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Potential energy profiles along the doubly degenerate vibrational modes in conjugated molecules

I. General theory based on the perturbation method

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In order to predict the molecular symmetries and the geometrical structures of conjugated molecules having the doubly degenerate first-order Jahn–Teller active modes (Q_1 and Q_2) or the doubly denegerate modes through which the second-order vibronic couplings occur (Q'_1 and Q'_2), the potential energy curves along these modes are expressed as the power series, including up to the third power. It is shown that although there are cases in which we cannot practically differentiate between the potential energy profiles along Q_1 and Q_2 or Q'_1 and Q'_2, in so far as we can differentiate between them, a potential energy minimum should always be located along Q_1 or Q'_1 that distorts a molecule in a more symmetrical way. This is in agreement with the available experimental facts. Finally on the basis of the perturbation theory, the coefficients of various powers (up to the third power) in the expansion of the electronic part of potential energy in the power series of the relevant mode are expressed in terms of the zeroth-order electronic wavefunctions and energies.

Key words: Potential energy surface—first-order Jahn–Teller effect—second-order Jahn–Teller effect

1. Introduction

The Jahn–Teller theorem [1] gives a substantial clue for determining the molecular symmetries and predicting the geometrical structures of molecules having degenerate ground states. Nuclear distortions due to the Jahn–Teller effect have been

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predicted for a wide variety of molecules, though the experimental evidence of their existence is very scarce. The effect is called the first-order Jahn–Teller (FOJT) effect, since it arises from the energy lowering due to the first-order terms in Eq. (1):

$$E(Q_1, Q_2, \ldots) = E^0 + \sum_i \left(\frac{\partial E}{\partial Q_i}\right)_0 Q_i + \frac{1}{2}\sum_i \sum_j \left(\frac{\partial^2 E}{\partial Q_i \partial Q_j}\right)_0 Q_i Q_j + \frac{1}{6}\sum_i \sum_j \sum_k \left(\frac{\partial^3 E}{\partial Q_i \partial Q_j \partial Q_k}\right)_0 Q_i Q_j Q_k + \cdots \tag{1}$$

where Q_i is the small nuclear displacement along the ith nuclear (symmetry) coordinate and E^0 is the original energy at point $Q_i = 0$ $(i = 1, 2, \ldots)$.

In recent years, the second-order Jahn–Teller (SOJT) effect, which manifests in molecules having nondegenerate ground states, has received wide attention, the effect being associated with the energy lowering due to the second-order terms in Eq. (1). Pearson [2] has demonstrated how well the symmetry rules derived from the SOJT effect work in predicting the geometrical structures for a variety of inorganic and simple organic molecules. Nakajima [3] and Nakajima et al. [4] have successfully applied the SOJT effect to the prediction of the geometrical structures with respect to C–C bond lengths of the ground and lower excited states of conjugated hydrocarbons.

It is the purpose of the present and the following paper to examine on the basis of Eq. (1) the potential energy profiles of conjugated molecules along the doubly degenerate FOJT active modes (Q_1 and Q_2) or along the doubly degenerate modes through which the second-order vibronic couplings responsible for the second-order terms in Eq. (1) occur (SO coupling modes[1], Q_1' and Q_2'). As an example of molecules treated, in Fig. 1 are shown the doubly degenerate FOJT active modes (E'), Q_1 and Q_2, for the cyclopropenyl radical belonging to D_{3h}. The FOJT theorem provides no information as to along which of Q_1 and Q_2 a minimum of potential energy exists. In order to answer this question we have to take into account the second-order terms with respect to the FOJT active modes.

