRC's from the normal coordinates defined at the potential minimum when the constituent atoms move away from the equilibrium positions. The non-linear relationship between an IRC and the normal coordinates should thus be described uniquely in terms of the anharmonic force constants. The present work has been initiated to search for such a relationship in a general form, and to utilize it to examine the behavior of an IRC near the minimum of an experimentally determined potential function of polyatomic molecules containing anharmonic terms.

Theory

Following the standard perturbation theory, we expand the potential function of a polyatomic molecule as a power series of its normal coordinates in the form

$$V = \frac{1}{2}\sum_i \lambda_i Q^{i2} + \frac{\varepsilon}{6}\sum_{ijk} K_{ijk}Q^iQ^jQ^k + \frac{\varepsilon^2}{24}\sum_{ijkl} K_{ijkl}Q^iQ^jQ^kQ^l + \cdots, \quad (1)$$

where λ_i is the ith frequency parameter related to the normal frequency ω_i in cm^{-1} and the light velocity c by

$$\lambda_i = (2\pi c\omega_i)^2,$$

and ε is an ordering parameter. In analysing spectroscopic data, the higher-order force constants are usually given in the system of the dimensionless normal coordinates. The cubic and quartic constants in this system, k_{ijk} and k_{ijkl}, are transformed to those in Eq. 1 through the relations

$$K_{ijk} = (1+\delta_{ij})(1+\delta_{ik}+\delta_{jk})(h/2\pi)^{3/2}(\lambda_i\lambda_j\lambda_k)^{1/4}k_{ijk} \quad (2)$$

and

$$K_{ijkl} = (1+\delta_{ij})(1+\delta_{ik}+\delta_{jk})(1+\delta_{il}+\delta_{jl}+\delta_{kl}) \times (h/2\pi)^2(\lambda_i\lambda_j\lambda_k\lambda_l)^{1/4}k_{ijkl}, \quad (3)$$

respectively, where h is Planck's constant and δ_{ij} is Kronecker's delta. Differentiating Eq. 1 with respect to Q^i leads to

$$(\partial V/\partial Q^i) = \lambda_i Q^i + \frac{\varepsilon}{2}\sum_{jk} K_{ijk}Q^jQ^k + \frac{\varepsilon^2}{6}\sum_{jkl} K_{ijkl}Q^jQ^kQ^l + \cdots. \quad (4)$$

Whenever the molecule is distorted along an IRC in the vicinity of the potential minimum, any pairs of non-degenerate normal coordinates, Q^i and Q^j, should satisfy the IRC equation[1]

$$dQ^i/(\partial V/\partial Q^i) = dQ^j/(\partial V/\partial Q^j), \quad (5)$$

or

$$(\partial V/\partial Q^i)dQ^j - (\partial V/\partial Q^j)dQ^i = 0. \quad (6)$$

The form of Eq. 5 is the same as that in the case of the mass-weighted Cartesian coordinates[2] because of the orthogonality condition between the two coordinate systems.

Now we suppose that there is an IRC which converges into the normal coordinate Q^i when the molecular configuration approaches that at the potential minimum. In order to specify the position of a configuration point moving on this IRC, we may take the distance from the origin to the point measured along the IRC, s^i, as an independent variable, and represent each element of the position vector in the normal coordinate space as a function of s^i satisfying Eq. 5. In the vicinity of the potential minimum, such a function may be expanded as a power series of s^i in the form

$$Q^j = a^j_i s^i + \frac{\varepsilon}{2}a^j_{it}s^{i2} + \frac{\varepsilon^2}{6}a^j_{iit}s^{i3} + \cdots. \quad (7)$$

