A theoretical study on the first ionic state of benzene with analysis of vibrational structure of the photoelectron spectrum

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Ab initio calculations have been performed to study the vibrational levels of the first ionic state ($^2E_{1g}$) of benzene. The equilibrium molecular structure and vibrational modes of the state are presented. The theoretical ionization intensity curve including the vibrational structure is also presented and compared with the photoelectron spectrum. A number of new assignments of the photoelectron spectra are proposed.

I. INTRODUCTION

The electronic configuration of the ground state of benzene is represented by a $...(3e_{1u})^4(1a_{2u})^2(3e_{2g})^4(1e_{1g})^4$ with the D_{6h} symmetry point group. The first ionic state of $^2E_{1g}$ is a doubly degenerate state. The molecular structure of the degenerated state should distort to those of the lower symmetric point group such as a D_{2h} symmetry by the Jahn–Teller distortion effect. The $^2E_{1g}$ state of the D_{6h} symmetry point group correlates to the $^2B_{2g}$ and $^2B_{3g}$ states of the D_{2h} symmetry point group. *Ab initio* calculation on the distorted molecular structure of the $^2B_{2g}$ and $^2B_{3g}$ states within the D_{2h} symmetry have been reported.[1,2]

The experimental investigation of cationic states of benzene have been performed by means of the 584 Å photoelectron (PE) spectra. The PE spectra have been observed in the energy range from 9.25 to 17.5 eV.[3–5] The first band was observed in the region from 9.25 to 10 eV. The PE spectra of the first band shows vibrational structure. The assignment of the vibrational structure has been discussed by Turner *et al.*[3] and Potts *et al.*[4] These assignments were based on the vibrational frequency of the ground state.

As a molecule is ionized, the equilibrium molecular structure and the vibrational mode are changed from those of the ground state. The vibrational structure of the PE spectrum reflects these changes. It is, therefore, interesting to investigate theoretically the vibrational structure associated with the change in the equilibrium molecular structure and the vibrational mode by ionization. The theoretical intensity of the band is obtained by the calculation of the Franck–Condon factor (FCF). FCF usually has a large value for the vibrational transitions to the totally symmetric modes of the cationic state. The a_{1g} and e_{2g} modes of the D_{6h} symmetry group correlate to the a_g totally symmetric modes of the D_{2h} symmetry group. There are two a_{1g} modes and four e_{2g} modes.

In this work, we studied the equilibrium molecular structure of the ground state and the lowest ionic state by using the *ab initio* self-consistent-field (SCF) method. Within the framework of the adiabatic approximation and the harmonic oscillator approximation, we calculated the harmonic force constant matrix elements over variables of the totally symmetric distortion of the D_{2h} symmetry and the vibrational frequencies of the totally symmetric modes. We obtained approximate theoretical intensity curves using the Franck–Condon factor (FCF) which was given by the square of the overlap integrals between the vibrational wave function of the ground state and that of the ionic state. Based on these calculations, we discuss the vibrational levels of the first band compared to the photoelectron spectrum.

II. METHOD OF CALCULATIONS

We used the basis sets of the MIDI-4-type prepared by Tatewaki and Huzinaga.[6] These were augmented by one p-type polarization function for H and one d-type polarization function for C. The exponents of the polarization function for H and C were 0.68 and 0.61, respectively.

The gradient technique for the Roothaan's restricted Hartree–Fock (RHF) method was employed to determine the optimum molecular structure of the ground state and the cationic states.

The single and double excitation configuration interaction (SDCI) method was employed to obtain more accurate ionization energies for the estimation of the vertical ionization energy (VIE) and adiabatic ionization energy (AIE). A single reference configuration of an SCF wave function of the respective state were employed. In the SDCI method, singly and doubly excited configuration state functions (CSFs) were generated where the inner shells were kept frozen. The generated CSFs were then restricted to the first-order interacting space.[7] The dimensions of the CI were too large (beyond 130 000), we have adopted a CSF selection process by the use of second-order perturbation theory. The threshold for the selection was 8 μhartree. We have reduced the dimensions of the CI about 17 000. We have estimated the total energy including the contribution from the rejected CSFs by a second-order perturbation theory.[8]

The harmonic force constant matrix elements were calculated by means of the gradient technique with an RHF wave function; the second derivative was estimated by the numerical differentiation of the analytically calculated first derivative. We calculated the FCFs of only the totally symmetric vibrational modes. In calculating FCFs, we approximated the vibrational wave functions by those obtained by the harmonic oscillator model. We assumed that the initial state was the zero-point vibrational level of the ground state. The method of calculation of the FCF and theoretical intensity curves was the same as we used in the previous paper.[9]

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TABLE I. Optimized molecular structure and magnitude of the change in the geometry by ionization.