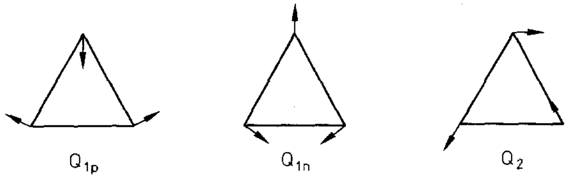

Fig. 1. The FOJT active degenerate modes (E') of the cyclopropenyl radical. Suffixes p and n indicate the positive and negative directions of Q_1, respectively

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[1] The SO coupling mode does not always bring about the SOJT effect: if in a molecule the energy gap between the ground and excited states that couple through the SO coupling mode is larger than a certain critical value, the molecule does not undergo the SOJT effect [2, 3]

If an energy minimum is predicted to exist along Q_1 by examining the second-order terms, which is true of this molecule (*vide infra*), we need the further information as to along which of the positive and negative directions of Q_1 the energy minimum is located. This is because, obviously, nuclear distortions along the mutually opposite directions of Q_1 produce the different molecular shapes: an oblate triangle form in the positive direction (Q_{1p}) and a prolate triangle form in the negative direction (Q_{1n}). In order to predict which of the two forms corresponds to the true energy minimum, the third-order term with respect to Q_1 should at least be taken into account.

An example of cases in which the SO coupling modes are (doubly) degenerate is given by the lowest excited triplet state ($^3B_{1u}$) and the second excited singlet state ($^1B_{1u}$) of benzene. The SO coupling modes, Q_1' and Q_2', through which the $^3B_{1u}$ and $^1B_{1u}$ states vibronically couple with the nearby higher degenerate excited $^3E_{1u}$ and $^1E_{1u}$ states, respectively, belong to E_{2g} and are shown in Fig. 2. As will be shown later, a minimum of potential energy is found along Q_1' in both cases. Now that the nuclear distortions along mutually opposite directions of Q_1' give different molecular shapes, the quinoid and antiquinoid forms, in order to predict which form is energetically more favorable, we have to invoke at least the third-order term with respect to Q_1'.

Liehr [5] has examined semiquantitatively the potential energy profiles of the cyclopropenyl radical and shown that an energy minimum should lie in one direction of Q_1 and a saddle point in the other. He has not, however, mentioned along which of the positive and negative directions of Q_1 the energy minimum is located. Öpik and Pryce [6] have studied theoretically the molecular shapes of octahedral metal complexes having the degenerate ground states (^2E_g) such as $Cu(H_2O)_6^{2+}$. Taking into account the third-order terms with respect to the FOJT active modes, together with the electrostatic interactions between Cu^{2+} and the water molecules, they have concluded that in $Cu(H_2O)_6^{2+}$ the tetragonally elongated form is energetically more stable than the tetragonally compressed one. As to the octahedral Cu^{2+} complexes, Jotham and Kettle [7] have reached the same conclusion by assuming that a section of the potential well might be described by the familiar Morse curve and by examining the restoring forces for this case.

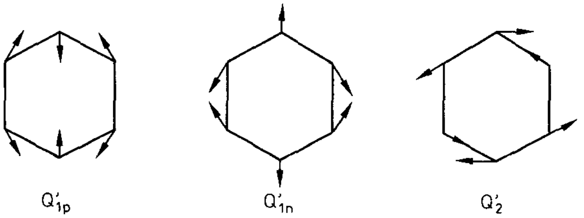

Fig. 2. The SO coupling degenerate modes (E_{2g}) of the lowest excited triplet state ($^3B_{1u}$) and the second excited singlet state ($^1B_{1u}$) of benzene

In this paper, we develope a general theory for predicting along which of the doubly degenerate FOJT active or SO coupling modes of conjugated molecules an energy minimum may possibly exist and furthermore along which of the mutually opposite directions of thus decided mode the energy minimum should be located. For this purpose, we examine the sections of potential energies along the relevant modes by taking into account up to the third-order terms in Eq. (1). Applications of the general theory to individual molecules will be made in the following paper.

2. Theory

We start by assuming for a conjugated molecule a fully-symmetrical arrangement of carbon nuclei, and then distort the nuclei from the symmetrical arrangement by means of a pair of degenerate nuclear coordinates Q_1 and Q_2 or Q_1' and Q_2'. The sections of potential energy along these modes are expressed as the power series of the relevant modes, including up to the third power.

