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A theoretical study on the ionization of thiophene with analysis of vibrational structure of the photoelectron spectra

Kouichi Takeshita [a], Yuichi Yamamoto [b]

[a] *Faculty of Bioindustry, Tokyo University of Agriculture, Abashiri, Hokkaido 099-24, Japan*
[b] *The Center for Information Processing Education of Hokkaido University, Sapporo 060, Japan*

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A theoretical study on the ionization of thiophene with analysis of vibrational structure of the photoelectron spectra

Kouichi Takeshita [a], Yuichi Yamamoto [b]

[a] *Faculty of Bioindustry, Tokyo University of Agriculture, Abashiri, Hokkaido 099-24, Japan*
[b] *The Center for Information Processing Education of Hokkaido University, Sapporo 060, Japan*

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Abstract

Ab initio calculations have been performed to study the molecular structures and the vibrational levels of the low-lying ionic states ($^2A_2$, $^2B_1$, $^2A_1$ and $^2B_2$) of thiophene. The equilibrium molecular structures and vibrational modes of these states are presented. The theoretical ionization intensity curves including the vibrational structures of the two low-lying ionic states are also presented and compared with the photoelectron spectrum. Several new assignments of the photoelectron spectra are proposed.

1. Introduction

The electronic configuration of the ground state of thiophene is represented by $\ldots(6b_2)^2\ (10a_1)^2\ (7b_2)^2\ (2b_1)^2\ (11a_1)^2\ (3b_1)^2\ (1a_2)^2$.

The photoelectron (PE) spectroscopy investigations of thiophene have been reported by many workers [1–8]. The first band from 8.9 to 9.8 eV contains the $^2A_2$ and $^2B_1$ states. The $^2A_2$ state shows well resolved vibrational structures. The assignment of the vibrational levels was tried by Derrick et al. [3]. They interpreted the vibrational structure by taking account of the vibrational frequencies of the ground state. The spectrum of the $^2B_1$ state overlaps the tail of that of the $^2A_2$ state. The spectrum shows no vibrational structure. The second band of the 12–16 eV region contains several electronic states.

Theoretical approaches on thiophene have been reported [9,10]. However, no study on the molecular structure of the ionic states and the assignment of the vibrational structure of the PE spectrum has been reported.

When a molecule is ionized, the equilibrium molecular structure and the character of the vibrational mode should change from those of the ground state. The vibrational structure of the PE spectrum reflects these changes. It is, therefore, interesting to investigate the vibrational structure associated with the change in the equilibrium molecular structure and the vibrational mode by ionization.

In this work, we determine the equilibrium molecular structures of the ground and lower ionic states 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 and the vibrational frequencies of the totally symmetric modes. We obtained approximate theoretical intensity curves using the Franck–Condon factor (FCF), which is given by the square of the overlap integrals between the vibrational wavefunction of the ground state and that of the ionic state. Based on these calculations, we discuss the

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vibrational levels of the low-lying ionic states compared to the photoelectron spectrum.

2. Methods of calculation

We used the basis sets of the MIDI-4-type prepared by Tatewaki and Huzinaga [11,12]. These were augmented by one p-type polarization function for H and one d-type polarization function for C and S. The exponents of the polarization function for H, C and S are 0.68, 0.61 and 0.46, respectively.

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

The single and double excitation configuration interaction (SDCI) method was used to get more accurate vertical ionization energy (VIE) and adiabatic ionization energy (AIE). A single reference configuration of the SCF wave function of the respective state was used. 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 [13]. The dimensions of the CI were too large; we used a CSF selection process by a second-order perturbation theory. The threshold for the selection was 8 μhartree. The number of generated CSFs was reduced from about 200000 to 15000. We estimated the total energy including the contribution from the rejected CSFs by a second-order perturbation theory [14]. The harmonic force constant matrix elements were calculated by the gradient technique with the 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 [15].

This work was carried out using the computer program system GRAMOL [16] for the gradient technique and the calculation of normal modes, and MICA3 [17] for the CI calculations.

3. Results and discussion

Table 1 shows the optimized geometrical parameters of the ground and ionic states. The numbering of each atom is illustrated in Fig. 1. The optimized geometric parameters of the ground state are in good agreement with the experimental ones [18]. Table 1 also shows

Table 1
Optimized molecular structure of thiophene and magnitude of the change in the geometry by ionization