State	C_1–C_2(ΔC_1–C_2)	C_2–C_3(ΔC_2–C_3)	C_1–H(ΔC_1–H)	C_2–H(ΔC_2–H)
^1A_g	1.388	1.388	1.083	1.083
Expt.[a]	1.397	1.397	1.084	1.084
$^2B_{2g}$	1.380(−0.008)	1.446(+0.058)	1.080(−0.003)	1.082(−0.001)
$^2B_{3g}$	1.425(+0.037)	1.357(−0.031)	1.083(0.000)	1.081(−0.002)

State	C_6–C_1–C_2(ΔC_6–C_1–C_2)	C_3–C_2–H(ΔC_3–C_2–H)
^1A_g	120.00	120.00
Expt.[a]	120.00	120.00
$^2B_{2g}$	118.05(−1.95)	118.39(−1.61)
$^2B_{3g}$	121.81(+1.81)	121.56(+1.56)

[a] Herzberg (Ref. 12). Bond lengths are in angstroms, angles in degrees. The values in parentheses are the magnitude of the change in geometry by ionization. Raghavachari *et al.* (Ref. 1) have obtained the following optimized geometries. For $^2B_{2g}$, C_1–C_2=1.386, C_2–C_3=1.447, C_1–H=1.070, C_2–H=1.072, C_6–C_1–C_2=119.65 and C_3–C_2–H=119.23. For $^2B_{3g}$, C_1–C_2=1.428, C_2–C_3=1.359, C_1–H=1.073, C_2–H=1.071, C_6–C_1–C_2=121.4, and C_3–C_2–H=121.4. Kato *et al.* (Ref. 2) have reported the following optimized geometries. For $^2B_{2g}$, C_1–C_2=1.382, C_2–C_3=1.445, C_1–H=1.069, C_2–H=1.072, C_6–C_1–C_2=118.9, and C_3–C_2–H=118.8. For $^2B_{3g}$, C_1–C_2=1.425, C_2–C_3=1.356, C_1–H=1.073, C_2–H=1.072, C_6–C_1–C_2=121.0, and C_3–C_2–H=123.4.

This work has been carried out by using the computer program system GRAMOL[10] for the gradient technique and the calculation of normal modes, and MICA3[11] for the CI calculations.

III. RESULTS AND DISCUSSION

The results of the optimized molecular structure of the ^1A_g, $^2B_{2g}$, and $^2B_{3g}$ states are listed in Table I. The numberring of each atom is illustrated in Fig. 1. The results are in good agreement with other calculations. Raghavachari *et al.*[1] reported the optimized geometries obtained by means of the UHF method with 6-31 G basis set. Kato *et al.*[2] obtained the optimized geometries at the UHF/4-31 G level. Their results are listed in the footnote of Table I.

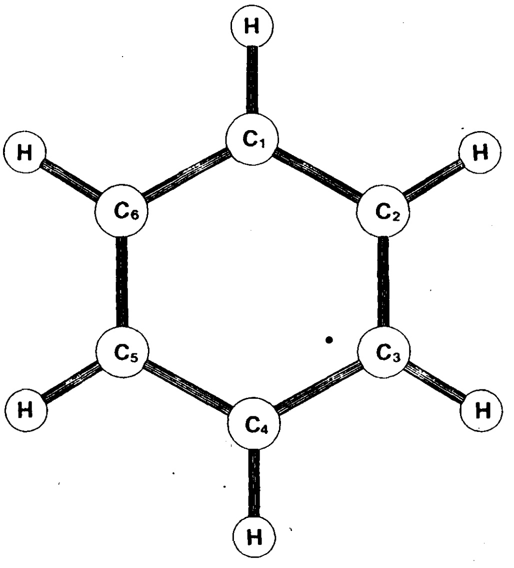

FIG. 1. A numberring of each atom.

A magnitude of the change in the geometry by ionization is shown in Table I. We find that there are obvious changes in the C–C bond distance. The bond length of the C_2–C_3 bond of the $^2B_{2g}$ state becomes longer. The bond lengths of the C_1–C_2 and C_2–C_3 bonds of the $^2B_{3g}$ state become longer and shorter, respectively. We also notice that the C–C–C and C–C–H bond angles change.