First, we treat the nondegenerate case. The potential energy surface as a function of Q_1 and Q_2 of a nondegenerate ground state, ψ_0, is given by

$$E_0(Q_1, Q_2) \equiv \langle \psi_0(Q_1, Q_2)|H'|\psi_0(Q_1, Q_2)\rangle \tag{2}$$

where the brackets mean the integration with respect to electronic coordinates, and H' is defined as

$$H' = H'(Q_1, Q_2) = H(Q_1, Q_2) - E_0^0 \tag{3}$$

whre E_0^0 is the ground-state energy of the original structure.

For molecules having doubly degenerate ground states, ψ_{01} and ψ_{02}, the potential energy surface is composed of the two parts, one belonging to a totally symmetric representation

$$\begin{aligned} E_{0,s}(Q_1, Q_2) = \{&\langle \psi_{01}(Q_1, Q_2)|H'|\psi_{01}(Q_1, Q_2)\rangle \\ &+\langle \psi_{02}(Q_1, Q_2)|H'|\psi_{02}(Q_1, Q_2)\rangle\}/2 \end{aligned} \tag{4}$$

and the other to a nontotally symmetric degenerate one of the original point group

$$\begin{aligned} E_{0,n1}(Q_1, Q_2) = \{&\langle \psi_{01}(Q_1, Q_2)|H'|\psi_{01}(Q_1, Q_2)\rangle \\ &-\langle \psi_{02}(Q_1, Q_2)|H'|\psi_{02}(Q_1, Q_2)\rangle\}/2 \end{aligned} \tag{5-1}$$

$$E_{0,n2}(Q_1, Q_2) = \langle \psi_{01}(Q_1, Q_2)|H'|\psi_{02}(Q_1, Q_2)\rangle. \tag{5-2}$$

Note that for the degenerate SO coupling modes, Q_1 and Q_2 in Eqs. (2)–(5) should be replaced by Q_1' and Q_2', respectively. We now expand Eqs. (2), (4) and (5) in the power series of Q_1 and Q_2 up to the third power. In Table 1 are shown degenerate nuclear distortions (up to the third power) that form the bases for irreducible representations of the point groups, D_{3h}, D_{5h}, D_{6h}, and D_{7h}. The nuclear distortions that form the bases for doubly degenerate representations of these point groups have the two components which are of different symmetry

Table 1. Irreducible representations to which belong Q_1 and Q_2, their squares and cubes, and their binary products for various types of modes

Nuclear distortions	Types of modes 1 D_{3h}	 D_{6h}	 2 D_{5h}		 3 D_{7h}		
Q_1, Q_2	E'	E_{2g}	E'_1	E'_2	E'_1	E'_2	E'_3
$Q_1^2+Q_2^2$	A'_1	A_{1g}	A'_1	A'_1	A'_1	A'_1	A'_1
$Q_1^2-Q_2^2$	E'	E_{2g}	E'_2	E'_1	E'_2	E'_3	E'_1
$2Q_1Q_2$							
$(Q_1^2+Q_2^2)Q_1$	E'	E_{2g}	E'_1	E'_2	E'_1	E'_2	E'_3
$(Q_1^2+Q_2^2)Q_2$							
$Q_1^3-3Q_1Q_2^2$	A'_1	A_{1g}	E'_2	E'_1	E'_3	E'_1	E'_2
$Q_2^3-3Q_1^2Q_2$	A'_2	A_{2g}					

with respect to operation σ_v: one is symmetric and the other antisymmetric. The two components belong to the different irreducible representations of the reduced point group if it still includes σ_v, as in the case of the above four point groups. Further, it is apparent that Table 1 holds true also for the degenerate ground-state wavefunctions, that is, Q_1 and Q_2 can be replaced by ψ_{01} and ψ_{02}, respectively. Throughout this paper we define the choice of Q_1 and Q_2 and that of ψ_{01} and ψ_{02} as follows:

$$\sigma_v(Q_1, Q_2) = (Q_1, -Q_2) \tag{6-1}$$

$$\sigma_v(\psi_{01}, \psi_{02}) = (\psi_{01}, -\psi_{02}). \tag{6-2}$$

With the degenerate SO coupling modes, Table 1 is read with Q_1 and Q_2 being replaced by Q'_1 and Q'_2, respectively. It is thus shown that in molecules belonging to D_{3h}, D_{5h}, D_{6h}, and D_{7h}, the FOJT active or SO coupling degenerate modes Q_1 and Q_2 or Q'_1 and Q'_2 bring about distorted structures belonging to the different point groups.

In the case of molecules belonging to point groups which do not have operation σ_v, e.g., C_{3h}, distorted structures brought about by the FOJT or SOJT effect belong to the same point group: in case of C_{3h}, both the two distorted structures belong to C_s. We cannot energetically distinguish between the two distorted structures belonging to the same point group in the framework of the present group theoretical treatment. We have thus excluded C_{3h}, C_{4h}, C_{5h}, C_{6h} etc. Furthermore, in molecules belonging to D_{4h}, e.g., cyclobutadiene, the FOJT effect is absent and the SO coupling mode (B_{2g}) is not degenerate. In its cation and anion radicals, the FOJT active mode is not degenerate and the SO coupling degenerate modes (E_u), if these radicals undergo the SOJT effects, bring about distorted structures both belonging to C_{2v}. A similar situation is found in molecules belonging D_{4nh} ($n > 1$) and their cation and anion radials so that these point groups also are excluded.

In Table 1 we classify the modes of nuclear distortion into three types from the following reasons. When in a molecule Q_1 and Q_2, and $(Q_1^2-Q_2^2)$ and $2Q_1Q_2$

belong to a unique (doubly) degenerate irreducible representation, E' of D_{3h} and E_{2g} of D_{6h}, modes Q_1 and Q_2 of the molecule are of Type 1. Note that Q_1 and Q_2, and $(Q_1^2+Q_2^2)Q_1$ and $(Q_1^2+Q_2^2)Q_2$ belong to the same representation for all the types. In Type 2, $(Q_1^2-Q_2^2)$ and $2Q_1Q_2$, and $(Q_1^3-3Q_1Q_2^2)$ and $(Q_2^3-3Q_1^2Q_2)$ belong to the same representation, which is different from that of Q_1 and Q_2. For modes of Type 3, Q_1 and Q_2, $(Q_1^2-Q_2^2)$ and $2Q_1Q_2$, and $(Q_1^3-3Q_1Q_2^2)$ and $(Q_2^3-3Q_1^2Q_2)$ belong to the three different doubly degenerate representations, e.g., E_1', E_2', and E_3', respectively. The cyclic permutation produces the remaining two cases.

3. Sections of potential energy surfaces along the FOJT active or SO coupling modes

3.1. *The* SO *coupling modes for molecules having nondegenerate ground state*

The simplest example of this type of molecule is given by the ground state of the cyclopropenyl cation (D_{3h}). In this molecule, the SO coupling modes (E') are degenerate on account of the existence of a lower doubly degenerate excited state and are of Type 1. $E_0(Q_1', Q_2')$ for the SO coupling modes of Type 1 takes the following form;

$$E_0(Q_1', Q_2') = b_1'(Q_1'^2+Q_2'^2)+c_2'(Q_1'^3-3Q_1'Q_2'^2) \tag{7}$$

where b_1' and c_2' are numerical numbers. For the SO coupling modes of Types 2 and 3, we have

$$E_0(Q_1', Q_2') = b_1'(Q_1'^2+Q_2'^2). \tag{8}$$

Eqs. (7) and (8) are obtained by noting that all the expansion terms of $E_0(Q_1', Q_2')$ given by Eq. (2) should be totally symmetric. It is shown from Eq. (7) that since it does not contain terms with $Q_2'^3$, for modes of Type 1 a potential energy minimum should exist along Q_1'. Along which of the positive and negative directions of Q_1' the energy minimum is located is governed by the signed value of c_2'. For the modes of Types 2 and 3, Eq. (8) indicates that there is no difference in energy between the sections of potential energy along Q_1' and Q_2'.

