

Theoretical Investigation of Molecular Properties of the First Excited State of the Thiophenoxyl Radical

Chi-Wen Cheng, Yuan-Pern Lee, and Henryk A. Witek*

Institute of Molecular Science and Department of Applied Chemistry, National Chiao Tung University, 30010 Hsinchu, Taiwan

Received: June 9, 2008; Revised Manuscript Received: September 29, 2008

Accurate ab initio study of the lowest excited state (A^2B_2) of the thiophenoxyl radical is presented. The calculated equilibrium geometries, excitation energies, and harmonic vibrational frequencies show that the $A^2B_2 \leftarrow X^2B_1$ excitation in C_6H_5S has different characteristics than the analogous transition in the phenoxyl radical. Vertical excitation energies for other low-lying (<4.5 eV) excited states of the thiophenoxyl radical are also presented and compared with available experimental data.

Introduction

Sulfur-containing radicals attracted considerably less attention than their oxygen analogues. Accordingly, the structure and spectroscopy of the thiophenoxyl radical (C_6H_5S , aka the phenylthiyl, phenylsulfyl, or phenylsulfur radical) is far less studied than the corresponding properties of the phenoxyl radical.

A number of absorption bands were reported in solution,^{1–11} solid matrix,^{12–14} and gas-phase^{15–17} experiments. No definitive assignment of the observed peaks to particular electronic states of C_6H_5S was given. Most of the experimental effort was devoted to kinetics and possible reaction pathways of the C_6H_5S radical, which was produced via flash photolysis,^{2–6} laser flash photolysis,^{1,7} or pulse radiolysis^{8,9,11} of liquid or solvated aromatic sulfur compounds. The main spectral tool to monitor this radical was the broad transient UV–vis absorption near 297 and 490 nm. It is noteworthy that the vibrational structure of these bands is not well-defined. Upon photolysis of solid samples of thiophenol or diphenyl disulfide, two bands appeared in the emission spectra. These experiments were performed in 3MP (3-methylpentane) or EPA (a mixture of ethyl ether, isopentane, and ethanol) matrices at 77K. The first band^{12–14} was observed in the region 626–770 nm (red emission, 1.61–1.98 eV) and had a long lifetime. The second band^{13,14} had a short lifetime with maximal intensity at 435 nm (broad intense blue emission, 2.85 eV).

Two transient absorption bands were attributed to gaseous C_6H_5S , one around 310 nm^{15,18} and the other around 470–520 nm.¹⁶ The laser-induced fluorescence excitation spectrum¹⁷ of gaseous C_6H_5S in the region 490–520 nm exhibited a transition origin at 517.38 nm (2.396 eV). The transition origin was tentatively assigned to the $^2A_2 \leftarrow ^2B_2$ excitation. (Note that this assignment is erroneous; the lower state should be 2B_1 .) Three vibrational frequencies (275, 410, and 483 cm^{-1}) were determined for the 2A_2 electronic state. A recent dynamic investigation^{19–21} of photodissociation of thiophenol revealed that the lowest excited state (A^2B_2) of C_6H_5S might be located at 2580 cm^{-1} (0.32 eV).

Six fully symmetric vibrational frequencies (436, 724, 991, 1073, 1180, and 1551 cm^{-1}) for the ground electronic state of C_6H_5S in solution were reported by Tripathi et al. based on their resonance Raman experiment. This study indicated that the CS

bond in C_6H_5S has essentially a single character with the unpaired electron localized on the sulfur atom.¹⁰ Three vibrational frequencies (430, 610, and 1165 cm^{-1}) were determined for the ground electronic state from observed progressions in the dispersed fluorescence spectrum of gaseous C_6H_5S .¹⁷ No experimental information on the equilibrium structure of C_6H_5S is available.

Theoretical calculations of equilibrium geometry and harmonic vibrational frequencies were reported for the ground (X^2B_1) state^{10,22–25} and the first excited (A^2B_2) state.²⁴ No reliable quantum chemical predictions are available for higher electronic states of C_6H_5S .

In a recent study²⁶ we presented an analysis of molecular properties of the phenoxyl radical (C_6H_5O) in its first excited state, A^2B_2 . A comparison of calculated equilibrium geometries and vibrational frequencies between the ground and excited states showed relatively large structural changes upon the $A^2B_2 \leftarrow X^2B_1$ transition. The $A^2B_2 \leftarrow X^2B_1$ excitation energy^{27,28} for C_6H_5O (1.1 eV) is significantly larger than the corresponding experimental value reported recently for C_6H_5S (0.32 eV).^{19–21} It is of fundamental interest²⁹ to understand how the replacement of oxygen by sulfur alters the energetics, structure, and vibrational spectra upon analogous excitation. A detailed theoretical analysis of various molecular properties of the lowest excited A^2B_2 state of C_6H_5S , together with a comparison with C_6H_5O , is presented in this study. The main motivation for our study is a perspective of accurate experimental characterization of the optically forbidden $A^2B_2 \leftarrow X^2B_1$ transition of C_6H_5S using the cavity ringdown absorption technique, which requires detailed information on energetics and vibrational frequencies of the A^2B_2 state.

Computational Details

Most of computational details are identical to those in the previous study of the phenoxyl radical.²⁵ The molecular model of the thiophenoxyl radical is shown in Figure 1. The symmetry of the ground state is described as a doublet B_1 and the symmetry of the first excited state as a doublet B_2 . The presented energetics and equilibrium geometries have been calculated using complete active space second-order perturbation theory^{30,31} (CASPT2) and density functional theory (DFT). In addition, the cluster-corrected (Davidson correction) multireference configuration interaction (MRCI+Q) vertical and adiabatic excita-

* Corresponding author. E-mail: hwitek@mail.nctu.edu.tw.