Substituting Eq. 7 with $j=i$, j, k, and l into Eq. 4 and multiplying the result by the differential of Eq. 7, we obtain the first term of Eq. 6 as

$$(\partial V/\partial Q^j)dQ^j = [\lambda_i a_i^i a_i^j s^i + \frac{\varepsilon}{2}\{\lambda_i(2a_i^i a_{ii}^j + a_{iii}^i a_i^j) + a_i^j \sum_{kl} K_{ikl} a_i^k a_i^l\} s^{i2} + \frac{\varepsilon^2}{6}\{\lambda_i(3a_i^i a_{iii}^j + 3a_{ii}^i a_{ii}^j + a_{iii}^i a_i^j) + a_{ii}^j \sum_{kl} K_{ikl} a_i^k a_i^l + a_i^j(3\sum_{kl} K_{ikl} a_i^k a_{ii}^l + \sum_{klm} K_{iklm} a_i^k a_i^l a_i^m)\} s^{i3} + \cdots]ds^i. \quad (8)$$

The second term of Eq. 6 can also be expressed by Eq. 8 provided that the superscripts i and j of the a coefficients are interchanged with each other and the subscript i of the force constants λ and K's is replaced by j. Since Eq. 6 holds for any displacements of the nuclei along the IRC under consideration, the coefficient of each power of s^i in the left hand side should vanish separately. The linear term gives the relation

$$(\lambda_i - \lambda_j)a_i^i a_i^j = 0, \quad (9)$$

which implies that

$$a_i^j = 0, \quad (10)$$

when both the conditions $\lambda_i \neq \lambda_j$ and $a_i^i \neq 0$ hold. This property of IRC's has already been pointed out by Fukui *et al.*[2]

Prior to estimation of a_{ii}^j, we shall determine the first two coefficients of the expansion of Q^i in terms of s^i. It follows from the definition of s^i that

$$\sum_k (dQ^k)^2 = (ds^i)^2. \quad (11)$$

Substituting Eqs. 7 and 10 into Eq. 11 and taking the term not including s^i, we have

$$a_i^i = \pm 1, \quad (12)$$

where the plus sign may be adopted without loss of generality. Since the coefficient of the term linear in s^i in Eq. 11 vanishes while a_i^i does not, it should hold that

$$a_{ii}^i = 0. \quad (13)$$

Substituting Eqs. 8, 10, 12, and 13 into Eq. 6, and taking the term quadratic in s^i, we obtain

$$a_{ii}^j = K_{jii}/(2\lambda_i - \lambda_j). \quad (14)$$

The coefficients of the cubic term in the expansions of Q^i and Q^j are derived similarly from Eq. 11 as

$$a_{iii}^i = -\sum_k (a_{ii}^k)^2, \quad (15)$$

and from Eq. 8 as

$$a_{iii}^j = (K_{jiii} + 3\sum_k K_{jik} a_{ii}^k - 3K_{iii} a_{ii}^j)/(3\lambda_i - \lambda_j), \quad (16)$$

respectively. The denominators in Eqs. 14 and 16 indicate that the expansion of Q^j in power series of s^i cannot be accomplished when λ^j is an integral multiple of λ_i. The form of $Q^j(s^i)$ in such a case is given in Appendix.

Once the expansion coefficients in Eq. 7 are determined by using Eqs. 14—16, we can calculate the values of normal coordinates corresponding to any small values of s^i given arbitrarily. The atomic displacements along with the increase of s^i can then be traced by converting the normal coordinates into the Cartesians $\boldsymbol{X}$ according to

$$\boldsymbol{X} = \boldsymbol{L}_x \boldsymbol{Q}. \quad (17)$$

Since the same relation as Eq. 17 holds for the derivatives of X's and Q's with respect to s^i, it is also possible to evaluate the components of the principal normal of an IRC by differentiating Eq. 7 at a given point near the potential minimum. Similarly, the curvature of an IRC near the equilibrium is obtained from the second derivatives of Eq. 7.[3]