Table II shows the VIE and AIE at the SCF and SDCI levels. Although the structure of the $^2B_{2g}$ and $^2B_{3g}$ states are different from each other, the calculated AIE of the $^2B_{2g}$ and $^2B_{3g}$ states gives almost the same value at the SDCI level. Table II also shows the energy lowering of the equilibrium structure compared with the vertical ionized state. The energies lowering of the $^2B_{2g}$ and $^2B_{3g}$ states are 0.20 eV at the SDCI level.

Table III gives the vibrational frequencies of the six totally symmetric modes of the D_{2h} symmetry. The vibrational frequencies are arranged from ν_1 to ν_6 modes in order of magnitude. The calculated frequencies of the ground state are compared to the observed values. The calculated values are overestimated about 8.4%–11.8%. The vibrational frequencies of the $^2B_{2g}$ and $^2B_{3g}$ states are almost the same values compared to those of the ground state except for the ν_3 mode.

We characterized each mode by the use of the conventional potential energy distribution (Table IV) and the classical half-amplitude of the zero-point vibrational levels (Table

TABLE II. Ionization energies (eV).

	VIE[a]		AIE[a]		Δ(VIE−AIE)	
State	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2B_{2g}$	8.30	8.89	8.11	8.69	0.19	0.20
$^2B_{3g}$	8.28	8.88	8.08	8.68	0.20	0.20

[a] VIE: Vertical ionization energy: AIE: Adiabatic ionization energy. Total energies (a.u.) of ^1A_g: −230.442 437 (SCF) and −231.118 882 (SDCI).

TABLE III. Vibrational frequencies (cm^{-1}) of the totally symmetric modes of the point group D_{2h}.

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
${}^1A_g$	3369	3339	1788	1271	1079	660
Obs.[a]	3073	3056	1599	1178	995	608
${}^2B_{2g}$	3401	3381	1731	1280	1042	641
${}^2B_{3g}$	3401	3377	1828	1293	1041	637

[a] Herzberg (Ref. 12). The a_g modes of ν_1, ν_2, ν_3, ν_4, ν_5, and ν_6 (point group D_{2h}) correlate to the $\nu_1(a_{1g})$, $\nu_{15}(e_{2g})$, $\nu_{16}(e_{2g})$, $\nu_{17}(e_{2g})$, $\nu_2(a_{1g})$, and $\nu_{18}(e_{2g})$ modes (point group D_{6h}), respectively.

V). For the ${}^1A_g$ state, Table IV shows that the ν_1 and ν_2 modes are a mixture of the ΔS_3 and ΔS_4 symmetry coordinates which describe the C–H stretching motion. Table V shows that the ν_1 and ν_2 modes are in-phase modes and out-of-phase modes of the C–H stretching motion, respectively. The ΔS_1 and ΔS_2 symmetry coordinates which correspond to the C–C stretching motion contribute mainly to the ν_3 and ν_5 modes. Table V shows that the ν_3 and ν_5 modes are characterized as out-of-phase and in-phase C–C stretching modes, respectively. The ν_4 mode is the C–C–H bending mode, and the ν_6 mode is the C–C–C ring deformation mode. The character of the ν_3, ν_4, ν_5, and ν_6 modes of the ${}^2B_{2g}$ and ${}^2B_{3g}$ states are almost the same as those of the ground state. Although the phase of motion of the ν_1 and ν_2 modes are not changed, the conventional potential energy distribution of the ΔS_1 and ΔS_2 symmetry coordinates change according to the change of the bond length.

The 0–0 ionization energies and the FCF of the 0–0 vibrational transition are given in Table VI. The 0–0 ionization energies of the ${}^2B_{2g}$ and ${}^2B_{3g}$ states are the same values.

TABLE IV. Conventional potential energy distribution (%).