It should be added that whether a molecule of the type under consideration is actually distorted along the SO coupling modes or not depends on the actual value of b_1': if it is positive, the molecule does not actually undergo the molecular-symmetry reduction due to the SOJT effect.

3.2. *The* FOJT *active modes for molecules having (doubly) degenerate ground states*

The potential energy $E_0(Q_1, Q_2)$ for a molecule with doubly degenerate ground states is composed of two parts with different symmetries (Eqs. (4) and (5)). Since by definition ψ_{01} is symmetric with respect to operation σ_v and ψ_{02} antisymmetric, Eq. (5-1) includes only the symmetric terms, while Eq. (5-2) only the antisymmetric ones.

For the modes of Type 1 (for example, the E' modes of the cyclopropenyl radical) we have

$$\begin{aligned} E_s(Q_1, Q_2) &= b_1(Q_1^2+Q_2^2)+c_2(Q_1^3-3Q_1Q_2^2) \\ E_{n1}(Q_1, Q_2) &= aQ_1-b_2(Q_1^2-Q_2^2)+c_1(Q_1^2+Q_2^2)Q_1 \\ E_{n2}(Q_1, Q_2) &= aQ_2+b_2(2Q_1Q_2)+c_1(Q_1^2+Q_2^2)Q_2 \end{aligned} \tag{9}$$

where we have omitted suffix 0.

Our next task is to take out the components along Q_1 and Q_2 from the potential energy surfaces given by Eq. (9). For this purpose, we have to define the degenerate wavefunctions along the Q_1 and Q_2 modes. The wavefunctions for Q_1 are taken to be $\psi_{01}(Q_1, 0)$ and $\psi_{02}(Q_1, 0)$ by definition. Those along Q_2 are then given by

$$\begin{aligned} \psi_{0+}(0, Q_2) &= \frac{1}{\sqrt{2}}(\psi_{01}(0, Q_2)+\psi_{02}(0, Q_2)), \\ \psi_{0-}(0, Q_2) &= \frac{1}{\sqrt{2}}(\psi_{01}(0, Q_2)-\psi_{02}(0, Q_2)). \end{aligned} \tag{10}$$

For the modes of Type 1 we thus obtain the potential energy curves along Q_1 and Q_2 as follows: along Q_1 we have

$$\begin{aligned} \langle\psi_{01}(Q_1, 0)|H'|\psi_{01}(Q_1, 0)\rangle &= aQ_1+(b_1-b_2)Q_1^2+(c_1+c_2)Q_1^3 \\ \langle\psi_{02}(Q_1, 0)|H'|\psi_{02}(Q_1, 0)\rangle &= -aQ_1+(b_1+b_2)Q_1^2+(-c_1+c_2)Q_1^3 \end{aligned} \tag{11}$$

and along Q_2

$$\begin{aligned} \langle\psi_{0+}(0, Q_2)|H'|\psi_{0+}(0, Q_2)\rangle &= aQ_2+b_1Q_2^2+c_1Q_2^3 \\ \langle\psi_{0-}(0, Q_2)|H'|\psi_{0-}(0, Q_2)\rangle &= -aQ_2+b_1Q_2^2-c_1Q_2^3. \end{aligned} \tag{12}$$

Comparing the possible signed values of the coefficients of the second-order terms of Eq. (12) with those of Eq. (11), we can conclude that a potential energy minimum should be located along Q_1. Along which of the positive and negative directions of Q_1 there exists the energy minimum is governed by the signed values of b_1, b_2, c_1, and c_2. It is noted that in this particular case, the differentiation between the potential energy profiles along the mutually opposite directions of Q_1 can be made even by the second-order terms.