State	$S–C_2(\Delta S–C_2)$	$C_2–C_3(\Delta C_2–C_3)$	$C_2–H(\Delta C_2–H)$	$C_3–H(\Delta C_3–H)$
$^1A_1$	1.729	1.349	1.079	1.081
exp.[a]	1.714	1.370	1.078	1.081
$^2A_2$	1.716(−0.012)	1.411(+0.061)	1.083(+0.004)	1.081(−0.001)
$^2B_1$	1.744(+0.016)	1.335(−0.014)	1.079(+0.000)	1.082(+0.001)
$^2A_1$	1.781(+0.052)	1.333(−0.016)	1.078(−0.001)	1.084(+0.003)
$^2B_2$	1.905(+0.176)	1.317(−0.032)	1.093(+0.014)	1.083(+0.002)
State	$C_2–S–C_5(\Delta C_2–S–C_5)$	$S–C_2–C_3(\Delta S–C_2–C_3)$	$S–C_2–H(\Delta S–C_2–H)$	$C_2–C_3–H(\Delta C_2–C_3–H)$
$^1A_1$	91.26	111.81	120.39	123.58
exp.[a]	92.2	111.5	119.8	123.3
$^2A_2$	89.70(−1.56)	113.31(+1.50)	120.67(+0.28)	122.68(−0.90)
$^2B_1$	93.63(+2.37)	109.88(−1.93)	120.03(−0.36)	123.89(+0.31)
$^2A_1$	98.50(+7.24)	103.01(−8.80)	120.80(+0.41)	120.38(−3.20)
$^2B_2$	80.68(−10.58)	116.88(+5.07)	100.73(−19.66)	121.81(−1.77)

[a] Nygaard et al. [18].

Bond lengths are in angstroms, angles in degrees. The values in parentheses are the magnitude of the change in geometry by ionization.

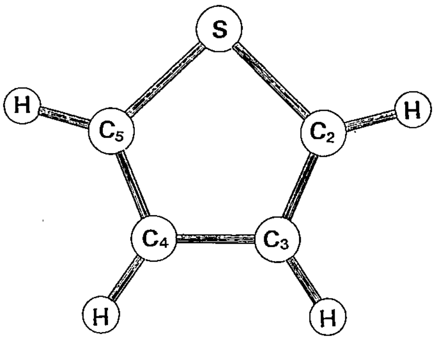

Fig. 1. Numbering of each atom.

Table 2
Ionization energies (eV) of thiophene

State	VIE		AIE		Δ(VIE–AIE)	
	SCF	SDCI	SCF	SDCI	SCF	SDCI
$^2A_2$	8.06	8.65	7.78	8.33	0.28	0.32
$^2B_1$	8.52	8.98	8.42	8.91	0.10	0.07
$^2A_1$	11.42	11.77	10.89	11.32	0.53	0.45
$^2B_2$	13.23	13.32	12.08	12.48	1.15	0.84

Total energies (au) of $^1A_1$: −550.687022(SCF) and −551.277283(SDCI).

Table 3
0–0 ionization levels of thiophene

State	0–0 IE	FCF
$^2A_2$	8.34	0.155
$^2B_1$	8.90	0.425
$^2A_1$	11.32	0.003
$^2B_2$	12.48	0.000

the magnitude of the change in the equilibrium molecular structure by ionization.

Table 2 shows the VIE and AIE at the SCF and SDCI levels. In the SDCI calculations, the weight of the reference function of the $^1A_1$, $^2A_2$, $^2B_1$, $^2A_1$ and $^2B_2$ states at the optimized geometry are 85.4, 85.5, 85.3, 85.1 and 84.8%, respectively. Table 2 shows the energy lowering of the AIE compared with the VIE. The energy lowering of the $^2A_2$ and $^2B_1$ states at the SDCI level are 0.32 and 0.07 eV, respectively, while those of the $^2A_1$ and $^2B_2$ states are 0.45 and 0.84 eV, respectively.

The 0–0 ionization energies and the FCFs of the 0–0 transitions are listed in Table 3. The FCF of the $^2A_2$ state is so large that the 0–0 transition should be observed. Derrick et al. reported that the observed 0–0 band of the $^2A_2$ state was 8.9 eV. The present calculated value underestimates by 0.56 eV in comparison with their value. The $^2A_1$ state should contribute to the beginning region of the second band. However, the zero-point vibrational level of the $^2A_1$ state should not be observed, because the FCF is negligibly small.

The vibrational frequencies of the ground and ionic states are shown in Table 4. The frequencies are arranged in order of magnitude. Compared with the observed values [19] of the $^1A_1$ state, we overestimate the frequencies by 5.8–13.0%. Each mode is characterized by using the conventional potential energy distribution (PED) and the classical half amplitude of the zero-point vibrational level. Table 5 shows the PED, which is described using the totally symmetrical displacement coordinate. The classical half amplitude is shown in Table 6.

For the interpretation of each mode of the $^1A_1$ state, Table 5 shows that the ΔS_3 and ΔS_4 totally symmetrical displacement coordinates contribute mainly to the PED of the ν_1 and ν_2 modes, respectively. The ΔS_3 and ΔS_4 coordinates are connected to the C_2–H (and C_5–H) and

Table 4
Vibrational frequencies (cm^{-1}) of thiophene

State	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
$^1A_1$	3415	3381	1586	1509	1179	1101	880	654
obs. [a]	3108	3084	1404	1358	1079	1032	832	604
$^2A_2$	3415	3396	1643	1459	1204	1145	911	661
$^2B_1$	3429	3400	1681	1429	1198	1037	810	614
$^2A_1$	3457	3366	1597	1409	1156	1053	738	552
$^2B_2$	3377	3268	1724	1417	1120	1088	573	470

[a] Herzberg [19].