State	Component[a]	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
${}^1A_g$	ΔS_1	0.7	0.1	24.9	7.0	67.1	1.1
	ΔS_2	0.3	0.2	49.1	13.8	32.1	2.0
	ΔS_3	33.4	65.5	0.1	0.0	0.3	0.0
	ΔS_4	65.6	33.6	0.0	0.0	0.5	0.0
	ΔS_5	0.0	0.6	10.6	0.5	0.0	76.5
	ΔS_6	0.0	0.0	15.2	78.6	0.0	20.4
${}^2B_{2g}$	ΔS_1	0.9	0.0	32.2	17.7	47.8	0.7
	ΔS_2	0.1	0.3	36.9	9.2	49.5	3.1
	ΔS_3	67.5	31.8	0.2	0.0	0.3	0.0
	ΔS_4	31.5	67.4	0.0	0.0	0.6	0.0
	ΔS_5	0.1	0.5	10.7	0.9	0.9	75.3
	ΔS_6	0.0	0.0	20.0	72.1	0.9	20.9
B_{3g}	ΔS_1	0.4	0.2	17.1	1.6	79.9	1.6
	ΔS_2	0.6	0.1	59.3	17.3	17.9	1.3
	ΔS_3	11.4	87.5	0.1	0.0	0.3	0.0
	ΔS_4	87.5	11.6	0.2	0.0	0.5	0.0
	ΔS_5	0.1	0.6	9.2	0.3	0.7	77.0
	ΔS_6	0.0	0.0	14.0	80.8	0.7	20.1

The definitions of the total symmetrical coordinates are as follows: $\Delta S_1=(\Delta C_1-C_2+\Delta C_1-C_6+\Delta C_3-C_4+\Delta C_4-C_5)/2$;$\Delta S_2=(\Delta C_2-C_3+\Delta C_5-C_6)/\sqrt{2}$; $\Delta S_3=(\Delta C_2-H+\Delta C_4-H)/\sqrt{2}$;$\Delta S_4=(\Delta C_2-H+\Delta C_3-H+\Delta C_5-H+\Delta C_6-H)/2$; $\Delta S_5=(\Delta C_2-C_1-C_5+\Delta C_3-C_4-C_5)/\sqrt{2}$; and $\Delta S_6=(\Delta C_3-C_2-H+\Delta C_2-C_3-H+\Delta C_6-C_5-H+\Delta C_5-C_6-H)/2$.

TABLE V. Classical half-amplitude of the zero-point vibrational levels.

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
${}^1A_g$	ΔC_1-C_2	−0.004	−0.001	0.017	−0.007	0.020	0.002
	ΔC_2-C_3	−0.004	0.003	−0.034	0.014	0.020	−0.005
	ΔC_1-H	0.043	0.060	0.002	−0.000	0.002	0.000
	ΔC_2-H	0.042	−0.030	−0.001	0.000	0.002	−0.000
	$\Delta C_6-C_1-C_2$	0.0	0.5	−1.7	0.3	−0.0	3.0
	ΔC_3-C_2-H	−0.0	−0.0	2.0	3.6	−0.0	1.6
${}^2B_{2g}$	ΔC_1-C_2	−0.004	0.000	0.018	−0.011	0.016	0.002
	ΔC_2-C_3	−0.002	−0.004	−0.032	0.013	0.027	−0.006
	ΔC_1-H	0.060	−0.041	0.003	−0.001	0.002	−0.000
	ΔC_2-H	0.029	0.043	−0.000	−0.001	0.002	0.000
	$\Delta C_6-C_1-C_2$	0.2	−0.5	−1.7	0.4	0.3	3.0
	ΔC_3-C_2-H	−0.0	0.0	2.2	3.4	0.3	1.6
${}^2B_{3g}$	ΔC_1-C_2	−0.003	−0.002	0.015	−0.004	0.023	0.003
	ΔC_2-C_3	−0.005	0.002	−0.035	0.015	0.014	−0.004
	ΔC_1-H	0.025	0.069	0.002	0.000	0.002	−0.000
	ΔC_2-H	0.049	−0.018	−0.002	0.001	0.002	0.000
	$\Delta C_6-C_1-C_2$	−0.1	0.5	−1.6	0.2	−0.3	3.0
	ΔC_3-C_2-H	0.0	−0.0	1.9	3.6	−0.3	1.6

Bond lengths are in angstroms, angles in degrees.

The FCFs are so large that the 0–0 transitions are able to be observed.

Using the 0–0 IEs from the SDCI energies and vibrational frequencies and FCFs, we obtained the theoretical intensity curve of ionization by assuming a half-width of 0.08 eV for each transition band. The result is illustrated in Fig. 2. It is compared with the observed PE spectrum by Turner *et al.*[3] The theoretical intensity curve imitates well the vibrational structure of the observed PE spectrum except for the magnitude of the fourth peak.