TABLE 1: Geometrical Parameters for the X 2B_1 and A 2B_2 States of the Thiophenoxyl Radical Optimized Using CASPT2 and B3LYP^a

	cc-pVDZ		aug-cc-pVDZ		cc-pVTZ		aug-cc-pVTZ	
	CASPT2	B3LYP	CASPT2	B3LYP	CASPT2	B3LYP	CASPT2	B3LYP
	X 2B_1							
r_{C_1S}	1.727	1.733	1.727	1.734	1.712	1.724	1.711	1.723
$r_{C_1C_2}$	1.430	1.422	1.432	1.422	1.418	1.414	1.419	1.414
$r_{C_2C_3}$	1.401	1.390	1.402	1.391	1.388	1.382	1.388	1.382
$r_{C_3C_4}$	1.412	1.403	1.414	1.403	1.400	1.395	1.401	1.395
$r_{C_2H_1}$	1.094	1.091	1.093	1.089	1.080	1.081	1.081	1.081
$r_{C_3H_2}$	1.094	1.092	1.093	1.090	1.080	1.082	1.081	1.082
$r_{C_4H_3}$	1.094	1.092	1.093	1.091	1.081	1.082	1.081	1.082
$\alpha_{C_6C_1C_2}$	118.5	118.4	118.7	118.5	118.6	118.4	118.7	118.4
$\alpha_{C_1C_2C_3}$	120.6	120.6	120.4	120.5	120.5	120.6	120.4	120.6
$\alpha_{C_2C_3C_4}$	120.1	120.1	120.1	120.1	120.1	120.1	120.1	120.1
$\alpha_{C_1C_2H_1}$	118.5	118.4	118.4	118.6	118.4	118.5	118.4	118.6
$\alpha_{C_4C_3H_2}$	120.0	120.0	120.0	120.0	120.0	120.0	119.9	120.0
	A 2B_2							
r_{C_1S}	1.769	1.774	1.771	1.774	1.753	1.763	1.753	1.763
$r_{C_1C_2}$	1.414	1.406	1.415	1.406	1.402	1.398	1.402	1.398
$r_{C_2C_3}$	1.406	1.397	1.408	1.397	1.394	1.389	1.394	1.389
$r_{C_3C_4}$	1.407	1.398	1.409	1.398	1.395	1.390	1.395	1.390
$r_{C_2H_1}$	1.094	1.092	1.093	1.092	1.081	1.081	1.082	1.081
$r_{C_3H_2}$	1.095	1.093	1.093	1.093	1.081	1.082	1.081	1.082
$r_{C_4H_3}$	1.094	1.092	1.093	1.092	1.080	1.081	1.081	1.081
$\alpha_{C_6C_1C_2}$	119.7	119.6	119.9	119.6	119.9	119.6	119.9	119.6
$\alpha_{C_1C_2C_3}$	119.8	119.8	119.7	119.8	119.7	119.8	119.7	119.8
$\alpha_{C_2C_3C_4}$	120.6	120.7	120.7	120.7	120.6	120.7	120.6	120.7
$\alpha_{C_1C_2H_1}$	120.1	120.2	120.2	120.1	120.1	120.2	120.1	120.2
$\alpha_{C_4C_3H_2}$	120.2	120.2	120.1	120.2	120.2	120.1	120.1	120.1

^a All CASPT2 calculations use the same $(0a_1, 2a_2, 5b_1, 1b_2)$ active space described in detail in the text. Distances are given in Å and bonds in deg. For an explanation of geometrical parameters, see Figure 1.

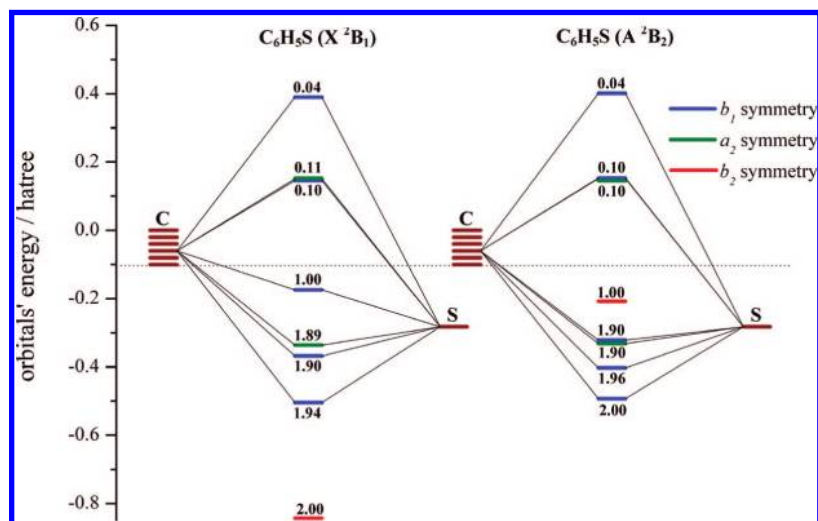


Figure 2. Orbital energy diagram for the seven active π orbitals and one active σ orbital of C_6H_5S in the X 2B_1 and A 2B_2 states obtained from the CASSCF($0a_1, 2a_2, 5b_1, 1b_2$)/aug-cc-pVDZ calculations. Occupation numbers are given for every orbital.

earlier for the phenoxy radical.²⁶ The only important difference concerns the chemical character of the singly occupied b_1 orbital (SOMO), which is almost completely localized on sulfur in C_6H_5S and strongly delocalized over oxygen and the aromatic ring in C_6H_5O . (See also the discussion in refs 9 and 10.) For C_6H_5S , the delocalization is hindered—as can be seen from the atomic spin densities shown in Figure 3—owing to a much larger distance between sulfur and the aromatic ring. This larger distance, originating from the larger size of the sulfur atom, does not permit effective overlap of the atomic p orbitals constituting the π manifold and consequently separates the π

electron densities of the ring and sulfur. In C_6H_5O , where the distance is approximately 0.5 Å shorter, the coupling of the p orbitals is much larger. (Note that conventional chemical explanation in terms of the large difference between the atomic orbital energies does not apply here. The one-electron energy of the carbon 2p orbital is -0.467 hartree. For the sulfur 3p orbital, one has -0.428 hartree and for oxygen 2p orbital -0.616 hartree.⁴⁶) Strong localization of the unpaired electron on sulfur for the X 2B_1 state of the thiophenoxyl radical can also be inferred from the experimental ESR and resonance Raman