Table 5
Conventional potential energy distribution (%) of thiophene

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
$^1A_1$	ΔS_1	0.2	0.0	0.5	11.0	0.4	1.6	38.3	6.6
	ΔS_2	0.8	0.1	43.7	7.1	12.5	4.0	0.3	0.0
	ΔS_3	84.3	11.8	0.2	0.0	0.0	0.1	0.0	0.0
	ΔS_4	11.2	85.8	0.0	0.2	0.0	0.4	0.0	0.0
	ΔS_5	2.0	0.2	23.6	12.6	1.2	22.1	7.7	61.1
	ΔS_6	1.4	2.0	20.9	19.6	0.0	29.6	52.1	32.2
	ΔS_7	0.0	0.0	2.9	24.9	47.5	18.7	1.4	0.1
	ΔS_8	0.0	0.1	8.1	24.5	38.4	23.5	0.2	0.0
$^2A_2$	ΔS_1	0.0	0.3	2.6	8.4	2.2	0.3	42.3	3.5
	ΔS_2	0.5	0.1	6.0	27.9	0.0	35.2	0.1	0.0
	ΔS_3	13.4	79.6	0.0	0.1	0.1	0.1	0.1	0.0
	ΔS_4	85.3	12.6	0.4	0.0	0.2	0.2	0.0	0.0
	ΔS_5	0.5	2.5	0.3	36.4	9.7	37.9	4.1	58.9
	ΔS_6	0.1	4.7	61.3	3.8	1.3	1.0	51.6	37.6
	ΔS_7	0.0	0.0	2.5	23.3	2.6	24.0	1.7	0.1
	ΔS_8	0.0	0.1	27.0	0.0	84.0	1.2	0.2	0.0
$^2B_1$	ΔS_1	0.2	0.0	0.6	6.7	0.1	3.0	30.7	13.3
	ΔS_2	1.1	0.1	52.6	6.0	7.4	9.3	0.4	0.0
	ΔS_3	82.8	13.6	0.3	0.0	0.0	0.2	0.0	0.0
	ΔS_4	13.0	84.4	0.1	0.2	0.0	0.6	0.0	0.0
	ΔS_5	1.8	0.2	20.9	7.5	0.1	20.0	9.7	64.6
	ΔS_6	1.2	1.7	16.5	14.3	0.2	44.3	58.8	21.9
	ΔS_7	0.0	0.0	2.5	31.7	47.7	15.4	0.4	0.2
	ΔS_8	0.0	0.1	6.6	33.8	44.5	7.4	0.0	0.1
$^2A_1$	ΔS_1	0.2	0.0	0.0	5.4	0.1	0.2	22.6	20.5
	ΔS_2	0.9	0.3	53.0	7.4	1.8	8.2	0.6	0.2
	ΔS_3	94.4	1.0	0.4	0.1	0.0	0.1	0.0	0.0
	ΔS_4	0.8	97.7	0.0	0.1	0.0	0.5	0.0	0.0
	ΔS_5	1.8	0.0	20.3	10.7	0.9	15.5	16.1	63.9
	ΔS_6	1.7	1.0	19.1	17.2	0.2	38.8	60.4	14.9
	ΔS_7	0.0	0.0	1.5	23.5	49.1	33.4	0.0	0.5
	ΔS_8	0.0	0.1	5.7	35.7	48.0	3.3	0.1	0.0
$^2B_2$	ΔS_1	0.0	0.0	1.2	5.3	0.9	1.4	4.0	42.6
	ΔS_2	0.8	1.2	58.5	5.2	3.8	6.7	0.1	0.1
	ΔS_3	2.3	90.8	0.9	0.5	0.0	0.1	0.0	0.1
	ΔS_4	96.4	2.5	0.1	0.1	0.0	0.5	0.0	0.0
	ΔS_5	0.2	3.2	20.9	7.4	0.7	26.8	35.2	55.0
	ΔS_6	0.4	2.2	12.3	28.2	2.5	18.9	60.0	2.1
	ΔS_7	0.0	0.1	1.6	20.9	43.6	34.4	0.6	0.0
	ΔS_8	0.0	0.0	4.6	32.4	48.5	11.4	0.1	0.1

The definitions of the totally symmetrical displacement coordinates are as follows:
$\Delta S_1 = (\Delta\text{S–C}_2 + \Delta\text{S–C}_5)/\sqrt{2}$,
$\Delta S_2 = (\Delta\text{C}_2\text{–C}_3 + \Delta\text{C}_5\text{–C}_4)/\sqrt{2}$,
$\Delta S_3 = (\Delta\text{C}_2\text{–H} + \Delta\text{C}_5\text{–H})/\sqrt{2}$,
$\Delta S_4 = (\Delta\text{C}_3\text{–H} + \Delta\text{C}_4\text{–H})/\sqrt{2}$,
$\Delta S_5 = \Delta\text{C}_2\text{–S–C}_5$,
$\Delta S_6 = (\Delta\text{S–C}_2\text{–C}_3 + \Delta\text{S–C}_5\text{–C}_4)/\sqrt{2}$,
$\Delta S_7 = (\Delta\text{S–C}_2\text{–H} + \Delta\text{S–C}_5\text{–H})/\sqrt{2}$,
$\Delta S_8 = (\Delta\text{C}_2\text{–C}_3\text{–H} + \Delta\text{C}_5\text{–C}_4\text{–H})/\sqrt{2}$.

