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ON THE JAHN-TELLER SPLITTING FOR THE $^2T_2$ STATE OF CH_4^+

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The magnitude of the Jahn-Teller splitting of the $^2T_2$ ionic state of methane was successfully calculated without determining the potential surface of the ionic state. This method can be easily applied to analyses of Jahn-Teller splittings observed in photoelectron spectroscopy.

Ejection of an electron from a fully occupied degenerate orbital in a molecule induces an orbitally degenerate doublet state of the corresponding ion. The degeneracy of such an ionic state can be lifted along the normal coordinate of nontotally symmetric vibrations.[1,2] This evidence called as Jahn-Teller (J-T) effect is certified in the photoelectron (PE) spectroscopy. In most cases the J-T split PE bands are broad and are overlapped severely, so that there are only a few studies on the J-T splittings and on the order of the J-T split ionic states.[3] The analyses of J-T distortions give an important and valuable information for the degenerate ionic states. For the Jahn-Teller distortion of CH_4^+, Dixon[4] calculated the vibronic potential surface of the $^2T_2$ state and force constants of ionic and neutral methane by an ab initio method, and estimated the J-T splittings and a spectral pattern for the PE spectrum of methane. However it seems to be somewhat laborious to apply this method to calculations of J-T splittings about various molecules because of taking account of the vibronic potential surface of the ionic state. We present a simpler calculation method to estimate the magnitude of J-T splittings obtained in various PE spectra. A procedure to calculate the J-T splitting is as follows: 1) A distorted coordinate of a maximum vibrational probability density is determined from force constants and vibrational frequencies obtained by a force gradient method for a neutral molecule. 2) The ab initio SCF MO calculations are carried out at this coordinate according to a semi-classical Franck-Condon approximation. 3) The ionization energies, that is, J-T splittings are obtained by assuming Koopmans' theorem.

The vibrational wavefunction of v" = 0 is usually given by

$$\Psi_0(Q_i) = (\gamma_i/\pi)^{1/4}\exp(-\gamma_i Q_i^2/2) \qquad (1)$$

where $\gamma_i = 4\pi^2\nu_i/h$, and ν_i and Q_i are a vibrational frequency (in s^{-1}) and a normal coordinate of J-T active vibration, respectively. For a doubly degenerate vibration (Q_{ix} and Q_{iy}), a vibrational probability density is expressed by $2\pi Q_i\Psi_0^2$, and a coordinate (Q_{im}) of the maximum density equals to $(2\gamma_i)^{-\frac{1}{2}}$, provided

$Q_i^2 = Q_{ix}^2 + Q_{iy}^2$ as a cylindrical symmetry.[5] For a triply degenerate vibration, Q_{im} equals to $\gamma_i^{-\frac{1}{2}}$. In order to obtain the Q_{im}, calculations of all vibrational frequencies for a molecule are carried out with the GF matrix method,[6] using force constants (F) obtained by a force gradient method.[7] An outline of the force gradient method is as follows. Assuming the potential curve near the equilibrium geometry as harmonic, total energy is given by

$$E = E_0 - \sum_i \phi_i Q_i + \frac{1}{2} \sum_{ij} F_{ij} Q_i Q_j \qquad (2)$$

where $\phi_i = -(\partial E/\partial Q_i)|_{Q_i=0}$ and $F_{ij} = \partial \phi_i / \partial Q_j$. The ϕ_i is the internal force and F_{ij} is the force constant. The ϕ_i was obtained analytically, whereas the F_{ij} was calculated numerically, using the following relation

$$F_{ij} = \{\phi_i(\Delta Q_j) - \phi_i(-\Delta Q_j)\}/(2\Delta Q_j) \qquad (3)$$

The position of $\phi_i = 0$ should correspond to the equilibrium geometry of a molecule and vibrational frequencies are calculated at the position. Programs JAMOL3[8] and GRAMOL[8] were used to calculate the ab initio SCF MO of methane and force constants, respectively, with basis set of MIDI4 + polarization function.[9]

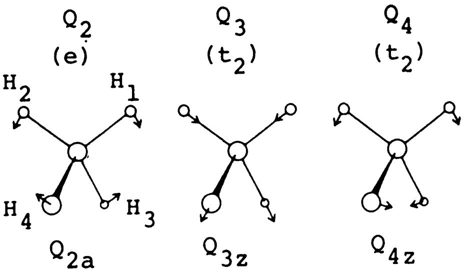

Fig. 1. Normal coordinates of CH_4.