In order to discuss the more detailed vibrational structure of each band, we illustrate the theoretical intensity curve with a half-width of 0.02 eV for each state. The theoretical intensity curves for the ${}^2B_{2g}$ and ${}^2B_{3g}$ states are illustrated in Figs. 3 and 4, respectively. Although a molecule distorts to the different geometry by the Jahn–Teller distortion, the theoretical vibrational structure of the two states coincides with each other.

The assignment of the vibrational structure of the ${}^2B_{2g}$ and ${}^2B_{3g}$ states are shown in Tables VII and VIII, respectively. The intensity of transition is classified into S(strong), M(medium), or W(weak) according to the magnitude of FCF. The assignment by Turner *et al.* and Potts *et al.* are listed in Table IX. We must note that the present notation of the mode is different from their notation. They used the notation of ν_2, ν_{17}, and ν_{18} of the D_{6h} point group. We change it to the notation of ν_5, ν_4, and ν_6 of the D_{2h} point group.

TABLE VI. 0–0 ionization levels.

State	0–0 IE[a]	FCF
${}^2B_{2g}$	8.69	0.233
${}^2B_{3g}$	8.69	0.225

[a] Observed 0–0 IE is 9.25 (Refs. 3 and 4).

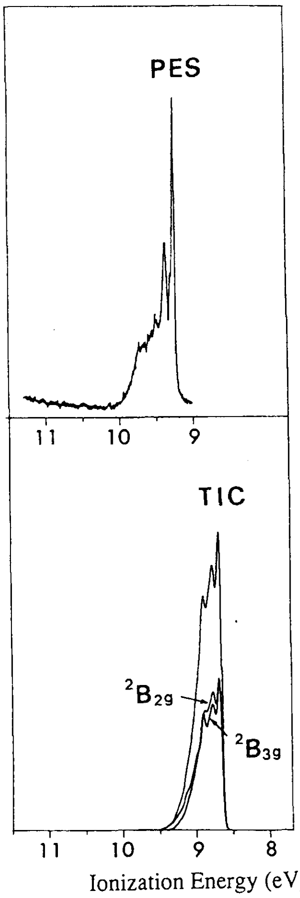

FIG. 2. The theoretical intensity curves of ionization of the $^2E_{1g}$ state with a half-width of 0.08 eV and the observed photoelectron spectrum by Potts *et al.* (Ref. 3). TIC: Theoretical intensity curve; PES: PE spectrum.

The first strong peak is the 0–0 transition. The second peak is the vibrational (0 0 0 0 0 1) level. The present assignment of the second peak is consistent with that of Turner *et al.* and Potts *et al.* Turner *et al.* discussed another possibility of the (0 0 0 1 0 0) level. In the present calculation, this level contributes to the third peak and it has weak intensity. The observed frequency were 610 cm^{-1} by Turner *et al.* and 670 cm^{-1} by Potts *et al.* The calculated frequencies of the ν_6 mode of the $^2B_{2g}$ and $^2B_{3g}$ states are 637 and 641 cm^{-1}, respectively. The ν_6 mode is characterized as a mixture of the C–C–C and C–C–H bending motions. This mode corresponds to the ν_{18} mode (e_{2u}) of the ground state. The vibrational excitation of the ν_6 mode associates to the molecular distortion of the C–C–C and C–C–H bond angle by the Jahn–Teller effect (see Tables I and V).

The third peak of the theoretical intensity curve corresponds to the (0 0 0 0 0 2) and (0 0 0 0 1 0) vibrational levels. The intensity of the (0 0 0 0 1 0) vibrational level are larger than that of the (0 0 0 0 0 2) level by 1.4 times. Turner *et al.* and Potts *et al.* assigned the third peak only to the (0 0 0 0 1 0) level. The frequencies obtained by Turner *et al.* and Potts *et al.* were 930 and 970 cm^{-1}, respectively. The calculated frequencies of the ν_5 mode of the $^2B_{2g}$ and $^2B_{3g}$ states are 1041 and 1042 cm^{-1}, respectively. The vibrational excitation of the ν_5 mode corresponds to the change of the C_1–C_2 and C_2–C_3 bond distance. This change is out of phase, whereas the ν_5 mode causes in phase change.