Application

Let us consider an isolated formaldehyde molecule undergoing a certain distortion which starts in the direction of the ν_6 mode at the equilibrium and proceeds as described by Eq. 7 in the normal coordinate space. The relevant expansion coefficients $a^j{}_{66}$ and $a^j{}_{666}$ are listed in Table 1 for two sets of force constants, Sets I and II, together with the frequency parameters λ_j which are common to the two sets. Set I was obtained previously by the least squares fitting of the observed values of 31 vibrational frequencies of H_2CO, HDCO, and D_2CO and 30 vibration-rotation interaction constants of H_2CO and D_2CO.[4] Set II was the same as Set I except that the cubic interaction constant between the CO stretching and the HCO deformation coordinates, $K_{R\phi\phi}$, was set equal to zero. This constant is given a relatively large absolute value, 0.963×10^{-8} N/rad^2, in Set I, so it is desirable to check its reality from a nonspectroscopic point of view. Since λ is nearly twice as large as λ_6, the denominator in Eq. 14 causes an appreciable difference in $a^2{}_{66}$ between Sets I and II, and even larger difference in $a^2{}_{666}$ results from the square of $a^2{}_{66}$ according to Eq. 15. Because of these differences, the in-plane normal coordinates calculated for Sets I and II exhibit quite different trends of the dependence on s^6 from each other as shown in Fig. 1. The energy for Set I increases more rapidly than that for Set II at larger values of s^6. The atomic displacements derived from the changes of Q^j's through Eq. 17 are shown in Fig. 2 together with a schematic view of the distorted molecule.

The IRC's of formaldehyde for the dissociation reaction

$$H_2CO \longrightarrow H_2 + CO$$

and the isomerization reaction

$$H_2CO \longrightarrow HC\text{–}OH$$

were studied by Yamashita *et al.* by means of an *ab initio* MO calculation.[5] For each of these reactions, the IRC traced from the transition point back to the starting

TABLE 1. COEFFICIENTS $a^j{}_{66}$ AND $a^j{}_{666}$ AND FREQUENCY PARAMETERS λ_j OF FORMALDEHYDE

j	Set I		Set II		λ_j[c]
	$a^j{}_{66}$[a]	$a^j{}_{666}$[b]	$a^j{}_{66}$[a]	$a^j{}_{666}$[b]	
1	0.00183	0.0	0.00165	0.0	5.1054
2	0.04924	0.0	0.01190	0.0	1.8277
3	0.00254	0.0	0.00484	0.0	1.3550
4	0.0	0.0	0.0	0.0	0.8293
5	0.0	0.000108	0.0	0.000040	5.4176
6	0.0	0.001623	0.0	0.000112	0.9679

a) In amu$^{-1/2}$ pm^{-1}. b) In amu^{-1} pm^{-2}. c) In N cm^{-1} amu^{-1}.

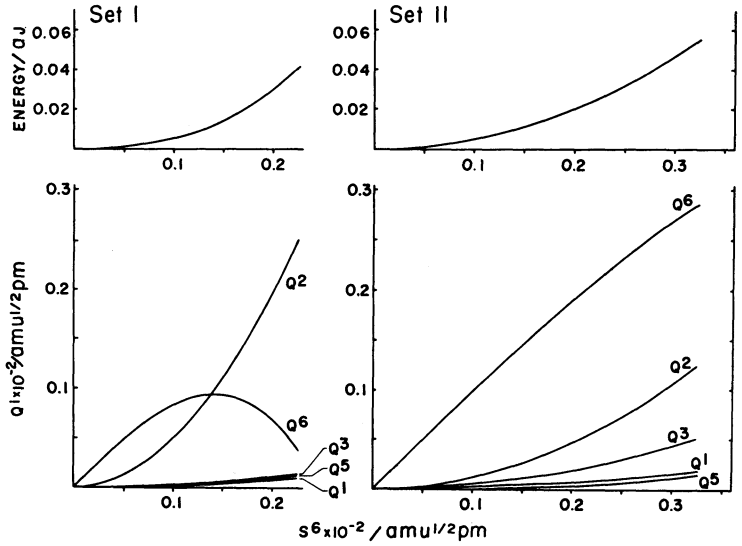

Fig. 1. Dependence of the potential energy and the in-plane normal coordinates on s^6 of formaldehyde molecule.