Table 6
Classical half amplitude of the zero-point vibrational levels

State	Component	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
$^1A_1$	$\Delta S\text{–}C_2$	−0.003	0.001	0.004	−0.015	−0.002	−0.003	0.037	0.023
	$\Delta C_2\text{–}C_3$	−0.005	−0.002	−0.038	0.012	−0.012	−0.005	−0.003	−0.000
	$\Delta C_2\text{–}H$	0.068	−0.025	−0.003	0.001	−0.001	−0.001	0.001	0.000
	$\Delta C_3\text{–}H$	0.025	0.069	−0.001	0.003	−0.001	−0.002	0.001	0.000
	$\Delta C_2\text{–}S\text{–}C_5$	−0.3	0.1	−1.1	0.6	−0.2	−0.5	0.7	−2.7
	$\Delta S\text{–}C_2\text{–}C_3$	0.3	−0.3	1.0	0.8	−0.0	−0.6	−1.7	2.0
	$\Delta S\text{–}C_2\text{–}H$	−0.2	0.0	−1.7	3.9	4.3	2.0	1.2	−0.5
	$\Delta C_2\text{–}C_3\text{–}H$	0.1	−0.3	2.9	3.9	−3.8	2.2	0.5	−0.2
$^2A_2$	$\Delta S\text{–}C_2$	−0.001	−0.003	−0.007	−0.015	−0.004	−0.002	0.037	0.018
	$\Delta C_2\text{–}C_3$	−0.005	−0.002	−0.012	0.034	0.000	−0.027	−0.002	0.002
	$\Delta C_2\text{–}H$	0.027	0.068	−0.001	0.002	−0.001	−0.002	0.002	−0.000
	$\Delta C_3\text{–}H$	0.068	−0.027	0.004	0.001	−0.001	−0.002	0.000	0.001
	$\Delta C_2\text{–}S\text{–}C_5$	−0.1	−0.3	−0.1	1.2	−0.3	−0.9	0.4	−2.7
	$\Delta S\text{–}C_2\text{–}C_3$	−0.1	0.4	1.2	−0.4	−0.1	0.1	−1.5	2.1
	$\Delta S\text{–}C_2\text{–}H$	−0.1	−0.2	1.3	4.9	−0.9	3.6	1.4	−0.5
	$\Delta C_2\text{–}C_3\text{–}H$	−0.2	0.3	4.2	−0.0	4.9	−0.8	0.5	−0.1
$^2B_1$	$\Delta S\text{–}C_2$	−0.003	0.001	0.004	−0.011	−0.001	−0.004	0.037	0.030
	$\Delta C_2\text{–}C_3$	−0.006	−0.002	−0.038	0.010	−0.009	−0.007	−0.004	−0.001
	$\Delta C_2\text{–}H$	0.067	−0.027	−0.004	0.001	−0.000	−0.001	0.002	−0.000
	$\Delta C_3\text{–}H$	0.027	0.068	−0.002	0.002	−0.001	−0.002	0.000	0.000
	$\Delta C_2\text{–}S\text{–}C_5$	−0.3	0.1	−1.1	0.5	−0.0	−0.5	0.9	−2.8
	$\Delta S\text{–}C_2\text{–}C_3$	0.3	−0.3	1.0	0.7	−0.1	−0.7	−2.1	1.6
	$\Delta S\text{–}C_2\text{–}H$	−0.2	0.0	−1.5	4.3	4.3	1.7	0.7	−0.6
	$\Delta C_2\text{–}C_3\text{–}H$	0.1	−0.3	2.5	4.4	−4.1	1.2	0.1	−0.4
$^2A_1$	$\Delta S\text{–}C_2$	−0.003	0.000	0.000	−0.011	−0.001	−0.001	0.034	0.038
	$\Delta C_2\text{–}C_3$	−0.006	−0.003	−0.039	0.011	−0.004	−0.008	−0.005	−0.004
	$\Delta C_2\text{–}H$	0.072	−0.007	−0.004	0.001	0.000	−0.001	0.002	−0.000
	$\Delta C_3\text{–}H$	0.007	0.073	−0.001	0.002	0.000	−0.002	0.000	0.001
	$\Delta C_2\text{–}S\text{–}C_5$	−0.4	0.0	−1.1	0.6	0.1	−0.5	1.2	−2.7
	$\Delta S\text{–}C_2\text{–}C_3$	0.3	−0.3	1.0	0.8	0.1	−0.7	−2.2	1.3
	$\Delta S\text{–}C_2\text{–}H$	−0.2	−0.0	−1.2	3.8	4.4	3.0	0.3	−1.0
	$\Delta C_2\text{–}C_3\text{–}H$	0.2	−0.2	2.4	4.5	−4.2	0.9	0.4	−0.2
$^2B_2$	$\Delta S\text{–}C_2$	0.000	−0.000	0.007	−0.012	−0.004	−0.004	−0.024	0.053
	$\Delta C_2\text{–}C_3$	−0.005	−0.006	−0.038	0.009	−0.006	−0.006	0.002	−0.001
	$\Delta C_2\text{–}H$	0.011	0.073	−0.006	0.004	−0.000	−0.001	0.001	−0.003
	$\Delta C_3\text{–}H$	0.072	−0.012	−0.002	0.002	0.001	−0.002	−0.001	0.001
	$\Delta C_2\text{–}S\text{–}C_5$	−0.1	−0.4	−0.9	0.4	−0.1	−0.5	−2.2	−1.8
	$\Delta S\text{–}C_2\text{–}C_3$	−0.2	0.5	0.8	0.9	0.2	−0.5	3.1	0.4
	$\Delta S\text{–}C_2\text{–}H$	−0.1	−0.3	−1.3	3.6	4.2	2.9	−1.5	0.0
	$\Delta C_2\text{–}C_3\text{–}H$	−0.2	0.2	2.1	4.4	−4.4	1.7	0.6	−0.4