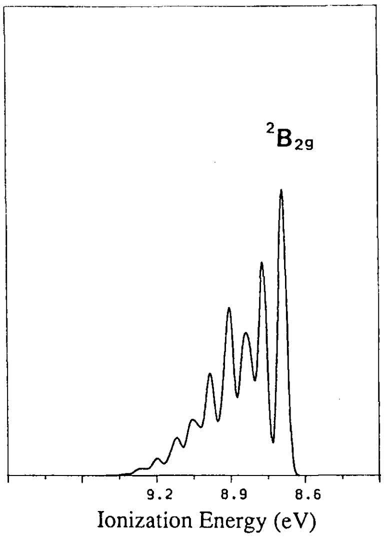

FIG. 3. The theoretical intensity curves of ionization of the $^2B_{2g}$ state with a half-width of 0.02 eV.

The fourth peaks are assigned mainly to the (0 0 0 0 1 1) and (0 0 1 0 0 0) levels. The theoretical intensity of this peak is larger than that of the third peak, whereas the observed intensity of the fourth peak is smaller than that of the third peak. Potts *et al.* found the weak band peak at 9.407 eV which was missed by Turner *et al.* The present fourth band should correspond to the fourth and fifth bands assigned by Potts *et al.* The large intensity of the present calculation may be caused by a calculational error of frequency and by overlapping several vibrational levels of nearly the same ionization energy. Turner *et al.* assigned the fourth band to the (0 0

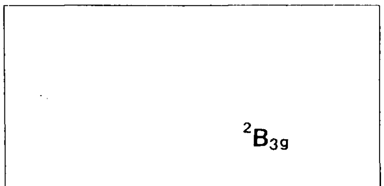

FIG. 4. The theoretical intensity curves of ionization of the $^2B_{3g}$ state with a half-width of 0.02 eV.

TABLE VII. Assignment of each peak of the $^2B_{2g}$ state.

No.[a]	IE	Vibrational levels			
1	8.69	S(0 0 0 0 0 0)			
2	8.77	S(0 0 0 0 0 1)			
3	8.82–8.85	M(0 0 0 0 0 2),	S(0 0 0 0 1 0),		W(0 0 0 1 0 0)
4	8.90–8.95	W(0 0 0 0 0 3),	M(0 0 0 0 1 1), W(0 0 0 0 2 0)	M(0 0 1 0 0 0),	W(0 0 0 1 0 1)
5	8.98–9.03		W(0 0 0 0 1 2),	M(0 0 1 0 0 1), W(0 0 1 0 1 0)	W(0 0 0 1 0 2)
6	9.06			W(0 0 1 0 0 2)	
7	9.11			W(0 0 1 0 1 1)	

[a]No.: Numbering of peak. IE: Ionization energy. Intensity is classified into S, M, or W according to magnitude of FCF as follows: S:0.08<FCF<0.23; M:0.03<FCF<0.07; or W:0.008<FCF<0.03.

0 0 1 1) or (0 0 0 1 1 0) level. The theoretical calculation shows that the FCF of the (0 0 0 1 1 0) level is smaller than 0.008. Potts *et al.* assigned the fourth band to the (0 0 0 1 0 0) level. The theoretical intensity of this level is weak. The fourth and fifth bands found by Potts *et al.* should be assigned by using the (0 0 0 0 1 1) and (0 0 1 0 0 0) levels which have large intensity. However, in our present level of calculation, we are not able to establish their assignment. The ν_3 mode contributes to intensity. The contribution on this mode was missed by Turner *et al.* and Potts *et al.* The ν_3 mode of the $^2B_{3g}$ state has a particularly large contribution to intensity. The character of the ν_3 mode is the out-of-phase mode of the C_1-C_2 and C_2-C_3 bond stretching motion. This situation is connected by the change in the C_1-C_2 and C_2-C_3 bond distances whose distortion is out of phase.

The fifth peak is assigned to the (0 0 0 1 0 1) level. This peak corresponds to the sixth peak by Potts *et al.* who assigned it to the (0 0 0 0 2 0) level. Turner *et al.* also assigned the fifth peak to the (0 0 0 0 2 0) level. The theoretical intensity of this level is smaller than that of the (0 0 0 1 0 1) level by 0.2 times. Therefore, the contribution of this level to intensity should be neglected.

We assign the sixth peak to the (0 0 1 0 0 2) level of the $^2B_{2g}$ and $^2B_{3g}$ states. It is also assigned to (0 0 1 1 0 0) and (0 0 1 0 1 0) levels of the $^2B_{3g}$ state. This peak was assigned to the (0 0 0 0 2 1) level by Turner *et al.* and Potts *et al.* However, the calculated FCF of this level is smaller by 0.008.