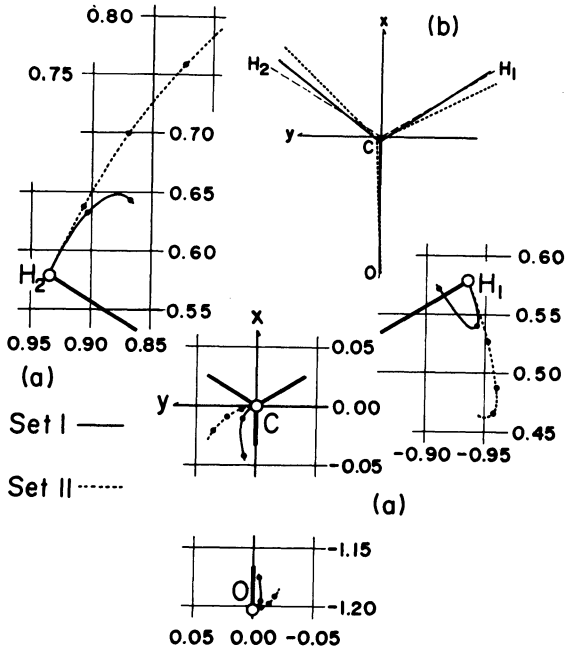

Fig. 2. (a) Atomic displacements of formaldehyde along s^6. The x and the y axes are scaled in a unit of 100 pm =Å. Filled circles on the atomic loci indicate the atomic positions corresponding to every increase of s^6 by 10 amu$^{1/2}$ pm. (b) A schematic view of undistorted and distorted molecules. Broken line: $s^6=0.0$. Solid line: $s^6=20$ amu$^{1/2}$ pm (Set I). Dotted line: $s^6=30$ amu$^{1/2}$ pm (Set II).

system converges into the ν_6 mode of formaldehyde. According to the present calculation, the spectroscopic data support the existence of an IRC which starts in the direction of the ν_6 mode at the equilibrium and proceeds toward the dissociation. In the framework of the harmonic approximation, the ν_6 mode is the CH_2 rocking mode in the course of which the two H–C=O angles close and open in turn. The hydrogen atom H_1 in Fig. 2 starts to close the H_1–C=O angle, but soon displays a

Table 2. Ground state rotational constants (cm^{-1}) of formaldehyde and its isotopic species

Molecule	Rotational constant	Obsd[a]	Calcd	
			Set I	Set II
H_2CO	*A*	9.40546	9.4158	9.4243
	B	1.29543	1.2952	1.2985
	C	1.13419	1.1354	1.1381
$H_2{}^{13}CO$	*A*	9.40628	9.4156	9.4238
	B	1.26124	1.2611	1.2644
	C	1.10789	1.1091	1.1118
$H_2C^{18}O$	*A*	9.40516	9.4157	9.4242
	B	1.23099	1.2309	1.2341
	C	1.08447	1.0856	1.0882
HDCO	*A*	6.60830	6.6298	6.6364
	B	1.16450	1.1646	1.1670
	C	0.98605	0.9873	0.9891
D_2CO	*A*	4.72504	4.7359	4.7401
	B	1.07686	1.0764	1.0781
	C	0.87345	0.8744	0.8757
$D_2C^{18}O$	*A*	4.72487	4.7358	4.7401
	B	1.02057	1.0202	1.0219
	C	0.83601	0.8369	0.8381

a) H_2CO, $H_2{}^{13}CO$ and $H_2C^{18}O$ from Ref. 7, the other from Ref. 6.

180° turn to move toward the correct direction for the dissociation. This reversal of the translation direction of H_1 takes place as a result of the increase of the contribution of the ν_2 mode and the corresponding decrease of that of the ν_6 mode in the IRC as shown in Fig. 1. Comparison between Sets I and II indicates that the turning point of H_1 is made nearer the equilibrium and the curvature around the turning point is increased by introduction of $K_{R\phi\phi}$. In Fig. 2, the locus of the hydrogen atom H_2 for Set I also shows a large curvature around the point where $s^6=17$ amu$^{1/2}$ pm. The turning of H_2 seems to be somewhat exaggerated, however, by errors associated with the truncation of Eq. 7 which contains large expansion coefficients.