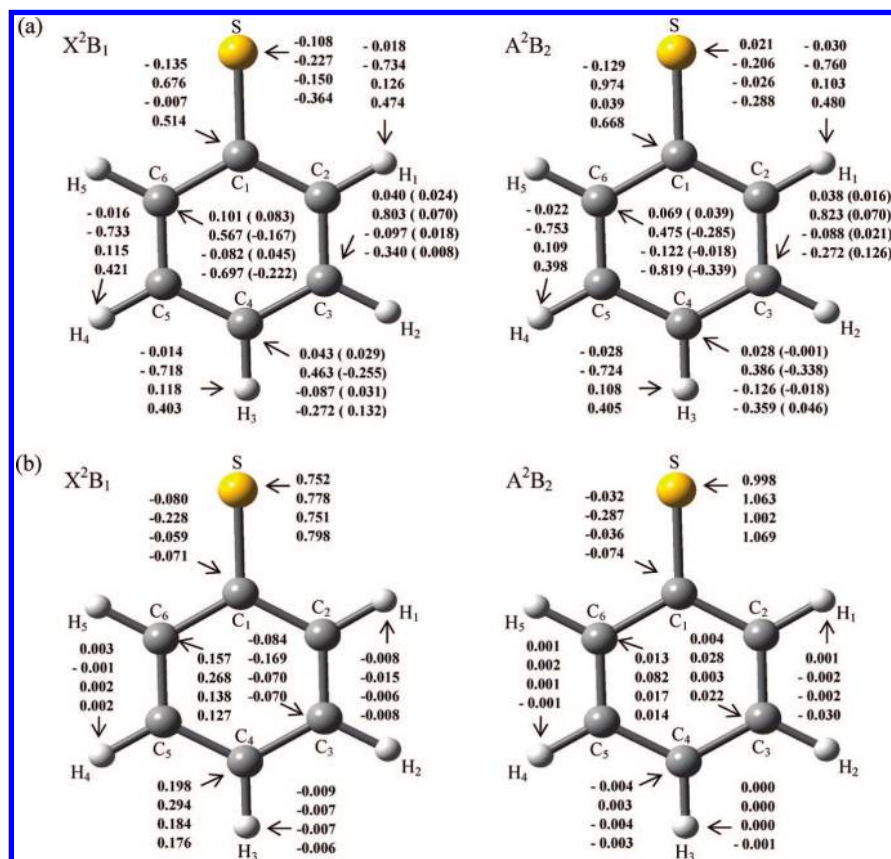


Figure 3. Mulliken charges (a) and spin densities (b) for the X^2B_1 and A^2B_2 states of C_6H_5S obtained from DFT calculation in four basis set (cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ). Values in parentheses are atomic charges with hydrogens summed into heavy atoms.

studies.¹⁰ Another experimental evidence of spin localization is the formation of $C_6H_5SSC_6H_5$ as the dominant combination product.¹⁰

b. Vertical and Adiabatic $A^2B_2 \leftarrow X^2B_1$ Excitation Energies and Assignment of Higher Electronic States. The computed vertical, adiabatic, and 0–0 excitation energies for the $X^2B_1 \rightarrow A^2B_2$ transition are given in Table 2. All the employed methods give rather similar theoretical estimates of the excitation energy. The results do not depend strongly on the quality of the basis set used in the calculations. The computed MRCI+Q, CASPT2, DFT, and TDDFT adiabatic and vertical excitation energies do not differ by more than 0.12 eV than the reported experimental value of 0.323 eV.^{19–21} Bearing in mind that the accuracy of the employed computational methods is probably not better than 0.1 eV, the agreement between theory and experiment can be considered as good. The best agreement between theory and experiment is found for the MRCI+Q/aug-cc-pVTZ method with the assumption that the experimentally determined value corresponds to adiabatic excitation energy. Excellent agreement with experiment for the previously reported^{19,20} CASPT2 excitation energy (0.332 eV), which was computed in smaller active space, is probably somewhat fortuitous. The experimental excitation energy was reported by Kim and co-workers, who investigated the photolysis of thiophenol (C_6H_5SH or C_6H_5SD) at 243 nm using the H^+ (D^+) velocity map imaging technique.^{19–21} Two distinct anisotropic rings observed in the H^+ (D^+) images were identified to correspond to production of two lowest electronic states of the C_6H_5S radical upon H (D) detachment. A value of 0.323 ± 0.024 eV (2600 ± 200 cm^{-1}) determined from the difference in threshold translational energy between these two channels was attributed to the energy difference between the A^2B_2 and

X^2B_1 states of C_6H_5S . Is it possible that the experimental value of 0.323 eV corresponds to the energy separation between the X^2B_1 and A^2B_2 states of the thiophenoxy radical *at the frozen equilibrium geometry of C_6H_5S* ? If this interpretation is correct, the somewhat larger value obtained in our calculations and excellent agreement between MRCI+Q, CASPT2, DFT, and TDDFT can be easily understood. We hope that our future study of the A^2B_2 state of the thiophenoxy radical using cavity ringdown absorption spectroscopy will help to shed more light on this issue.

