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A Molecular Orbital Approach to the Fragmentation of the Acetaldehyde Cation Radical

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The microscopic process of the α-cleavage of the acetaldehyde cation radical is treated by means of the molecular orbital method. Two kinds of transition state for two different dissociation channels are located on the multi-dimensional potential surface. Supposing the Franck–Condon principle in the ionization process, the importance of the non-equilibrium initial state where two specific modes are excited is emphasized. In order to clarify the mechanism of these fragmentation processes a simple model of the intra-molecular energy transfer is constructed considering the anharmonicity of the potential energy function.

Key words: Acetaldehyde cation radical

1. Introduction

The dissociation process of organic molecules in mass spectroscopy has long been studied based on the quasi-equilibrium theory (QET) [1]. In this theory the initial distribution of excited states among various vibrational modes of an ionized molecule is assumed to be in the thermal equilibrium prior to the fragmentation and the statistical reaction probability mainly depends on the activation energy corresponding to the barrier height. However, QET may not be adequate to describe such a reaction process as the system is not in the thermal equilibrium but only in some specific excited vibrational state, the relaxation of which is slower than the bond cleavage. For example, the mass spectrum of the α-cleavage of the acetaldehyde cation radical [2] shows two characteristic peaks for HCO^+ (appearance ratio (a.r.) = 100, appearance potential (a.p.) = 12.53 eV) corresponding to C–C bond cleavage and CH_3CO^+ (a.r. = 38, a.p. = 11.38 eV) corresponding to C–H bond cleavage. On the contrary, when the system is reached in the thermal

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equilibrium by collision with the inert gas (He), the spectrum [3] shows a strong peak for CH_3CO^+ and a weak one for HCO^+. This is usually called the "collisional" activation spectrum. These fragmentation processes are considered as the reaction on the ground electronic state of the cation radical, since the appearance potentials are significantly lower than the observed second ionization potential (13.09 eV) [4]. The latter case is considered in the thermal equilibrium and may reasonably be treated by QET. In the former case, it is clear that the amount of HCO^+ produced over a higher barrier[1] overcomes that of CH_3CO^+ produced over a lower barrier. This fact implies that the initial system prepared by ionization is not in thermal equilibrium but only in one of a few specific excited states of vibrational modes. Thus, the α-cleavage of the acetaldehyde cation radical observed in mass spectrum may be a typical example to be treated as a case of the non-equilibrium system.

Prior to our present study, Salem *et al.* discussed the mechanism of this α-cleavage by using state correlation diagrams only for C–C bond cleavage [5]. In the present study, we attempt to make clear the mechanism of this α-cleavage for both C–C bond and C–H bond cleavages by considering the vibronic states of the ion to cleave. Suppose the first step of the dissociation is the ionization process accompanying excitations of several vibrational modes and this process is well described by the Franck–Condon principle. In this case, the electron to be removed is one of the lone pair electrons of the oxygen atom in acetaldehyde and not the electron forming the bond that breaks and leads to the fragmentation. As the second step of the fragmentation, it is then necessary to consider the mechanism of the intramolecular energy transfer through the intramolecular charge transfer. The importance of such an effect was discussed in our earlier paper on the electron-impact fragmentation of ethylamine [6]. In this paper, we consider the anharmonicity of the vibrational modes which causes the intramolecular energy transfer among the specific modes. The anharmonic terms on the multi-dimensional potential surface giving the strength of the coupling of normal modes are calculated directly by means of the molecular orbital (MO) method.

2. Calculations of Critical Points on the Potential Surface

The dissociation processes of acetaldehyde in mass spectroscopy are characterized by the initial stable conformations of neutral and ionized acetaldehyde, transition states and the final states of products. These critical points on the multi-dimensional potential surface of the dissociation process were calculated by the use of the MINDO/3 method [7a]. The open shell species were calculated by the unrestricted Hartree-Fock (UHF) method [7b].

The equilibrium nuclear configurations of neutral and ionized species were obtained by the energy-minimization method proposed by McIver and Komornicki [8]. The gradient of potential energy was obtained by the MINDO/3

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[1] The appearance potential corresponds to the barrier height plus a small amount of the translational energy.