Recently, very precise values of the ground state rotational constants of various isotopic species of formalde-

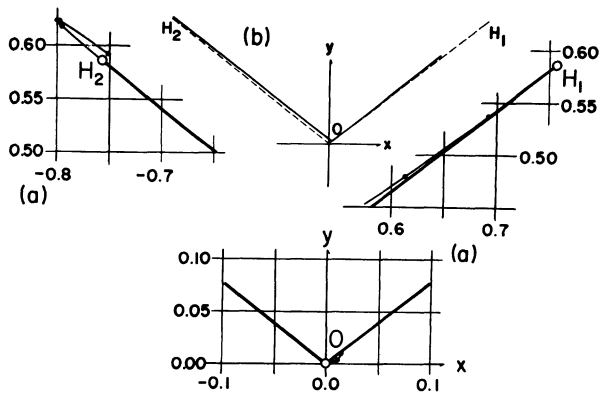

Fig. 3. (a) Atomic displacements of water along s^3. The axes are scaled and the atomic positions are indicated as in Fig. 2. (b) A schematic view of undistorted and distorted molecules. Broken line: $s^3=0.0$. Solid line: $s^3=30$ amu$^{1/2}$ pm.

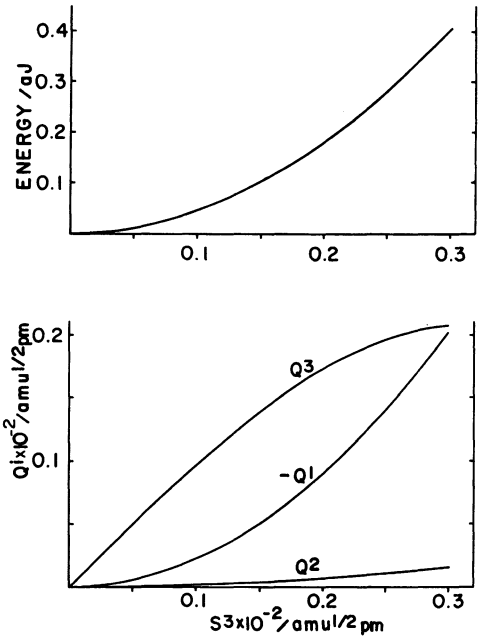

Fig. 4. Dependence of the potential energy and the normal coordinates on s^3 of water molecule.

hyde have been determined from the microwave spectra.[6-8] Some of them are compared with those calculated from Sets I and II in Table 2. Obviously, Set I is superior to Set II in reproducing the observed data, indicating the importance of the cubic constant $K_{R\phi\phi}$. For both Sets I and II, the mixing of the ν_5 mode takes place with the correct phase which brings about stretching of the C–H_1 bond, though the rate of the mixing is rather small compared with the result of the *ab initio* MO calculation.[5]

There are many normal modes for which the atomic path defined by Eq. 7 does not lead to any dissociation into molecular fragments. Figure 3 shows the atomic displacements of an isolated water molecule calculated by applying the same procedure as above to the ν_3 mode. The corresponding changes of the energy and the normal coordinates are plotted against s^3 in Fig. 4. The force constants were taken from the general quartic force field (iii) of Smith and Overend.[9] According to the sign of the coefficient $a^1{}_{33}$, the mixing of Q^1 and Q^3 in s^3 takes place with the opposite phase, leading to a sharp turning of the hydrogen atom H_2 in Fig. 3 which starts to stretch the O–H_2 bond at the potential minimum. Since the atom H_1 starts to approach the oxygen atom, the molecular distortion along s^3 cannot lead to any dissociation eventually. There are a number of symmetric triatomic molecules for which the antisymmetric stretching mode ν_a has a higher frequency than the symmetric stretching mode ν_s, and the relevant cubic constant K_{saa} is negative.[10] Absence of any IRC's which start in the direction of the antisymmetric stretching mode at the equilibrium should be a general feature for these molecules.

Combination of Eqs. 7 and 17 may thus be utilized for discussing whether a given normal coordinate is connected with any IRC's as well as for examining the behavior of an IRC in the vicinity of the equilibrium configuration of a molecule. Such an information offers important reference data in estimation of higher-order force constants, and should be useful to check the accuracy of a MO calculation when reliable force constants are available from a large number of experimental data.