Bond lengths are in angstroms, angles in degrees.

C_3–H (and C_4–H) stretching motions, respectively. Thus, the ν_1 and ν_2 modes should be interpreted as the C_2–H and C_3–H stretching motions, respectively. Table 5 also shows that the ΔS_4 and ΔS_3 components contribute to the PED of the ν_1 and ν_2 modes, respectively. Table 6 reveals that the C_2–H and C_3–H stretching motions mix with the in-phase mode for the ν_1 mode and with the out-of-phase mode for the ν_2 mode. Table 5 suggests that the ΔS_1 and ΔS_6 coordinates contribute to the ν_7 mode. The ΔS_1 and ΔS_6 coordinates describe the S–C_2 (and S–C_5) stretching and S–C_2–C_3 (and S–C_5–C_4) bending motions, respectively. Table 6 suggests that the S–C stretching and S–C–C bending motions mix with the out-of-phase mode. The PED of the ν_8 mode is a mixture of ΔS_5 and ΔS_6 coordinates. The symmetrical displacement coordinates of ΔS_5 and ΔS_6 are the C_5–S–C_2 and S–C_2–C_3 (and S–C_5–C_4) bending motions, respectively. It is found from Table 6 that the two motions couple with the out-of-phase mode. Therefore, the ν_8 mode is a mixture of the C–S–C and S–C–C bending motions coupled with the out-of-phase mode. It is seen from Tables 5 and 6 that the ν_5 mode is a mixture of the S–C_2–H and C_2–C_3–H bending motions coupled with the out-of-phase mode. We cannot make clear-cut interpretations of the ν_3, ν_4 and ν_6 modes. The ΔS_1, ΔS_2, ΔS_5, ΔS_6 and ΔS_7 coordinates contribute to these modes, while the contribution of the ΔS_3 and ΔS_4 coordinates is negligibly small.

The characters of the ν_1 and ν_2 modes of the $^2A_2$ state change from those of the $^1A_1$ state. Table 5 shows that the main components of the PED of the ν_1 and ν_2 modes are composed by the ΔS_4 and ΔS_3 totally symmetrical displacement coordinates, respectively. It also shows that the ΔS_3 and ΔS_4 coordinates contribute to the ν_1 and ν_2 modes, respectively. Table 6 suggests that the character of the ν_1 is a mixture of the C_3–H and C_2–H stretching motions coupled with the in-phase mode and that of the ν_2 mode is a mixture of the C_2–H and C_3–H stretching motions coupled with the out-of-phase mode. It is found from Tables 5 and 6 that the characters of the ν_7 and ν_8 modes are almost the same as those of the ground state. We cannot find any correspondence between the ν_3, ν_4, ν_5 and ν_6 modes of the $^2A_2$ state and those of the ground state.

For the $^2B_1$ state, it is found from Tables 5 and 6 that the character of each mode corresponds generally to that of the ground state.

The character of each vibrational mode of the $^2A_1$ state corresponds generally to that of the $^1A_1$ state. However, the contributions of S_4 to ν_1, S_3 to ν_2, S_2 to ν_5, S_8 to ν_6 and S_6 to ν_8 become small compared with those of the ground state.

The characters of the ν_1 and ν_2 modes of the $^2B_2$ state are different from those of the $^1A_1$ state. Each character of the ν_1 and ν_2 modes of the $^2B_2$ state corresponds to that of the $^2A_2$ state. Each character of the ν_3, ν_4, ν_5 and ν_6 modes of the $^2B_2$ state corresponds generally to that of the ground state. Tables 5 and 6 indicate that the character of the ν_7 and ν_8 modes does not correspond to any mode of the ν_7 and ν_8 modes of the ground state concerning the component of PED and the phase of the mode.