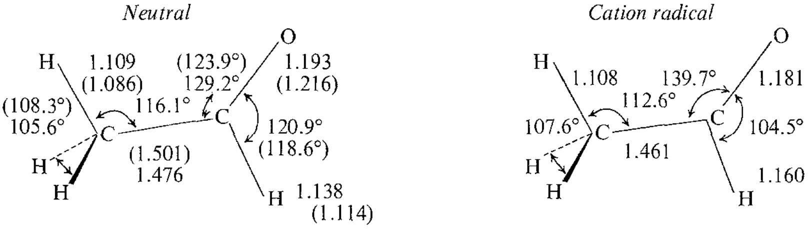

Fig. 1. Optimized geometries of the neutral molecule and the cation radical of acetaldehyde. The bond lengths are given in Å and values in parentheses are the experimental ones (Ref. [10])

version of its SCF formalism given by Gerat and Mills [9]. The calculated results for these two species, which were optimized in C_s symmetry, are shown in Fig. 1, being in good agreement with the experimental values for the neutral molecule [10]. Interestingly, the bond angles, ∢OCH and ∢CCO, are varied remarkably by ionization without accompanying the significant changes of bond lengths. The electron is removed from the lone pair orbital of the oxygen atom.

Spin transfer from the oxygen atom to the hydrogen atom of the formyl group is considerably large since the geometry of the ionized molecule is effective for the orbital interaction between the lone pair orbital of the oxygen atom and the C–H bonding orbital. Large positive spin on the oxygen and hydrogen atoms induces negative spin on the carbon atom in the formyl group. The calculated adiabatic ionization potential was obtained to be 9.42 eV, in good agreement with the experimental value, 10.19 eV, determined by electron-impact measurement [4]. The equilibrium geometries of the products, the CH_3 radical and the HCO cation after C–C bond cleavage as well as the CH_3CO cation after C–H bond cleavage were calculated in a similar way.

Characterization of the transition state is based on the category investigated by McIver and Komornicki [11]. The locations of the transition state on the potential energy surface were determined by using the algorithm described by Powell [12a, b]. Two kinds of the transition state were found, corresponding to C–C bond cleavage and C–H bond cleavage, respectively, as shown in Fig. 2. The

Table 1. Calculated charge density ρ and spin density s

	Neutral molecule	Cation radical		Transition state			
				(*A*)		(*B*)	
	ρ	ρ	s	ρ	s	ρ	s
C	+0.62	+0.62	−0.15	+0.77	−0.01	+0.78	−0.03
C (in CH_3)	−0.07	−0.06	+0.10	−0.14	+1.08	−0.10	+0.01
O	−0.46	−0.04	+0.72	−0.02	+0.04	−0.11	+0.04
H (in CH_3)	+0.02	+0.12	+0.01	+0.08	−0.04	+0.14	+0.01
H	−0.14	+0.13	+0.34	+0.20	+0.01	0.00	+0.97

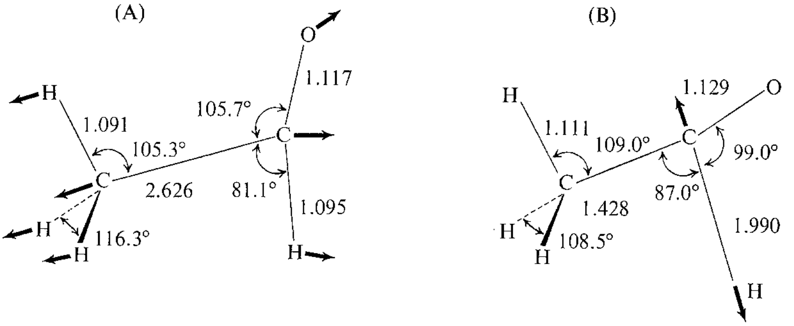

Fig. 2. Optimized geometries of the transition states (A) for C–C bond cleavage and (B) for C–H bond cleavage. The bond lengths are given in Å. The arrows indicate the displacement along the normal coordinate with negative force constant

arrows indicate the displacement along the normal coordinate with a negative force constant, which is uniquely determined since the transition state corresponds to a single saddle point on the potential energy surface. The structures of these two transition states resemble the products more closely than the reactants and the displacement vectors clearly show that the reaction proceeds toward, respectively, C–C and C–H bond cleavages.