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Appendix

The behavior of the IRC starting in the direction of the ν_i mode in the normal coordinate space may be described by taking Q^i itself instead of s^i as the independent variable. In this case, we divide Q^j in orders of magnitude as

$$Q^j = Q^j_0 + \varepsilon Q^j_1 + \varepsilon^2 Q^j_2 + \cdots. \tag{A1}$$

Substituting Eq. 4 and Al into Eq. 6 and rearranging, we obtain a series of differential equations which should hold separately in order that the choice of ε is arbitrary. The zeroth order equation

$$dQ^j_0/\lambda_j Q^j = dQ^i/\lambda_i Q^i$$

is immediately integrated to give the general expression for meta IRC's given by Tachibana and Fukui,[11]

$$Q^j_0 = C_{0j} Q^{i\lambda_j/\lambda_i}. \tag{A2}$$

If we take only those solutions of the zeroth order equation which are identically zero by putting $C_{0j}=0$ in Eq. A2, the first order equation is written simply as

$$(dQ^j_1/dQ^i) = (\lambda_j Q^j_1/\lambda_i Q^i) + (K_{jii}/2\lambda_i)Q^i. \tag{A3}$$

By introducing the integrating factor

$$\exp\{-(\lambda_j/\lambda_i)\int(1/Q^i)dQ^i\} = Q^{i\,-\lambda_j/\lambda_i},$$

Eq. A3 can be solved to give

$$Q^j_1 = (1/2)K_{jii}(\ln Q^i/\lambda_i)Q^{i2}, \tag{A4}$$

for the case where $\lambda_j=2\lambda_i$ and

$$Q^j_1 = (1/2)K_{jii}(2\lambda_i - \lambda_j)^{-1} Q^{i2}, \tag{A5}$$

for the case where $\lambda_j \neq 2\lambda_i$. The solution of the second order equation is given similarly as

$$Q_2^j = (1/6)(K_{jiii} + 3\sum_k K_{jik}a_{ii}^k - 3K_{iii}a_{ii}^j)(\ln Q^i/\lambda_i)Q^{i3}, \quad \text{(A6)}$$

when $\lambda_j = 3\lambda_i$. The solution for the case where $\lambda_j \neq 3\lambda_i$ is obtained by replacing $(\ln Q^i/\lambda_i)$ in Eq. A6 with $(3\lambda_i - \lambda_j)^{-1}$. These solutions of the first and the second order equations can also be expressed as functions of s^i simply by replacing Q^i in Eqs. A4—A6 with s^i, since the expansion of Q^i with respect to s^i does not include the quadratic term: see Eq. 13. The coordinate Q^j is then given as the sum of $Q_1{}^j$ and $Q_2{}^j$ under the approximation up to the second order. When neither $2\lambda_i$ nor $3\lambda_i$ equals to λ_j, this sum becomes identical to the expansion derived in the text.

References

1) K. Fukui, *J. Phys. Chem.*, **74**, 4161 (1970).
2) K. Fukui, S. Kato, and H. Fujimoto, *J. Am. Chem. Soc.*, **97**, 1 (1975).
3) S. Kato and K. Morokuma, *J. Chem. Phys.*, **73**, 3900 (1980).
4) Y. Tanaka and K. Machida, *J. Mol. Spectrosc.*, **64**, 429 (1977).
5) K. Yamashita, T. Yamabe, and K. Fukui, *Chem. Phys. Lett.*, **84**, 123 (1981).
6) D. Dangoisse, E. Willemot, and J. Bellet, *J. Mol. Spectrosc.*, **71**, 414 (1978).
7) D. T. Davies, R. J. Richards, and M. C. L. Gerry, *J. Mol. Spectrosc.*, **80**, 307 (1980).
8) R. Cornet and G. Winnewisser, *J. Mol. Spectrosc.*, **80**, 438 (1980).
9) D. F. Smith and J. Overend, *Spectrochim. Acta, Part A*, **28**, 471 (1972).
10) K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Jpn.*, **38**, 805, 814 (1965).
11) A. Tachibana and K. Fukui, *Theor. Chim. Acta*, **49**, 321 (1978).