In our recent studies^{26,47} of the first excited state of the phenoxy radical, we reported theoretical and experimental energy separation between the two lowest electronic states of C_6H_5O . Unfortunately, the previous experimental values^{27,28} of the separation could not be uniquely assigned as the vertical or adiabatic excitations due to discrepancies in our computed data. We try to compensate for this omission in the present work by comparing the experimental values for the phenoxy radical with accurate MRCI+Q theoretical data. As can be seen from data shown in Table 3, the MRCI+Q vertical excitation energies lie between the previously reported CASPT2 and B3LYP results and the MRCI+Q adiabatic excitation energies are almost identical to those computed with B3LYP.²⁶ The presented MRCI+Q results suggest that the previously published experimental excitation energies should be interpreted as vertical excitations. This is also consistent with the experimental adiabatic separation between these two states that was found by us to be 0.952 eV.⁴⁷

No definitive assignment of higher lying electronic states of the thiophenoxy radical is available. Since the only published theoretical study of excited states was performed using a low-level quantum chemical method (configuration interaction with

TABLE 2: Total Energies, Vertical Excitation Energies, and Adiabatic Excitation Energies for the X ²B₁ and A ²B₂ Electronic States of the Thiophenoxyl Radical Computed Using the CASSCF, CASPT2, MRCI+Q, and B3LYP Methods^d

basis set	total energies			A ² B ₂ ← X ² B ₁ excitation energies		
	X ² B ₁	A ² B ₂ (vertical)	A ² B ₂ (adiabatic)	vertical ^a	adiabatic	ΔE _H ^{0-0b}
CASSCF						
cc-pVDZ	-627.726063	-627.713627	-627.714759	0.338	0.308	0.303
aug-cc-pVDZ	-627.733670	-627.721080	-627.722244	0.343	0.311	0.310
cc-pVTZ	-627.795487	-627.783484	-627.784651	0.327	0.295	0.292
aug-cc-pVTZ	-627.797276	-627.785374	-627.786538	0.324	0.292	0.290
CASPT2						
cc-pVDZ	-628.552552	-628.537445	-628.538731	0.411	0.376	0.371
aug-cc-pVDZ	-628.598634	-628.582527	-628.583904	0.438	0.401	0.400
cc-pVTZ	-628.824789	-628.809950	-628.811244	0.404	0.369	0.366
aug-cc-pVTZ	-628.844566	-628.829445	-628.830767	0.412	0.376	0.374
MRCI+Q						
cc-pVDZ	-628.580901	-628.567184	-628.568948	0.373	0.325	0.320
aug-cc-pVDZ	-628.619835	-628.605467	-628.607377	0.391	0.339	0.338
cc-pVTZ	-628.830279	-628.816726	-628.818590	0.369	0.318	0.315
aug-cc-pVTZ	-628.846297	-628.832556	-628.834465	0.374	0.322	0.320
B3LYP						
cc-pVDZ	-629.842725	-629.826715	-629.827936	0.436 (0.403)	0.403	0.398
aug-cc-pVDZ	-629.856466	-629.840607	-629.841813	0.432 (0.412)	0.399	0.398
cc-pVTZ	-629.924651	-629.909312	-629.910475	0.417 (0.428)	0.386	0.383
aug-cc-pVTZ	-629.927282	-629.911999	-629.913156	0.416 (0.433)	0.384	0.382
exptl				0.323 ± 0.010 ^c		

^a Values in parentheses have been calculated using the TDDFT method. ^b Isotope substitution of hydrogen by deuterium does not alter these values. ^c References 19, 20, and 21. ^d All CASSCF, CASPT2, and MRCI+Q calculations use the same (0a₁, 2a₂, 5b₁, 1b₂) active space described in detail in the text. ΔE_H⁰⁻⁰ denotes the 0-0 excitation energy for C₆H₅S. Total energies are given in hartree and excitation energies in eV.

TABLE 3: Total Energies, Vertical Excitation Energies, and Adiabatic Excitation Energies for the X ²B₁ and A ²B₂ Electronic States of the Phenoxy Radical Computed Using the MRCI+Q Method at the Optimized CASPT2 Geometries^c

basis set	total energies			A ² B ₂ ← X ² B ₁ excitation energies			
	X ² B ₁	A ² B ₂ (vertical)	A ² B ₂ (adiabatic)	vertical ^a	adiabatic	ΔE _H ⁰⁻⁰	ΔE _B ⁰⁻⁰
MRCI+Q							
cc-pVDZ	-305.945344	-305.903375	-305.912976	1.142	0.881	0.880	0.878
aug-cc-pVDZ	-305.990382	-305.947200	-305.957020	1.175	0.908	0.904	0.903
cc-pVTZ	-306.210359	-306.167617	-306.177899	1.163	0.883	0.880	0.878
aug-cc-pVTZ	-306.228308	-306.185093	-306.195206	1.176	0.901	0.898	0.896
exptl				1.06, ^a 1.10 ^b			

^a Reference 27, in the gas phase. ^b Reference 28, in argon matrix. ^c All calculations use the same (0a₁, 2a₂, 5b₁, 1b₂) active space described in detail in ref 26. ΔE_H⁰⁻⁰ denotes the 0-0 excitation energy for C₆H₅O, and ΔE_B⁰⁻⁰ for C₆D₅O. Total energies are given in hartree and excitation energies in eV.

single excitations only), we use this opportunity to report here the low-lying doublet states of the thiophenoxyl radical. The calculated TDDFT and MS CASPT2 excitation energies are tabulated in Table 4 for all electronic states under 4.5 eV (275 nm). For the TDDFT method, the corresponding transition oscillator strengths are also given. The quality of the basis set does not have a substantial impact on the calculated excitation energies (except for the ²A₁ state at the CASPT2 level). A relatively large number of electronic states are located in the studied spectral region. It is not a difficult task to explain the reported experimental absorption and fluorescence data in terms of the calculated electronic spectrum. The fluorescence excitation signals observed¹⁷ by Shibuya et al. in the gas phase between 2.38 and 2.58 eV correspond to the ²A₂ state located by us at 2.44 (TDDFT) and 2.34 eV (CASPT2). This finding confirms the suggested experimental assignment for this state. The 0-0 band was assigned by Shibuya et al.¹⁷ at 2.40 eV and earlier by Okuyama et al.¹⁶ at 2.51 eV. The absorption attributed to the ²A₂ state is weak; the calculated oscillator strength is only 0.002.