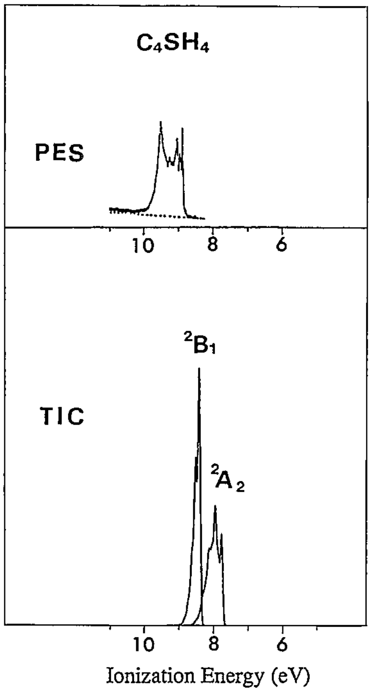

Fig. 2. The theoretical intensity curves of ionization of the $^2A_2$ and $^2B_1$ states with a half width of 0.08 eV and the observed photoelectron spectrum by Turner et al. [2]. TIC: theoretical intensity curve. PES: PE spectrum.

The theoretical intensity curves of the $^2A_2$ and $^2B_1$ states are illustrated in Fig. 2 by assuming a half width of 0.08 eV for each transition band. It is compared with the observed PE spectrum by Turner et al. [2]. It imitates well the vibrational structure of the observed PE spectrum. We illustrate the theoretical intensity curve with a half width of 0.02 eV to discuss the more detailed vibrational structure of each band. The result is shown in Figs. 3 and 4. The assignment of the vibrational structures of the $^2A_2$ and $^2B_1$ states is shown in Tables 7 and 8, respectively.

Table 7 shows the vibrational energy, intensity and assignment of each vibrational level found in Fig. 3. The vibrational levels whose FCF values are larger than 0.01 are listed. The intensity of each vibrational level is classified as S, M or W according to the magnitude of FCF. The present assignment is compared with the interpretation of the observed spectrum by Derrick et al. [3]. We note that they used the qualitative description of the vibrations according to Lord and Miller [20]. We convert their notation in Table 7 according

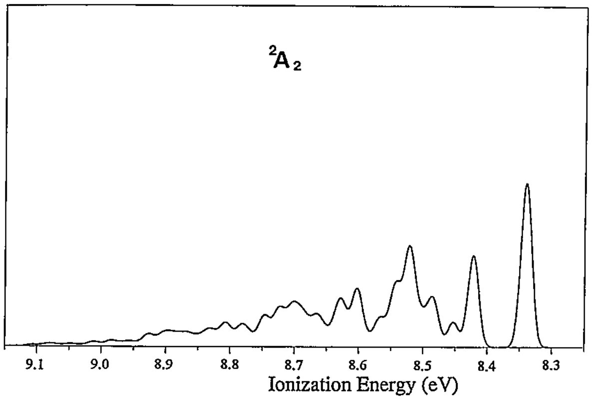

Fig. 3. The theoretical intensity curves of ionization of the $^2A_2$ state with a half width of 0.02 eV.

to Herzberg [19]. Comparing vibrational energies of the present calculation with that by Derrick et al., we overestimate from 2.5% to 6.9%. The three peaks with strong intensity at 8.34, 8.42 and 8.52 eV are shown in Fig. 3. The first peak is interpreted as the 0–0 transition. The second strong peak is assigned to the ν_8 mode. This assignment is consistent with that by Derrick et al. However, our interpretation of the third peak with strong intensity is different from their interpretation. We assign it as the ν_4 band. They interpreted it as the ν_3 band. The present calculation suggests that the ν_3 band is found at 8.54 eV with frequency 1643 cm^{-1}. Comparing the calculated frequency of the ν_3 mode with their value, we overestimate by 17.8%, which value is beyond the present accuracy of the calculation of frequency. Therefore, the third peak with the observed frequency of 1395 cm^{-1} should be assigned as the ν_4 band. The band with medium intensity centered at 8.49 eV is overlapping with the transitions of the ν_6, ν_5 and $2\nu_8$ modes. Derrick et al. interpreted it as the ν_5 and $2\nu_8$ bands. In their interpretation, the contribution of the ν_6 band was missed. They also should miss the ν_7 weak band, which is found between the 8.42 and 8.49 bands in the theoretical intensity curve. It is seen from Fig. 3 that a shoulder of the third strong band is found at 8.54 eV. It is assigned mainly to the ν_3 mode. The shoulder at 8.56 eV is assigned to the $\nu_6+\nu_8$ and $\nu_5+\nu_8$ band with equal intensity. This band was assigned as the $\nu_5+\nu_8$ only by Derrick et al. They proposed the $3\nu_8$ band with vibrational energy of 1879 cm^{-1}. The present calculation shows that the FCF of this transition is smaller than 0.01. Therefore, an observation of this transition should be impossible. The band at 8.60 eV is the $\nu_4+\nu_8$. This band corresponds to the observed band of 2017 cm^{-1}, which was interpreted as the $\nu_3+\nu_8$ band. Derrick et al. proposed that the vibrational frequency of 2230 cm^{-1} was assigned as the $2\nu_5$ band. This band should correspond to the present one at 8.63 eV, which is the $\nu_3+\nu_8$ and $\nu_4+\nu_7$ transitions. The calculated FCF of the $2\nu_5$ transition is negligibly small. The observed vibrational frequency of 2492 cm^{-1} was interpreted as the $\nu_3+\nu_5$ band. The $\nu_4+\nu_6$, $\nu_4+\nu_5$ and $\nu_4+2\nu_8$ transitions should correspond to the observed band.