Likewise, for the modes of Types 2 and 3 the potential energy profiles along Q_1 and Q_2 are given, respectively, by

$$\begin{aligned} \langle\psi_{01}(Q_1, 0)|H'|\psi_{01}(Q_1, 0)\rangle &= aQ_1+b_1Q_1^2+c_1Q_1^3 \\ \langle\psi_{02}(Q_1, 0)|H'|\psi_{02}(Q_1, 0)\rangle &= -aQ_1+b_1Q_1^2-c_1Q_1^3 \end{aligned} \tag{13}$$

and

$$\begin{aligned} \langle\psi_{0+}(0, Q_2)|H'|\psi_{0+}(0, Q_2)\rangle &= aQ_2+b_1Q_2^2+c_1Q_2^3 \\ \langle\psi_{0-}(0, Q_2)|H'|\psi_{0-}(0, Q_2)\rangle &= -aQ_2+b_1Q_2^2-c_1Q_2^3. \end{aligned} \tag{14}$$

Apparently, for these modes there is no difference between the potential energy curves along Q_1 and Q_2.

3.3 The SO *coupling modes for molecules having the degenerate ground states*

We now deal with the SO coupling modes for a molecule which undergoes the FOJT effect. We examine the potential energy profiles along the SO coupling modes that belong to a degenerate irreducible representation different from that to which the FOJT active modes belong. For example, in the lowest excited singlet state (E'_2) of the cyclopentadienyl cation, the SO coupling modes belong to E'_2 and the FOJT active modes to E'_1. Since in molecules whose FOJT active modes are of Type 1, the SO coupling modes belong to the same degenerate representation as the FOJT active modes, they are excluded from the present discussion.

First, we treat molecules whose SO coupling modes are of Type 2. The potential energy profiles along Q'_1 and Q'_2 are expressed, respectively, by

$$\begin{aligned}\langle\psi'_{01}(Q'_1,0)|H'|\psi'_{01}(Q'_1,0)\rangle &= (b'_1-b'_2)Q'^2_1+c'_2Q'^3_1\\ \langle\psi'_{02}(Q'_1,0)|H'|\psi'_{02}(Q'_1,0)\rangle &= (b'_1+b'_2)Q'^2_1-c'_2Q'^3_1\end{aligned}\tag{15}$$

and

$$\begin{aligned}\langle\psi'_{0+}(0,Q'_2)|H'|\psi'_{0+}(0,Q'_2)\rangle &= b'_1Q'^2_2+c'_2Q'^3_2\\ \langle\psi'_{0-}(0,Q'_2)|H'|\psi'_{0-}(0,Q'_2)\rangle &= b'_1Q'^2_2-c'_2Q'^3_2.\end{aligned}\tag{16}$$

Eqs. (15) and (16) indicate that irrespective of the signed values of b'_1 and b'_2, a minimum of the potential energy should be located along Q'_1. Along which of the positive and negative directions of Q'_1 the minimum point is found is governed by the signed values of c'_2. Along which of the FOJT active mode Q_1 and the SO coupling mode Q'_1 the true minimum exists is governed by the signed values of numerical coefficients of Eqs. (11) and (15) and cannot be decided by the present group theoretical treatment.

Next, we deal with the molecules whose SO coupling modes Q'_1 and Q'_2 are of Type 3. There are two cases to be treated separately. Case 1: quadratic terms $Q'^2_1-Q'^2_2$ and $2Q'_1Q'_2$ belong to the same degenerate representation as the FOJT active modes and cubic terms $Q'^3_1-3Q'_1Q^2_2$ and $Q'^3_2-3Q'^2_1Q'_2$ belong to the remaining one of the three degenerate representations. Case 2: cubic terms $Q'^3_1-3Q'_1Q'^2_2$ and $Q'^3_2-3Q'^2_1Q'_2$ and the FOJT active modes belong to the same degenerate representation, and quadratic terms $Q'^2_1-Q'^2_2$ and $2Q'_1Q'_2$ belong to the remaining one of the three representations (see Table 1).