This state is probably also responsible for the weak shoulder band observed¹¹ in absorption spectrum in solution at 2.44 eV. The main broad signal in the absorption spectrum in solution has a maximum at 2.70 eV together with intensive sideband at 2.57 eV.¹⁰ A similar broad signal is also observed in the emission spectrum.^{13,14} The position of the maximum in the absorption spectrum depends quite strongly on the solvent: 2.70 eV in water,^{10,11} 2.79 eV in decalin,¹ 2.91 eV in 3-methylpentane,¹³ and 2.92 eV in ethanol.² It is plausible to assign this band to the calculated ²B₁ state, which is located in our calculations at 3.00 (TDDFT) and 2.66 eV (CASPT2), and the observed sideband to progression associated with some ~1050 cm⁻¹ vibrational mode. It is possible that the 0-0 band is weak and both the observed bands correspond to progressions. The calculated oscillator strength for the ²B₁ state is large (0.059) and explains well the observed absorption spectrum. The most intensive peak in the absorption spectrum is located at 4.20 eV in aqueous solution^{10,11} and at 4.17 eV in cyclohexane and ethanol.² It is clear that the state responsible for this peak is

TABLE 4: Vertical Excitation Energies (in eV) for the Lowest Doublet Excited States of the Thiophenoxy Radical Computed Using the B3LYP and Multistate (MS) CASPT2 Method^h

	TDDFT				MS CASPT2				Exp.
	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	
X ² B ₁	-629.842725	-629.856466	-629.924651	-629.927282	-628.549286	-628.594568	-628.820821	-628.840438	
² B ₂	0.403 (0.000)	0.412 (0.000)	0.428 (0.000)	0.433 (0.000)	0.454	0.487	0.451	0.461	0.323 ^a
² A ₂	2.430 (0.003)	2.383 (0.002)	2.457 (0.003)	2.443 (0.002)	2.547	2.357	2.412	2.344	2.40 ^b , 2.51 ^c
² B ₁	3.001 (0.054)	2.952 (0.061)	3.013 (0.057)	2.999 (0.059)	2.718	2.633	2.693	2.664	2.70 ^d , 2.79 ^e , 2.91 ^f , 2.92 ^g
² A ₁	3.947 (0.003)	3.908 (0.002)	3.949 (0.003)	3.944 (0.002)	4.820	4.689	4.751	4.265	
² B ₁	4.186 (0.049)	4.133 (0.061)	4.223 (0.058)	4.197 (0.066)	4.729	4.604	4.746	4.662	4.20 ^d , 4.17 ^g
² B ₂	4.458 (0.000)	4.379 (0.000)	4.438 (0.000)	4.393 (0.000)	4.265	4.208	4.257	4.225	
² A ₂	4.536 (0.011)	4.424 (0.008)	4.514 (0.010)	4.459 (0.008)	5.262	5.063	5.196	5.084	

^a References 19, 20, and 21. Photoelectron spectroscopy in the gas phase. ^b Reference 13. Fluorescence in the gas phase. ^c Reference 12. Fluorescence in the gas phase. ^d References 11 and 14. Time-resolved absorption spectroscopy in aqueous solution. ^e Reference 1. Time-resolved absorption spectroscopy in liquid decalin. ^f Reference 17. Absorption spectrum in 3-methylpentane glass. ^g Reference 2. Absorption spectrum in cyclohexane and EtOH. ^h The lowest excited state in each symmetry is given. Values in parentheses are oscillator strengths.

TABLE 5: Harmonic Vibrational Frequencies for the X ²B₁ and A ²B₂ Electronic State of C₆H₅S Computed Using the B3LYP Method^c

symmetry	mode	X ² B ₁				A ² B ₂				
		exptl	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ
A ₁	<i>v</i> ₁		3117	3115	3105	3104	3111	3110	3099	3099
	<i>v</i> ₂		3104	3103	3093	3092	3097	3096	3086	3086
	<i>v</i> ₃		3084	3085	3073	3073	3079	3081	3069	3069
	<i>v</i> ₄	1551 ^a	1559	1549	1552	1549	1586	1574	1575	1571
	<i>v</i> ₅		1431	1423	1444	1441	1451	1442	1463	1460
	<i>v</i> ₆	1180 ^a , 1165 ^b	1153	1155	1166	1164	1160	1162	1173	1171
	<i>v</i> ₇	1073 ^a	1049	1044	1051	1051	1068	1063	1068	1066
	<i>v</i> ₈		1008	1004	1012	1010	1017	1013	1018	1017
	<i>v</i> ₉	991 ^a	976	968	980	979	976	971	983	983
	<i>v</i> ₁₀	724 ^a	708	706	711	710	683	683	687	686
	<i>v</i> ₁₁	436 ^a , 430 ^b	415	413	415	415	397	396	399	398
A ₂	<i>v</i> ₁₂		967	958	971	974	949	944	951	957
	<i>v</i> ₁₃		827	816	828	828	820	811	823	825
	<i>v</i> ₁₄		376	375	376	373	410	409	411	409
B ₁	<i>v</i> ₁₅		987	975	986	986	972	965	972	976
	<i>v</i> ₁₆		919	910	923	924	880	871	884	887
	<i>v</i> ₁₇		749	744	753	752	721	716	726	725
	<i>v</i> ₁₈		669	664	671	668	685	684	688	684
	<i>v</i> ₁₉		453	452	454	451	464	465	466	464
	<i>v</i> ₂₀		157	156	156	156	175	174	175	174
B ₂	<i>v</i> ₂₁		3113	3113	3102	3101	3101	3100	3090	3089
	<i>v</i> ₂₂		3093	3093	3083	3082	3085	3086	3075	3075
	<i>v</i> ₂₃		1539	1529	1534	1531	1566	1557	1558	1555
	<i>v</i> ₂₄		1414	1404	1422	1420	1414	1403	1421	1419
	<i>v</i> ₂₅		1310	1304	1306	1305	1308	1305	1316	1314
	<i>v</i> ₂₆		1262	1260	1265	1263	1265	1262	1255	1253
	<i>v</i> ₂₇		1134	1136	1147	1144	1137	1138	1149	1147
	<i>v</i> ₂₈		1059	1059	1065	1064	1062	1061	1066	1064
	<i>v</i> ₂₉	610 ^b	600	597	604	603	606	605	612	610
	<i>v</i> ₃₀		289	288	289	288	238	238	237	237

^a Reference 11. Resonance Raman in solution. ^b Reference 13. Fluorescence in the gas phase. ^c All values are given in cm⁻¹.