Now we signify activation energies, ΔE(exp.) and ΔE(calc.) in Table 2, as the difference between the appearance potential and the observed first ionization potential, and between the potential energy at the transition state and at the equilibrium point, respectively. Calculated results are in good agreement with experimental values. If this system is treated in a statistical way by assuming the thermal equilibrium of the vibrational modes, the amount of the products of C–H bond cleavage will overcome that of C–C bond cleavage since the statistical reaction probability mainly depends on the activation energy. This result coincides with the "collisional" activation spectra of the acetaldehyde cation radical. However, the experimental result of normal mass spectroscopy of acetaldehyde is quite different from the above, and consequently leads to the conception that the initial ionized state is not yet arrived at the thermal equilibrium and the vibrational relaxation is not accomplished prior to the fragmentation.

In order to show the possibility of such a non-equilibrium initial state as the energy is distributed among some specific modes, we calculate in the next section the

Table 2. Calculated activation energy and heat of formation (eV)

	$E_{\text{calc.}}$	$E_{\text{exp.}}$	$H_{\text{calc.}}$	$H_{\text{exp.}}$	Appearance potential
C–C Bond cleavage	2.15	2.39	2.02	2.34	12.53
C–H Bond cleavage	0.59	1.24	0.43	1.19	11.38

vibrational transition intensity considering the change of the vibrational structure in the ionization process.

3. Calculations of Vibrational Structures and Franck–Condon Factors

The normal coordinates are given as the eigenvectors of the following secular equation [13],

$$\det\left(\frac{\partial^2 W}{\partial x_i \partial x_j} - \kappa\,\delta_{ij}\right)=0$$

where W is the potential energy and x_i is the mass-weighted Cartesian coordinate. The second derivatives of potential energy were obtained by the numerical differentiation of potential gradients. The six eigenvalues corresponding to translation or rotation are zero. This means that the system is fixed in the laboratory space. The normal vibrations are classified into groups of a' and a'' as $10a'+5a''$ since the neutral and ionized molecules of acetaldehyde possess C_s symmetry in their equilibrium conformations. In Table 3, the vibrational frequencies and the main components of 15 normal coordinates are shown for both the neutral and ionized molecules. Some of the most important normal modes of the cation radical are illustrated in Fig. 3.

On the neutral molecule, comparing the calculated frequencies with experimental ones [14], stretching modes are systematically overestimated. In contrast to stretching modes, the calculated results tend to underestimate vibrational types, such as C–H bending and CH_3 deformation. Though the discrepancies are typical for the MINDO/3 method [15], almost all the qualitative trends are well reproduced by calculations.

Table 3. Calculated normal vibrations and fundamental frequencies

	CH_3CHO	$CH_3CHO(+)$	
Species	calc. (obs.)	calc.	Description
a' 1	3483 (2967)	3499	CH stretching in CH_3
2	3471 (2917)	3465	CH stretching in CH_3
3	3200 (2840)	2836	CH stretching
4	2012 (1743)	1895	CO stretching
5	1385 (1441)	1284	CH_3 deformation
6	1279 (1390)	765	CH bending
7	1290 (1352)	1218	CH_3 deformation
8	1144 (1122)	1092	CC stretching
9	901 (919)	897	CH_3 rocking
10	462 (509)	323	CCO bending
a'' 11	3478 (3024)	3489	CH stretching in CH_3
12	1295 (1441)	1234	CH_3 deformation
13	990 (867)	923	CH out-of-plane bending
14	711 (763)	622	CH_3 rocking
15	101 (150)	46	Torsion