The ν_3, ν_4, ν_5, ν_6, ν_7 and ν_8 modes contribute to the intensity of the spectrum of the $^2A_2$ state. The ν_4 and ν_8 modes have particularly strong intensity and most of the higher vibrational levels include these modes. This situation is connected to the change in the geometrical parameters by ionization. Table 1 reveals that the S–C$_2$ length becomes short and the C$_2$–C$_3$ length becomes long. It also shows that the C$_5$–S–C$_2$ bond angle becomes narrow and the S–C$_2$–C$_3$ angle becomes wide. Table 6 suggests that the character of the ν_4 mode contains a mixture of the S–C$_2$ and C$_2$–C$_3$ stretching motions coupled with the out-of-phase mode. This phase is consistent with the phase of the change in the S–C$_2$ and C$_2$–C$_3$ length. It also suggests that the character of the ν_8 mode is a mixture of the C$_5$–S–C$_2$ and S–C$_2$–C$_3$ bending motions coupled with the out-of-phase mode. This phase is consistent with the phase of the change in the C$_5$–S–C$_2$ and S–C$_2$–C$_3$

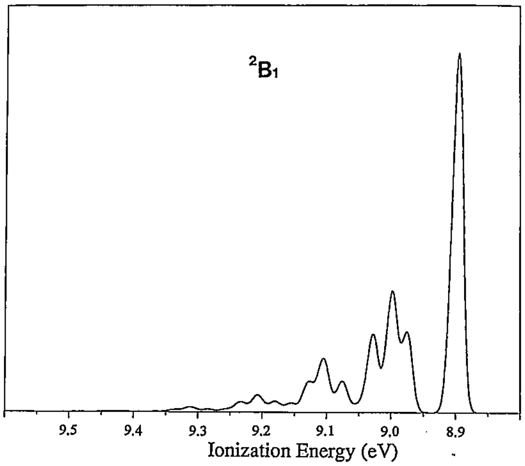

Fig. 4. The theoretical intensity curves of ionization of the $^2B_1$ state with a half width of 0.02 eV.

Table 7
Assignment of the vibrational structure of the $^2A_2$ state

IE	Present calculation			Derrick et al. [3]		
	vibrational energy (cm^{-1})	intensity	assignment	vibrational energy (cm^{-1})	intensity	assignment
8.34	0	S	0	0	VS	
8.42	661	S	ν_8	645	S	ν_8
8.45	911	W	ν_7			
8.48	1145	W	ν_6			
8.49	1204	W	ν_5	1137	M	ν_5
8.50	1322	W	$2\nu_8$	1290	W	$2\nu_8$
8.52	1459	S	ν_4	1395	S	ν_3
8.53	1572	W	$\nu_7+\nu_8$			
8.54	1643	M	ν_3			
8.56	1806	W	$\nu_6+\nu_8$			
8.57	1865	W	$\nu_5+\nu_8$	1760	W	$\nu_5+\nu_8$
8.60	2120	M	$\nu_4+\nu_8$	2017	W	$\nu_3+\nu_8$
8.63	2304	W	$\nu_3+\nu_8$			
8.63	2370	W	$\nu_4+\nu_7$	2230	W	$2\nu_5$
8.66	2604	W	$\nu_4+\nu_6$			
8.67	2663	W	$\nu_4+\nu_5$	2492	W	$\nu_3+\nu_5$
8.68	2781	W	$\nu_4+2\nu_8$			
8.69	2847	W	$\nu_3+\nu_5$			
8.70	2918	W	$2\nu_4$			
8.72	3102	W	$\nu_3+\nu_4$			
8.75	3286	W	$2\nu_3$			
8.78	3579	W	$2\nu_4+\nu_8$			
8.81	3763	W	$\nu_3+\nu_4+\nu_8$			

Intensity is classified as S, M or W according to magnitude of FCF as follows: S:0.16>FCF>0.08, M:0.06>FCF>0.04 and W:0.03>FCF>0.01.