In Case 1 we have

$$\begin{aligned}\langle\psi'_{01}(Q'_1,0)|H'|\psi'_{01}(Q'_1,0)\rangle &= (b'_1-b'_2)Q'^2_1\\ \langle\psi'_{02}(Q'_1,0)|H'|\psi'_{02}(Q'_1,0)\rangle &= (b'_1+b'_2)Q'^2_1\end{aligned}\tag{17}$$

and

$$\begin{aligned} \langle \psi'_{01}(0, Q'_2)|H'|\psi'_{01}(0, Q'_2)\rangle &= (b'_1 + b'_2)Q'^2_2 \\ \langle \psi'_{02}(0, Q'_2)|H'|\psi'_{02}(0, Q'_2)\rangle &= (b'_1 - b'_2)Q'^2_2. \end{aligned} \tag{18}$$

It is noted that in this case the wavefunctions along Q'_1 are taken to be $\psi_{01}(Q'_1, 0)$ and $\psi_{02}(Q'_1, 0)$ and those along Q'_2 to be $\psi_{01}(0, Q'_2)$ and $\psi_{02}(0, Q'_2)$. Eqs. (17) and (18) show that there is no difference in energy between the potential energy curves along Q'_1 and Q'_2.

In Case 2 we have

$$\begin{aligned} \langle \psi'_{01}(Q'_1, 0)|H'|\psi'_{01}(Q'_1, 0)\rangle &= b'_1 Q'^2_1 + c'_2 Q'^3_1 \\ \langle \psi'_{02}(Q'_1, 0)|H'|\psi'_{02}(Q'_1, 0)\rangle &= b'_1 Q'^2_1 - c'_2 Q'^3_1 \end{aligned} \tag{19}$$

and

$$\begin{aligned} \langle \psi'_{0+}(0, Q'_2)|H'|\psi'_{0+}(0, Q'_2)\rangle &= b'_1 Q'^2_2 + c'_2 Q'^3_2 \\ \langle \psi'_{0-}(0, Q'_2)|H'|\psi'_{0-}(0, Q'_2)\rangle &= b'_1 Q'^2_2 - c'_2 Q'^3_2 \end{aligned} \tag{20}$$

Inspecting Eqs. (19) and (20), we arrive at the same conclusions as obtained in Case 1.

All the above results are summarized as follows. For the SO coupling modes of Type 1 in molecules with nondegenerate ground states, the FOJT active modes of Type 1, and the SO coupling modes of Type 2 in molecules with (doubly) degenerate ground states, the minimum of the potential energy should be located along Q_1 and Q'_1. In all other cases, the potential energy profiles between along Q_1 and Q_2 or between along Q'_1 and Q'_2 cannot be differentiated in the present third-order perturbational approximation. Our results are in qualitative agreement with the experimental facts that the distorted structures due to the FOJT or SOJT effects confirmed so far are always those brought about by the distortion along Q_1 or Q'_1.

4. The coefficients in the expansion of electronic energy in power series of Q_i including up to the third power

In order to apply the general theory obtained above to actual molecules, we need to estimate the possible values of the coefficients of the various powers (up to the third power) in the expansion of electronic energy in power series of the relevant mode Q_i. Using the perturbation theory (see Appendix), we can express the coefficients in terms of the zeroth-order wavefunctions and energies. In cases in which the ground state is doubly degenerate, the perturbed energy for ψ_{01} is given by