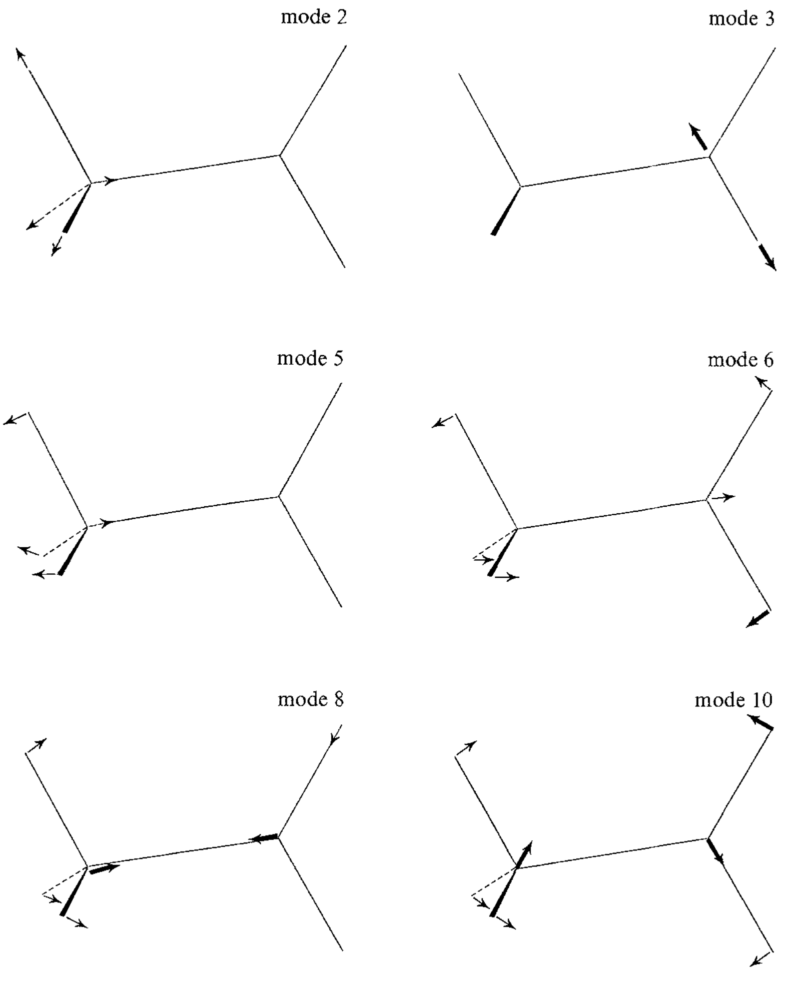

Fig. 3. Schematic representation of some vibrational modes of the cation radical. The arrows indicate the displacement along the normal coordinate

The large changes in frequencies by ionization are seen in several modes, particularly in C–H and CCO bending modes. The other stretching modes, such as C–H in the formyl group and C=O, also show the considerable decrease of vibrational frequencies. On the contrary, there is not so large a variation in the C–C stretching mode which may give the essential effect on C–C bond cleavage. As a matter of course these differences are mainly attributed to the change of the conformational structure by ionization.

As is well known, the Franck–Condon principle governs the relative transition probability to various vibrational levels of an electronic state for vertical excitation in the ionization process. So, we evaluate the Franck–Condon factor, i.e. the square of the vibrational overlap integrals between the initial (neutral) and final (ionized) states to understand the initial state prepared by ionization. The general

Table 4. Calculated Franck–Condon factor for multi-phonon system

Quanta in normal mode				Factor	Quanta in normal mode				Factor
n_5	n_8	n_6	n_{10}		n_5	n_8	n_6	n_{10}	
0	0	0	0	0.16[a]					
0	0	0	1	0.21	0	1	0	0	0.01
0	0	0	2	0.09	0	1	0	1	0.02
0	0	0	3	0.01	0	1	0	2	0.01
0	0	1	0	0.10	0	1	1	0	0.01
0	0	1	1	0.13	0	1	1	1	0.01
0	0	1	2	0.06	1	0	0	0	0.01
0	0	1	3	0.01	1	0	0	1	0.02
0	0	2	0	0.01	1	0	0	2	0.01
0	0	2	1	0.02	1	0	1	0	0.01
0	0	2	2	0.01	1	0	1	1	0.01

[a] 0 → 0 transition.

treatment of the Franck–Condon factor for the multi-dimensional polyatomic surface was formulated by Band and Freed [16a]. Here we consider only the case of the transition from the initial ground vibrational state to the final state where only one vibrational mode s is excited to the level n_s [16b]. The Franck–Condon factor is then of the form,

$$I(0,\ldots n_s,\ldots 0;\mathbf{0})=\left[\int \psi^f_{(0\cdots n_s\cdots 0)}(Q^f)\psi^i_{(\mathbf{0})}(Q^i)\,dQ^f\right]^2, \qquad (1)$$

where Q^f and Q^i are the nuclear displacement coordinates of final and initial electronic surfaces. The intensities for the multi-phonon transitions are calculated using the approximate relation of Ref. [16b]. The vibrational wavefunctions are approximated as harmonic. To evaluate the integral, we express the coordinates of the initial state by those of the final state through an Eckart transformation [17]. The overlap integrals are then evaluated using the generating function for Hermite polynomials.