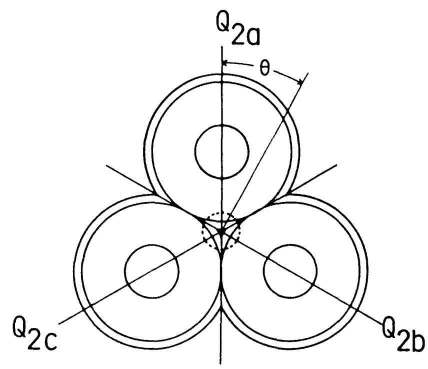

Fig. 2. Schematic contour lines of the lowest surface of CH_4^+. The dashed circle corresponds to Q_{2m} for CH_4.

The J-T active vibrations for $^2T_2$ state of methane are of one "e" and two "t_2" modes. The normal coordinates (Q) and certain elements of the vibrations are shown in Fig. 1. The normal coordinate of "e" mode is denoted by Q_2 which corresponds to a radial displacement in a xy plane expanded by Q_{2x} and Q_{2y} where exist three local minima[10] as shown in Fig. 2. The Q_{2a} shown in Fig. 1 is a displacement on an axis through one of the three minima. Then the geometry on the Q_{2a}, Q_{2b}, and Q_{2c} axis belongs to D_{2d} symmetry and the others to D_2. Both Q_3 and Q_4 are normal coordinates for two kinds of "t_2" mode and each component can be tentatively represented in terms of x, y, and z axis in the Cartesian coordinates. The Q_{3z} and Q_{4z} shown in Fig. 1 indicate displacements on z axes of Q_3 and Q_4 mode, respectively. The geometry on the x, y, and z axis belongs to C_{2v} and such as $|Q_{ix}| = |Q_{iy}| = |Q_{iz}|$ to C_{3v}.

The calculated vibrational frequencies for the J-T active vibrations are listed in Table 1, together with the Q_{im} and intramolecular coordinates (R_{im}). The C-H bond length obtained here is 1.091 Å for the equilibrium geometry of CH_4. The calculated frequencies are about 10% larger than experimental one[11] as usual. In order to determine bond lengths and angles at the most probable position of Q_{im}, normal coordinates must be transformed to the intramolecular coordinates shown in Table 1 by using the transformation matrix L which is an eigenvector of GF matrix. The intramolecular coordinates for the individual vibrational modes are summarized

Table 1. Calculated results of vibrational frequencies, most probable values of normal coordinate (Q_{im}) and intramolecular coordinate (R_m=LQ_m)[a] for the J-T active vibrations of methane

	Frequency / s^{-1}			Intramolecular coordinate / Å			
Mode	Calcd	Exptl[b]	Q_{im}	R_{1m}	R_{2m}	R_{3m}	R_{4m}
Q_2(e)	4.95×10^{13}	4.60×10^{13}	0.101	0.0	0.0	0.0923	-0.0923
$Q_3(t_2)$	9.86×10^{13}	9.05×10^{13}	0.101	-0.0752	0.0752	0.0111	-0.0111
$Q_4(t_2)$	4.30×10^{13}	3.92×10^{13}	0.153	-0.0032	0.0032	0.1540	-0.1540
		For all Q_{im}		-0.0783	0.0783	0.2573	-0.0727

a) Intramolecular coordinates are defined as follows: $R_1 = \sqrt{2}\delta r(C\text{-}H_1) = \sqrt{2}\delta r(C\text{-}H_2)$, $R_2 = \sqrt{2}\delta r(C\text{-}H_3) = \sqrt{2}\delta r(C\text{-}H_4)$, $R_3 = r\delta{<}H_1CH_2$, $R_4 = r\delta{<}H_3CH_4$. b) Ref. 11.

in Table 1. The calculations of ab initio SCF MO energies for methane at the Q_m displacements were carried out with the program of IMS version of GAUSSIAN 70 with the 4-31G basis set. All calculations were carried out at Computing Center, Hokkaido University. For the Q_2 mode, the MO energy diagram is shown in Fig. 3. The energy difference between the first and third MO energies scarcely depends on θ but the second MO energy changes largely from the 1st to 3rd MO's. Then, the spectrum should be indicated by the average over θ, so that the 2nd level may be located at the center of the three bands, which equals to the degenerate MO energy level.[12] Similar results were also obtained for the Q_3 and Q_4 modes. However the practical spectrum should be compared with the spectral pattern obtained by taking account of all displacements of the Q_2, Q_3, and Q_4 modes. Figure 4 shows the energy diagram for the angle θ in each combination of types I and IV listed in Table 2. Similar to the case of the Q_2 mode (Fig.3), the variation of the 2nd MO level largely depends on θ whereas the energy difference between the 1st and 3rd MO energy (ΔE)seems to be almost constant. Assuming that the averaged 2nd MO level equals to the degenerate MO's, we estimated the energy splitting between the 1st and 3rd MO's by the interpolation. The results are listed in Table 2 for some combinations of the Q_3 and Q_4 modes. The displacement of Q_{4z} was selected for the component of Q_4 because the results of ΔE are also reproduced in other selections for the