$$
\begin{aligned}
E(Q_i) = {} & E_0 + \left\langle \psi_{01} \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_{01} \right\rangle Q_i + \frac{1}{2}\left[\left\langle \psi_{01} \left| \left(\frac{\partial^2 H}{\partial Q_i^2}\right)_0 \right| \psi_{01} \right\rangle \right. \\
& \left. - 2 \sum_{n \neq 0} \frac{\left| \left\langle \psi_{01} \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_n \right\rangle \right|^2}{E_n - E_0} \right] Q_i^2 + \frac{1}{6}\left[\left\langle \psi_{01} \left| \left(\frac{\partial^3 H}{\partial Q_i^3}\right)_0 \right| \psi_{01} \right\rangle \right. \\
& - 3 \sum_{n \neq 0} \frac{ \left\langle \psi_{01} \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_n \right\rangle \left\langle \psi_n \left| \left(\frac{\partial^2 H}{\partial Q_i^2}\right)_0 \right| \psi_{01} \right\rangle + \left\langle \psi_{01} \left| \left(\frac{\partial^2 H}{\partial Q_i^2}\right)_0 \right| \psi_n \right\rangle \left\langle \psi_n \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_{01} \right\rangle }{E_n - E_0} \\
& \left. + 6 \sum_{n \neq 0} \sum_{m \neq 0} \frac{ \left\langle \psi_{01} \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_n \right\rangle \left\langle \psi_n \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_m \right\rangle \left\langle \psi_m \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_{01} \right\rangle }{(E_n - E_0)(E_m - E_0)} + 6A \right] Q_i^3
\end{aligned}
\tag{21}
$$

with term A is given by

$$
A = - \left\langle \psi_{01} \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_{01} \right\rangle \sum_{n \neq 0} \frac{ \left\langle \psi_{01} \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_n \right\rangle \left\langle \psi_n \left| \left(\frac{\partial H}{\partial Q_i}\right)_0 \right| \psi_{01} \right\rangle }{(E_n - E_0)^2} \tag{22}
$$

where ψ_{01} and ψ_{02} are the zeroth-order degenerate ground-state wavefunctions. The perturbed energy for ψ_{02} is obtained by replacing ψ_{01} with ψ_{02} in Eqs. (21) and (22). If the ground state is not degenerate, ψ_{01} and ψ_{02} are replaced by ψ_0, and the second term and term A should be deleted in Eq. (21). Eq. (21) thus obtained for the nondegenerate case is different in appearance from but essentially the same as the formula given by Salem [8].

In order to estimate the probable values of various matrix elements appearing in Eqs. (21) and (22) we fully use the selection rules based on the group theoretical argument.

Finally it is noted that the results obtained above hold also for excited states. For the lth excited states, ψ_0 or ψ_{01} and ψ_{02} should be replaced by ψ_l or ψ_{l1} and ψ_{l2}.

Appendix

In cases in which the ground state is doubly degenerate (ψ_{01} and ψ_{02}), it is shown by using the Rayleigh-Schrödinger perturbation theory [9] that in the perturbed energy for

ψ_{01} the following term B appears in addition to Eq. (21):

$$B=\sum_{m\neq 0}\sum_{n\neq 0}\frac{\langle\psi_{01}|V|\psi_m\rangle\langle\psi_m|V|\psi_{02}\rangle\langle\psi_{02}|V|\psi_n\rangle\langle\psi_n|V|\psi_{01}\rangle}{(E_m-E_0)(E_{01}^{(1)}-E_{02}^{(1)})(E_n-E_0)} \tag{A1}$$

where $E_{0j}^{(1)}=\langle\psi_{0j}|V|\psi_{0j}\rangle(j=1,2)$ and $V=(\partial H/\partial Q_i)_0Q_i$.

For the perturbed energy for ψ_{02} the additional term is $-B$. In Eq. (A1), if $\langle\psi_{01}|V|\psi_m\rangle$ is nonvanishing, $\langle\psi_m|V|\psi_{02}\rangle$ should vanish, and vice versa because in molecules treated in this paper, ψ_{01} and ψ_{02} are of opposite symmetry with respect to σ_v. Therefore, in Eq. (21) term B is omitted in both the degenerate and nondegenerate cases.

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