Table 4 shows the results for multi-phonon systems having significant intensities. In the case that a single mode is excited, the CCO bending mode has the largest intensity ($n_{10}=1$). Further, in the case of the multi-phonon system the coupling between C–H and CCO bending modes is more interesting. Therefore, we can represent an initial ionized state as both C–H and CCO bending modes are excited simultaneously, conserving the obtained excess electronic energy as the vibrational one.

4. Intramolecular Vibrational Energy Transfer

There are some previous attempts to develop a theory of internal energy exchange in isolated molecules [18a, b]. Gelbart, Rice and Freed [19] derived a weak-coupling master equation for intramolecular relaxation. In this case, the coupling of vibrational modes are determined by the anharmonic terms in the potential function of the system. That is, any harmonic model allows no vibrational relaxation.

Here, we try to calculate the anharmonic terms on the multi-dimensional potential surface giving the strength of the coupling of normal modes. From first-order perturbation theory, the transition probability between the states a and b is given by [20],

$$P_{a\to b}=\frac{2\pi}{\hbar}|\langle b|V|a\rangle|^2\rho_b(\varepsilon), \tag{2}$$

where V is the anharmonic terms in the expansion of potential energy W and $\rho_b(\varepsilon)$ is the state density of the final state b, approximated as the inverse of the vibrational frequency of normal mode b. Equation (2) corresponds to the intramolecular energy transfer by the anharmonic effect. Approximating V by quartic terms and referring to the coefficients of cubic and quartic terms as f_{iij} and f_{iiij}, these f_{iij} and f_{iiij}'s are calculated by the method presented in the Appendix.

Although the efficiency of the relaxation of vibrational energy is proportional to the product of the coupling matrix element and the state density, we can discuss qualitatively the characteristics of the energy transfer among various normal modes by considering only the absolute values of f_{iij} and f_{iiij}'s. In the previous section we obtained the initial prepared state where two special bending modes, C–H and CCO bending modes, are excited. Most dissociation processes involve the breaking of one bond which has enough energy for the reaction to take place. So, an initial energy distribution must be reorganized to concentrate the energy on the bond. That is, C–H and CCO bending modes play an important role in the vibrational energy transfer to the C–C stretching mode for C–C bond cleavage and to the C–H stretching mode for C–H bond cleavage.

The calculated $|f_{iij}|$ and $|f_{iiij}|$'s[2] (Table 5) show that there is specificity in the coupling of these two bending modes with other vibrational modes. The CCO bending mode has strong coupling with the C=O stretching mode through a cubic anharmonic term ($i=10, j=4$). The C–H bending mode couples with the C–H stretching mode through a cubic term ($i=6, j=3$) and with the C–C stretching mode through a quartic term ($i=6, j=8$). The excess vibrational energy may be more efficiently transferred to the C–H stretching mode through the cubic term of the C–H bending mode and the quartic term of the CCO bending mode, rather than to the C–C stretching mode through the quartic term of the C–H bending mode and the cubic term of the CCO bending mode. However, $\rho_b(\varepsilon)$ (Table 6) may profit the energy transfer to the C–C stretching mode. Thus, these situations suggest that the efficiency of energy transfer to C–H and C–C stretching modes are comparable. Now, there remains a question whether the transferred energy will be accumulated in these two stretching modes or not.

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[2] The standard deviations of the fit for the $\partial W/\partial Q$'s are within 0.0002 (8×10^{-5} ($i=10, j=4$), 2×10^{-4} ($i=6, j=3$), and 9×10^{-6} ($i=6, j=8$)).

Table 5. Absolute values of the coefficient of anharmonic terms

Mode			
i	j	$\lvert f_{iij}\rvert$	$\lvert f_{iiij}\rvert$
3	3	0.106 $E+01$	0.176 $E+01$
	4	0.204 $E+00$	0.226 $E+00$
	8	0.560 $E-01$	0.441 $E-01$
	9	0.434 $E-01$	0.0
	10	0.513 $E-01$	0.725 $E-01$
6	2	0.961 $E-02$	0.296 $E-02$
	3	0.834 $E-01$	0.112 $E-02$
	4	0.902 $E-02$	0.759 $E-02$
	6	0.743 $E-03$	0.878 $E-01$
	8	0.180 $E-02$	0.111 $E-01$
8	2	0.716 $E-02$	0.665 $E-03$
	4	0.150 $E-01$	0.828 $E-02$
	5	0.134 $E-01$	0.485 $E-02$
	7	0.801 $E-02$	0.362 $E-02$
	8	0.189 $E-01$	0.768 $E-02$
10	2	0.758 $E-02$	0.623 $E-03$
	3	0.139 $E-02$	0.548 $E-02$
	4	0.119 $E-01$	0.186 $E-03$
	8	0.456 $E-02$	0.283 $E-02$
	10	0.108 $E-02$	0.626 $E-02$