²B₁ with the calculated excitation energy of 4.20 (TDDFT) and 4.66 eV (CASPT2), and the largest oscillator strength (0.066) among all theoretically determined electronic states. There exists a large discrepancy between the TDDFT and CASPT2 methods for some higher lying states (the first ²A₁ and second ²A₂ states). Usually such large discrepancy is attributed to inaccuracies within the TDDFT scheme, but here it also can be caused by deficiencies in the choice of the active space or poor convergence of the perturbation series. (Note the large deviation of the ²A₁ ← X ²B₁ CASPT2 transition energy computed with various basis sets.) The lowest quartet state of the thiophenoxy radical (⁴B₁) is found at 4.35 eV in our B3LYP/cc-pVDZ

calculations. Clearly, higher spin states are not going to influence the observed absorption spectrum of C₆H₅S in the studied spectral region. Our calculations cannot account directly for the red emission observed^{13,14} in the photolysis of C₆H₅SH and C₆H₅SSC₆H₅ in 3-methylpentane and EPA glasses. (The emission maximum is located at 1.83 eV in 3MP and at 1.92 eV in EPA; well-structured vibrational progression of approximately 1350 cm⁻¹ is also observed.) The only electronic state located in this region is ²B₁, but the observed emission maxima differ by 0.5–0.6 eV to match this state. It is rather unlikely that there exists another electronic state with such energy, especially given that the positions of the next two observed states, ²A₂ with ²B₁,

TABLE 6: Harmonic Vibrational Frequencies for the X ²B₁ and A ²B₂ Electronic State of C₆D₅S Computed Using the B3LYP Method^a

symmetry	mode	X ² B ₁				A ² B ₂			
		cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ
A ₁	<i>v</i> ₁	2311	2310	2301	2301	2308	2307	2298	2298
	<i>v</i> ₂	2296	2295	2287	2286	2289	2289	2281	2280
	<i>v</i> ₃	2273	2273	2266	2266	2268	2270	2262	2262
	<i>v</i> ₄	1521	1510	1508	1505	1550	1538	1536	1532
	<i>v</i> ₅	1296	1286	1297	1295	1319	1309	1319	1316
	<i>v</i> ₆	1023	1016	1026	1026	1026	1020	1027	1026
	<i>v</i> ₇	935	928	940	939	936	931	942	941
	<i>v</i> ₈	843	844	853	851	849	850	860	858
	<i>v</i> ₉	807	808	816	815	813	813	821	820
	<i>v</i> ₁₀	670	668	673	673	650	650	655	654
	<i>v</i> ₁₁	407	405	408	407	390	389	391	391
A ₂	<i>v</i> ₁₂	786	781	789	793	770	769	772	779
	<i>v</i> ₁₃	643	634	644	644	639	631	640	642
	<i>v</i> ₁₄	327	325	327	325	357	355	358	356
B ₁	<i>v</i> ₁₅	826	821	829	827	808	809	810	813
	<i>v</i> ₁₆	756	751	761	761	725	722	731	732
	<i>v</i> ₁₇	630	624	632	631	609	604	611	610
	<i>v</i> ₁₈	520	514	521	520	535	530	536	535
	<i>v</i> ₁₉	400	398	400	398	408	407	409	407
	<i>v</i> ₂₀	148	146	147	146	164	163	164	163
	<i>v</i> ₂₁	2305	2304	2295	2295	2297	2296	2287	2287
B ₂	<i>v</i> ₂₂	2283	2283	2275	2275	2276	2277	2268	2269
	<i>v</i> ₂₃	1495	1485	1484	1481	1530	1520	1517	1514
	<i>v</i> ₂₄	1322	1314	1310	1308	1314	1304	1302	1300
	<i>v</i> ₂₅	1272	1263	1258	1256	1266	1257	1249	1247
	<i>v</i> ₂₆	998	996	1017	1016	1000	998	1018	1016
	<i>v</i> ₂₇	824	824	834	832	822	822	832	830
	<i>v</i> ₂₈	798	801	810	809	806	809	817	815
	<i>v</i> ₂₉	575	574	580	579	581	580	586	585
	<i>v</i> ₃₀	275	273	274	274	226	227	226	226

^a All values are given in cm⁻¹.

agree well with our calculations. We can see two potential explanations for this phenomenon.

(1) The emission corresponds rather to the B ²A₂ → A ²B₂ transition than the B ²A₂ → X ²B₁ transition. The calculated energy separation between the B ²A₂ and A ²B₂ states is 2.01 eV (TDDFT/aug-cc-pVTZ), which matches the experimental emission spectrum more closely than the energy separation between B ²A₂ and X ²B₁ (2.44 eV). Even better agreement is observed for the associated excitation spectrum (see Figure 2 of ref 14), which has a maximum located at 2.11 eV. This value almost perfectly agrees with the experimentally determined separation between the B ²A₂ and A ²B₂ states (2.08 eV).

(2) The equilibrium geometry of the B ²A₂ state computed with DFT is not planar. There exists a close structural similarity with the equilibrium geometry of the phenoxyl radical in the ²A'' state. (For details, see Figure 2 of ref 48.) It is clear that geometry relaxation leads to smaller energy separation between the B ²A₂ state and the two lower states. However, the energy of the B ²A₂ state is lowered only by 0.002 eV (B3LYP/cc-pVDZ) upon the relaxation. At the same time, the energy of the two lower states computed at the optimized geometry of the B ²A₂ state is elevated by 0.36 (X ²B₁) and 0.40 eV (A ²B₂). The zero-point energy corrections (cc-pVDZ, unscaled) to all three studied states are comparable (2.46, 2.46, and 2.37 eV for X ²B₁, A ²B₂, and B ²A₂, respectively). The experimental separation between the maxima of emission and absorption signals is 0.28 eV in 3MP and 0.19 eV in EPA. It is rather unlikely that this mechanism could account for the discrepancy of 0.5–0.6 eV for the B ²A₂ → X ²B₁ transition mentioned above.