Table 8
Vibrational levels of the $^2B_1$ state of thiophene

IE	Present calculation		
	vibrational energy (cm^{-1})	intensity	assignment
8.90	0	S	0
8.98	614	S	ν_8
9.00	810	S	ν_7
9.03	1037	S	ν_6
9.08	1424	M	$\nu_7+\nu_8$
9.10	1620	W	$2\nu_7$
9.10	1651	W	$\nu_6+\nu_8$
9.11	1681	M	ν_3
9.13	1847	M	$\nu_6+\nu_7$
9.21	2491	W	$\nu_3+\nu_7$

Intensity is classified as S, M or W according to the magnitude of FCF as follows: S:0.43>FCF>0.09, M:0.04>FCF>0.03 and W:0.03>FCF>0.01.

angles. Therefore, the higher vibrational excitation including the ν_4 and ν_8 modes mainly contributes the intensity.

Fig. 4 illustrates the theoretical intensity curve of the $^2B_1$ state. A well resolved vibrational structure is found. However, no vibrational structure of the observed PES has been reported. This should be connected with the fact that the tail of the first band of the $^2A_2$ state should overlap with the band of the $^2B_1$ state and the vibrational structure should not be distinguishable. Table 8 shows the assignment of the vibrational structure of the theoretical intensity curve. The first very strong band is the zero–zero transition. The second band at 8.98–9.03 eV with strong intensity is assigned to the ν_8, ν_7 and ν_6 modes. The ν_3 mode also contributes to the band at 9.11 eV.

In $^2B_1$ state, the 0–0 transition has strong intensity whose FCF is 0.43. The excitation of the ν_7 mode also contributes to the intensity. This feature is connected to the change in the geometrical parameters of the $^2B_1$ state by ionization. The obvious change is found from Table 1 in the parameters of the S–C_2, C_2–C_3, C_5–S–C_2 and S–C_2–C_2. However, the magnitude of these changes is less than that of the classical half amplitudes of the zero-point vibrational level (see Table 6). Thus, the intensity of the 0–0 transition is strong. Table 1 shows that the C_5–S–C_2 bond angle becomes narrow and the S–C_2–C_3 angle becomes wide. Table 6 suggests that the character of the ν_7 mode is a mixture of the C_5–S–C_2 and S–C_2–C_3 bending motions coupled with the out-of-phase mode. This phase is consistent with the phase of the change in the C_5–S–C_2 and S–C_2–C_3 angles. Therefore, the ν_7 mode has large intensity.

For the $^2A_1$ and $^2B_2$ states, we could not obtain reasonable theoretical intensity curves compared with the observed spectra. Large geometrical changes are found in the S–C_2 distance, C_5–S–C_2, and S–C_2–C_3 angles of the $^2A_1$ state, and the S–C_2 distance, C_5–S–C_2, S–C_2–C_3 and S–C_2–H angles of the $^2B_2$ state. The magnitude of these changes is larger than that of the classical half amplitudes of the zero-point vibrational level. Therefore, higher vibrational excitations contribute to the intensity.

4. Conclusion

The molecular equilibrium structures and vibrational frequencies were calculated for the ground and lower four ionic states. By using the FCFs, we obtained the theoretical intensity curve of the $^2A_2$ and $^2B_1$ states. The theoretical intensity curves were in good agreement with the observed PE spectra.

Derrick et al. interpreted the vibrational structure of the spectrum of the $^2A_2$ state by using the ν_8, ν_5 and ν_3 modes. The present calculation reveals that the ν_3, ν_4, ν_5, ν_6, ν_7 and ν_8 modes contribute to the intensity. The 0–0, ν_8 and ν_4 transitions have strong intensity. We propose that the observed frequency of 1395 cm^{-1} is the ν_4 band, whose frequency was interpreted as the ν_3 band by Derrick et al. We also propose that the frequencies of 2017 and 2492 cm^{-1} are the $\nu_4 + \nu_8$ and $\nu_4 + \nu_5$ bands, respectively. These frequencies were assigned as the $\nu_3 + \nu_8$ and $\nu_3 + \nu_5$ bands by them. The present calculation reveals that the ν_4 and ν_8 modes contribute to most of the higher vibrational excitations. This situation is connected to the change in the geometry where the S–C_2 length becomes short, the C_2–C_3 length becomes long, the C_5–S–C_2 bond angle becomes narrow and the S–C_2–C_3 angle becomes wide. The character of the ν_4 mode contains a mixture of the S–C_2 and C_2–C_3 stretching motions coupled with the out-of-phase mode and the ν_8 is a mixture of the C_5–S–C_2 and S–C_2–C_3 bending motions coupled with the out-of-phase mode. These phases are consistent with the phase of the change of geometry. Thus, the ν_4 and ν_8 modes contribute particularly to the intensity.

Although the theoretical intensity curve of the $^2B_1$ state shows a well resolved vibrational structure, no vibrational structure of the observed PES has been reported. This should be connected with the fact that the tail of the first band of the $^2A_2$ state should overlap with the band of the $^2B_1$ state and the vibrational structure should not be distinguishable.

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