Table 6. State densities

Mode	(kcal/mol)$^{-1}$ $\rho_b(\varepsilon)$
3	1.23 $E-01$
6	4.57 $E-01$
8	3.20 $E-01$
10	1.08

If the rate of dissipation of energy is faster than that of concentration, any vibrational energy will be accumulated in the bond stretching. On this point, we can make a clear explanation by considering the values of $|f_{iij}|$ and $|f_{iiij}|$'s[3] ($i=3$ and 8). That is, the transferred vibrational energy will be effectively accumulated in the C–C stretching mode, whereas the C–H stretching mode couples with other vibrational modes very strongly as contrasted with the C–C stretching mode.

Thus, the mechanism for the α-cleavage of the acetaldehyde cation radical in mass spectroscopy may be as follows. In the initial stage of reaction, the prepared state has a vibrational distribution where both CCO and C–H bending modes are highly excited conserving the excess electronic energy as the vibrational one, and they act as driving force to transfer the excess vibrational energy to other vibrational modes coupled with these two modes by anharmonic effects. The vibrational energy will be transferred to the C–C and C–H stretching modes. However, in contrast to in the C–H stretching mode, the energy is effectively accumulated in the C–C stretching mode to have enough energy to lead to dissociation. This contributes to the reason why the products from the C–C bond cleavage overcome

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[3] The standard deviations of the fit for the $(\partial W/\partial Q)$'s are within 8×10^{-7}.

those from the C–H bond cleavage in spite of the potential barrier being lower in the former case than the latter.

Our treatment of this fragmentation process is insufficient in that it is limited to the ground electronic state of the cation radical. However, the importance of the anharmonic effect on the intramolecular vibrational energy transfer in connection with dissociation mechanism is well elucidated there. Information for the life time of activated molecules for the dissociation process would be useful for the verification of the present idea. These calculations of anharmonic terms on the multi-dimensional potential surfaces could be one theoretical approach to discuss the mechanism of the unimolecular dissociation induced by vibrational excitation.

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Appendix

This appendix shows the procedure for calculation of the coefficient of anharmonic terms on the multi-dimensional potential surface.

The potential energy function, W, is represented as a power expansion in the complete set of the normal coordinates, Q_i's, at the equilibrium point,

$$W = W_0 + \frac{1}{2}\sum_i f_{ii} Q_i^2 + \frac{1}{3!}\sum_{ijk} f_{ijk} Q_i Q_j Q_k + \cdots \tag{A1}$$

where W_0 is the energy at minimum. Therefore we have,

$$\frac{\partial W}{\partial Q_s} = f_{ss} Q_s + \frac{1}{2}\sum_{ij} f_{ijs} Q_i Q_j + \cdots \tag{A2}$$

where the identity, $f_{ijs} = f_{isj} = f_{sij}$, is used. The gradient, $\partial W/\partial Q_s$, is equal to zero at the equilibrium point. If the geometry of the molecule is varied along the normal coordinate Q_t from the minimum on the potential energy surface, we obtain for the case of $t = s$,

$$\frac{\partial W}{\partial Q_s} = f_{ss} Q_s + \tfrac{1}{2} f_{sss} Q_s^2 + \cdots \tag{A3}$$

for the case of $t \neq s$,

$$\frac{\partial W}{\partial Q_s} = \tfrac{1}{2} f_{tts} Q_t^2 + \cdots \tag{A4}$$

since Q_i's $(i \neq t)$ are orthonormal to Q_t. Then, $(\partial W/\partial Q_s)$'s are plotted versus Q_t. Finally, the coefficient of anharmonic terms such as f_{iij} and f_{iiij}'s are determined using least squares fitting by the use of polynomials of Q_t.

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