The seventh peak was assigned to the (0 0 0 0 3 0) level by Turner *et al.* The FCF of this level is smaller than 0.008. We assign it to the (0 0 1 0 1 1) level of the $^2B_{2g}$ and $^2B_{3g}$ states and the (0 0 2 0 0 0) level of the $^2B_{3g}$ state.

IV. CONCLUSIONS

Within the D_{2h} symmetry point group, we calculated the equilibrium molecular structure of the $^2B_{2g}$ and $^2B_{3g}$ states by the Jahn–Teller distortion of the $^2E_{1g}$ state. We also calculated the vibrational frequencies of totally symmetric modes. We obtained the theoretical intensity curve. Although a molecule distorts to the different geometry, the theoretical vibrational structure of the two states coincides with each other. It imitates well the vibrational structure of the observed PE spectrum except for the magnitude of the fourth peak.

The present assignment of the vibrational structure is listed in Tables VII and VIII. We discuss the assignment of the vibrational structure compared with that by Turner *et al.* and Potts *et al.* They were assigned by using the ν_2, ν_{17}, and ν_{18} modes of the D_{6h} point group whose modes are correlated to the ν_5, ν_4, and ν_6 of the D_{2h} point group, respectively. The present calculation shows that the ν_5 and ν_6 modes contribute to intensity at the lower energy side and that the contribution of the ν_4 mode is small. We find that the ν_3 mode contributes to intensity at the higher energy side. The ν_3 mode correlates to the ν_{16} mode of the D_{2h} point

TABLE VIII. Assignment of each peak of the $^2B_{3g}$ state.

No.[a]	IE	Vibrational levels			
1	8.69	S(0 0 0 0 0 0)			
2	8.77	S(0 0 0 0 0 1)			
3	8.82–8.85	M(0 0 0 0 0 2),	S(0 0 0 0 1 0)		W(0 0 0 1 0 0)
4	8.90–8.95	W(0 0 0 0 0 3),	M(0 0 0 0 1 1), W(0 0 0 0 2 0)	S(0 0 1 0 0 0),	W(0 0 0 1 0 1)
5	8.98–9.01		W(0 0 0 0 1 2),	M(0 0 1 0 0 1),	W(0 0 0 1 0 2)
6	9.05–9.08		W(0 0 1 0 0 2),	W(0 0 1 1 0 0),	 W(0 0 1 0 1 0)
7	9.12–9.14			W(0 0 2 0 0 0),	W(0 0 1 0 1 1)
8	9.22			W(0 0 2 0 0 1)	

[a]No.: Numbering of peak. IE: Ionization energy. Intensity is classified into S, M, or W according to magnitude of FCF as follows: S:0.08<FCF<0.23; M:0.03<FCF<0.07, or W:0.008<FCF<0.03.

TABLE IX. Assignment of each peak by Turner *et al.* (Ref. 3) and Potts *et al.* (Ref. 4).

Turner *et al.*			Potts *et al.*		
No.[a]	Separation levels (cm^{-1})		No.	Separation levels (cm^{-1})	
1		(0 0 0 0 0 0)	1		(0 0 0 0 0 0)
2	610	(0 0 0 0 0 1) or(0 0 0 1 0 0)	2	670	(0 0 0 0 0 1)
3	930	(0 0 0 0 1 0)	3	970	(0 0 0 0 1 0)
			4	1220	(0 0 0 1 0 0)
4		(0 0 0 0 1 1) or(0 0 0 1 1 0)	5		(0 0 0 0 1 1)
5		(0 0 0 0 2 0)	6		(0 0 0 0 2 0)
6		(0 0 0 0 2 1) or(0 0 0 1 2 0)	7		(0 0 0 0 2 1)
7		(0 0 0 0 3 0)			

[a] No.: Numbering of peak. Separation: *A* separation of the peak from the band origin. The ν_4, ν_5, and ν_6 modes of the D_{2h} point group correlate to the ν_{17}, ν_2, and ν_{18} modes of the D_{6h} point group, respectively.

group. The character of the ν_3 mode is the out-of-phase mode of the C_1–C_2 and C_2–C_3 bond stretching motion. The ν_3 mode of the $^2B_{3g}$ state has a particularly large contribution to intensity. This situation is connected to the change in the C_1–C_2 and C_2–C_3 bond distances of the $^2B_{3g}$ state whose distortion is out of phase.

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