Note that none of these hypotheses fully explains the unusually long lifetime of the observed red emission. Jinguji et al.¹⁴ argue that the long emission lifetime is a consequence of the strongly forbidden character of the corresponding excitation. The computed TDDFT oscillator strengths for the B ²A₂ → A ²B₂ and B ²A₂ → X ²B₁ transitions are indeed small: 0.002 and 0.000, respectively.

There is no experimental evidence for other electronic states of the thiophenoxyl radical with excitation energies smaller than 4.5 eV.

c. Harmonic Vibrational Frequencies. Harmonic vibrational frequencies for the X ²B₁ and A ²B₂ states of C₆H₅S are given in Table 5. Analogous data for the isotope-substituted species (C₆D₅S) are given in Table 6. The presented (scaled) values are computed with B3LYP using a set of four basis sets. The scaling factors (0.971 for cc-pVDZ and aug-cc-pVDZ and 0.970 for cc-pVTZ and aug-cc-pVTZ) have been determined from separate DFT calculations for thiophenol (C₆H₅SH), for which experimental fundamental frequencies are available.⁴⁹ The frequencies computed with various basis sets are rather similar; the largest deviation observed upon basis set change is 21 cm⁻¹ for *v*₂₆ of C₆D₅S (X ²B₁) and *v*₅ of C₆H₅S (A ²B₂). As discussed in the previous study of the phenoxyl radical,²⁶ the smallest mean absolute deviation from experiment (approximately 25 cm⁻¹) can be expected for the cc-pVTZ basis set. Therefore, for the following discussion, the cc-pVTZ harmonic vibrational frequencies are used. A graphical description of some of the full-symmetric modes can be found in ref 10. Information for the remaining vibrational modes will be made available from the authors upon request.

The change in harmonic vibrational frequencies upon the $X^2B_1 \rightarrow A^2B_2$ excitation is small. The difference between the zero-point energies (ZPE) of both states is only 26 cm^{-1} for C_6H_5S and 37 cm^{-1} for C_6D_5S . On average, each vibrational level is displaced by 15 cm^{-1} for C_6H_5S and 13 cm^{-1} for C_6D_5S . The largest displacement is observed for the in-plane CS bending (ν_{30}): -51 cm^{-1} for C_6H_5S and -48 cm^{-1} for C_6D_5S . The change in other vibrational modes involving the sulfur atom—the out-of-plane CS bending (ν_{20}) and the CS stretch (ν_7)—is noticeably smaller. This situation is in contrast with that reported²⁶ for the phenoxy radical, where the corresponding vibrational modes (ν_6 , ν_{30} , and ν_{20}) were displaced by 167, 73, and 38 cm^{-1} (C_6H_5O) and 217, 65, and 37 cm^{-1} (C_6D_5O), respectively.

The computed harmonic vibrational frequencies of the ground state correspond well to the fundamental modes detected in the resonance Raman spectrum in solution (436, 724, 991, 1073, 1180, and 1551 cm^{-1})¹⁰ and in the gas-phase fluorescence spectrum (430, 610, and 1165 cm^{-1}).¹⁷ These modes can be easily assigned to ν_{11} , ν_{10} , ν_9 , ν_7 , ν_6 , and ν_4 (solution spectrum) and to ν_{11} , ν_{29} , and ν_6 (gas-phase spectrum). (For more detailed discussion, see ref 10.) The computed ground-state frequencies are in satisfactory agreement with other theoretical studies.^{10,22,25} Similar agreement is found for the X^2B_1 and A^2B_2 frequencies reported by Song et al.,²³ if one scales these frequencies by an appropriate factor. While no large discrepancies are found with the previous theoretical data, the present study probably can be considered as giving the most accurate set of harmonic vibrational frequencies for both electronic states of the thiophenoxy radical owing to the most complete character of employed basis sets.

The presented analysis confirms the observation made previously on the basis of optimized geometrical parameters about structural similarity between both electronic states of the thiophenoxy radical. The computed force fields are also similar giving an almost identical set of harmonic vibrational frequencies for both electronic states: X^2B_1 and A^2B_2 .

Conclusion

High-level ab initio techniques are employed to study the equilibrium geometry, excitation energies, and harmonic vibrational frequencies for the first excited electronic state (A^2B_2) of the thiophenoxy radical. The calculated properties are compared to analogous data for the ground state. The wave functions of both studied electronic states are well represented with single Slater determinants. The $A^2B_2 \leftarrow X^2B_1$ excitation can be concisely described as a transfer of a single electron between two atomic-like p orbitals localized on sulfur. The calculated excitation energies for the $A^2B_2 \leftarrow X^2B_1$ transition correspond well to experimental data. The change in molecular equilibrium geometry and harmonic vibrational frequencies is rather small upon the excitation. The presented results show that the $A^2B_2 \leftarrow X^2B_1$ excitation in C_6H_5S has a quite different characteristic than the analogous transition in the phenoxy radical (C_6H_5O), where the singly occupied orbital in the X^2B_1 state is largely delocalized over oxygen and the aromatic ring. The delocalization causes energetic stabilization of the X^2B_1 state of C_6H_5O and results in approximately double character of the CO bond. This effect is missing in C_6H_5S owing to a much larger distance between sulfur and carbon that does not permit large effective overlap of π densities on both atoms. Consequently, both studied electronic states of the thiophenoxy radical (A^2B_2 and X^2B_1) show close energetic and structural similarity.

In addition, a computational study of other low-lying ($<4.5\text{ eV}$) electronic states of the thiophenoxy radical is presented. The calculated TDDFT and CASPT2 excitation energies correspond well to the available experimental absorption and emission data. A reliable assignment of excited states of the thiophenoxy radical is given in Table 4. The lowest quartet state of C_6H_5S is found at 4.35 eV (B3LYP/cc-pVDZ).