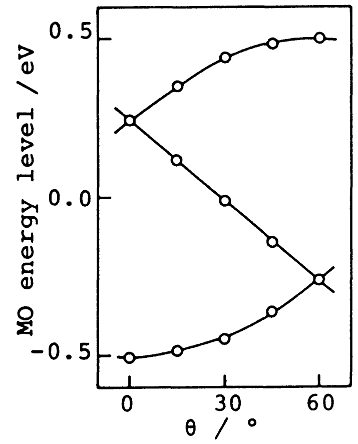

Fig. 3. Energy diagram of J-T split MO energies for the angle θ in Fig. 2.

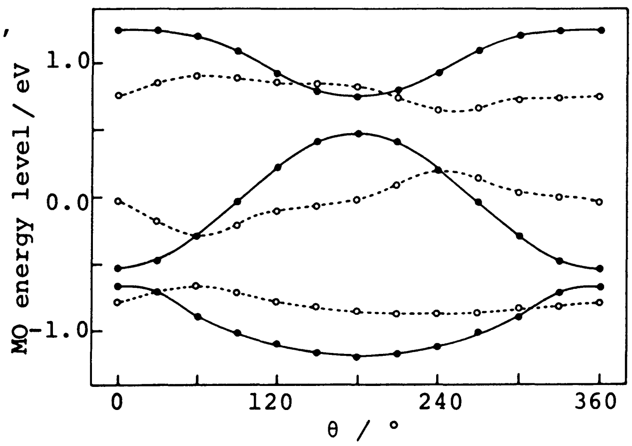

Fig. 4. Energy diagram of J-T split MO energies for θ in types I (—●—) and IV (···○···).

Table 2. The J-T splittings (ΔE) for combinations of Q_3 and Q_4

Type	Components of Q_3			Components of Q_4		MO energy / eV		J-T splitting	
	Q_{3x}	Q_{3y}	Q_{3z}	Q_{4x}, Q_{4y}	Q_{4z}	1st	3rd	ΔE	ΔE_{av}
I	0	0	Q_{3m}	0	Q_{4m}	-1.03	1.07	2.10	1.50
I'	0	0	$-Q_{3m}$	0	Q_{4m}	-0.48	0.42	0.90	
II	$\sqrt{1/2}Q_{3m}$	0	$\sqrt{1/2}Q_{3m}$	0	Q_{4m}	-0.97	0.97	1.94	1.51
II'	$\sqrt{1/2}Q_{3m}$	0	$-\sqrt{1/2}Q_{3m}$	0	Q_{4m}	-0.56	0.52	1.08	
III	$\sqrt{1/3}Q_{3m}$	$\sqrt{1/3}Q_{3m}$	$\sqrt{1/3}Q_{3m}$	0	Q_{4m}	-0.97	0.96	1.93	1.55
III'	$\sqrt{1/3}Q_{3m}$	$\sqrt{1/3}Q_{3m}$	$-\sqrt{1/3}Q_{3m}$	0	Q_{4m}	-0.61	0.56	1.17	
IV	Q_{3m}	0	0	0	Q_{4m}	-0.83	0.78	1.61	1.61

component of Q_4. Molecular geometries are unchanged by the plus and minus displcements of Q_{3m} for Q_{3x} and also by the interchange of Q_{3x} and Q_{3y} in types I, II,and IV. Since the experimental J-T splitting should correspond to the averaged value of all combinations, each mean value (E_{av}) in types I to III and the value in type IV may be compared with the experimental one. Figure 5 shows HeI PE spectrum of methane in the 12-17 eV region, which was measured with a photoelectron spectrometer (JASCO Ltd., model PE-1A).[13] This spectrum is in good agreement with previous ones.[14] We found three vertical ionization energies to be 13.6, 14.5,and 15.2 eV from the spectrum. The calculated results of the J-T splitting are in good agreement with the experimental ones.

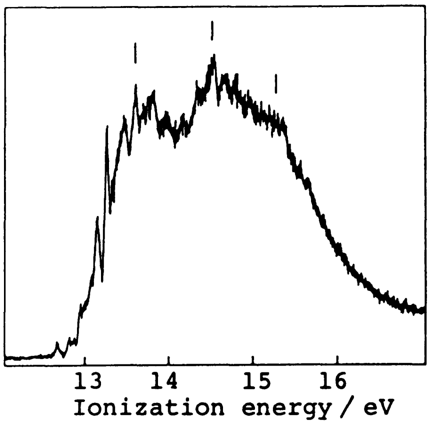

Fig. 5. HeI photoelectron spectrum of methane.

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