Acknowledgment. We thank Prof. Soji Tsuchiya for help and the National Center for High-Performance Computing for computer time. The National Science Council of Taiwan is acknowledged for financial support (grants NSC96-2113-M009-022 and NSC96-2113-M009-025). This research has also been supported by Institute of Nuclear Energy Research, Atomic Energy Council, Taiwan, under Contract No. 970147 L, and by the Ministry of Education (MOE-ATU project).

References and Notes

- (1) Scott, T. W.; Liu, S. N. *J. Phys. Chem.* **1989**, *93*, 1393.
- (2) Thyron, F. C. *J. Phys. Chem.* **1973**, *77*, 1478.
- (3) Gaspari, G.; Granzow, A. *J. Phys. Chem.* **1970**, *74*, 836.
- (4) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1983**, *105*, 1937.
- (5) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 1815.
- (6) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732.
- (7) Burkey, T. J.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 246.
- (8) Hermann, R.; Dey, G. R.; Naumov, S.; Brede, O. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1213.
- (9) Armstrong, D. A.; Sun, Q.; Schuler, R. H. *J. Phys. Chem.* **1996**, *100*, 9892.
- (10) Tripathi, G. N. R.; Sun, Q.; Armstrong, D. A.; Chipman, D. M.; Schuler, R. H. *J. Phys. Chem.* **1992**, *96*, 5344.
- (11) Bonifačić, M.; Weiss, J.; Chaudhri, S. A.; Asmus, K.-D. *J. Phys. Chem.* **1985**, *89*, 3910.
- (12) Feher, F.; Gladden, T.; Kurz, D. Z. *Naturforsch.* **1970**, *25b*, 1215.
- (13) Russell, P. G. *J. Phys. Chem.* **1975**, *79*, 1353.
- (14) Jinguji, M.; Imamura, T.; Obi, K.; Tanaka, I. *Chem. Phys. Lett.* **1984**, *109*, 31.
- (15) Porter, G.; Wright, F. J. *Trans. Faraday Soc.* **1955**, *51*, 1469.
- (16) Okuyama, M.; Takakura, T.; Kamada, H. *J. Spectrosc. Soc. Jpn.* **1977**, *26*, 164.
- (17) Shibuya, K.; Nemoto, M.; Yanagibori, A.; Fukushima, M.; Obi, K. *Chem. Phys.* **1988**, *121*, 237.
- (18) Norrish, R. G. W.; Zeelenberg, A. P. *Proc. R. Soc. London, Ser. A* **1967**, *240*, 293.
- (19) Lim, J. S.; Lim, I. S.; Lee, K. S.; Ahn, D. S.; Lee, Y. S.; Kim, S. K. *Angew. Chem., Int. Ed.* **2006**, *45*, 6290.
- (20) Lim, I. S.; Lim, J. S.; Lee, Y. S.; Kim, S. K. *J. Chem. Phys.* **2007**, *126*, 034306.
- (21) Lim, J. S.; Lee, Y. S.; Kim, S. K. *Angew. Chem., Int. Ed.* **2008**, *47*, 1853.
- (22) Kamisuki, T.; Hirose, C. *J. Mol. Struct. (THEOCHEM)* **2000**, *531*, 51.
- (23) Remacle, F.; Kryachko, E. S. *J. Mol. Struct.* **2004**, *708*, 165.
- (24) Song, L.; Bu, Y.; Li, P. *Int. J. Quantum Chem.* **2005**, *105*, 186.
- (25) Xu, W.; Gao, A. *J. Phys. Chem. A* **2006**, *110*, 997.
- (26) Cheng, C.-W.; Lee, Y.-P.; Witek, H. A. *J. Phys. Chem. A* **2008**, *112*, 2648.
- (27) Radziszewski, J. G.; Gil, M.; Gorski, A.; Spanget-Larsen, J.; Waluk, J.; Mróz, B. *J. Chem. Phys.* **2001**, *115*, 9733.
- (28) Gunion, R. F.; Gilles, M. K.; Polak, M. L.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.
- (29) Foster, S. C.; Miller, T. A. *J. Phys. Chem.* **1989**, *93*, 5986.
- (30) Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645.
- (31) Celani, P.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 5546.
- (32) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Phys. Chem.* **1998**, *108*, 4439.
- (33) Finley, J.; Malmqvist, P.-Å.; Roos, B. O.; Serrano-Andrés, L. *Chem. Phys. Lett.* **1998**, *288*, 299.
- (34) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (35) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6769.
- (36) Werner, H.-J.; Knowles, P. J.; Amos, R. D. et al., *MOLPRO*, a package of ab initio programs, version 2006.1.
- (37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B. et al. *Gaussian 03*, Revision A.1; Gaussian Inc.: Pittsburgh, PA, 2003.
- (38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (39) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (40) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

(41) NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 12, Aug 2005, Russell D. Johnson III, Ed. <http://srdata.nist.gov/cccbdb>.

(42) Hagen, K.; Hedberg, K. *J. Chem. Phys.* **1973**, *59*, 158.

(43) Chipman, D. M.; Liu, R.; Zhou, X.; Pulay, P. *J. Chem. Phys.* **1994**, *100*, 5023.

(44) Johansson, K. I.; Oldeberg, H.; Selen, H. *Ark. Fys.* **1967**, *33*, 313.

(45) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, S1.

(46) Visscher, L.; Dyall, K. G. *At. Data Nucl. Data Tables* **1997**, *67*, 207.

(47) Cheng, C.-W.; Witek, H. A.; Lee, Y.-P. *J. Chem. Phys.* In press.

(48) Liu, R.; Morokuma, K.; Mebel, A. M.; Lin, M. C. *J. Phys. Chem.* **1996**, *100*, 9314.

(49) Scott, D. W.; McCullough, J. P.; Hubbard, W. N.; Messerly, J. F.; Hossenlopp, I. A.; Waddington, G. *J. Am. Chem. Soc.* **1956**, *78*, 5463.

JP805045S