# Direct Identification of Photofragment Structures Formed in the 193 nm Photodissociation of Thiophene<sup>†</sup>

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An experimental scheme which involves vacuum ultraviolet photoionization mass spectrometric sampling of laser photodissociation products in a pulsed supersonic molecular beam has been used to identify the isomeric structures of the 193 nm photofragments from thiophene. The primary products observed are vinylacetylene (H<sub>2</sub>C=CH-C=CH), acetylene (C<sub>2</sub>H<sub>2</sub>), and thioketene (H<sub>2</sub>C=C=S). Using the 2 + 1 resonance-enhanced multiphoton (REMPI) scheme, we find that S atoms are produced predominantly ( $\geq$ 96%) in <sup>3</sup>P<sub>J</sub> states with a fine structure distribution of <sup>3</sup>P<sub>2</sub>:<sup>3</sup>P<sub>1</sub>:<sup>3</sup>P<sub>0</sub> = 0.82 ± 0.03:0.15 ± 0.03:0.03 ± 0.03. These experimental results indicate that the major dissociation channels are CH<sub>2</sub>=CH-C=CH + S(<sup>3</sup>P) and CH=CH + CH<sub>2</sub>=C=S. *Ab initio* multiconfiguration self-consistent-field calculations have been made to rationalize these experimental observations.

## I. Introduction

One of the important objectives for an experimental photochemical study is to identify the primary photoproduct structures and branching ratios for the dissociation channels at a known photodissociation wavelength. For polyatomic product species with unknown spectroscopic properties, laser spectroscopic detection schemes may not be useful for product structure identifications.

Because photoionization mass spectrometry is a mass and energy sensitive technique,<sup>1</sup> photoionization efficiency (PIE) measurements of a photoproduct near its ionization threshold can in principle be used effectively to identify the structures of primary photofragments. Although polyatomic molecules and radicals may exist in many isomeric forms, their ionization energies (IEs) are often sufficiently different to allow an unambiguous isomeric structure identification by vacuum ultraviolet (VUV) PIE measurements.<sup>2-6</sup> However, primary photofragments often contain excitations. As a result, the experimental IE observed for a photoproduct is expected to shift to a lower energy, which depends on the specific photochemical process involved. In order to overcome this problem, rare gas matrix isolation techniques<sup>7</sup> have been used for spectroscopic studies of transient photoproducts. For photoionization mass spectrometric sampling, a particularly attractive approach is to cool the primary photoproducts in a supersonic expansion prior to PIE measurements.<sup>2-6</sup> This can be accomplished by inducing the photochemical process in the high-pressure region of a free jet, i.e., close to the nozzle tip. It has been well-demonstrated that further expansion of the photoproducts together with the bath molecules or atoms can be an effective means of relaxing the internal photoproduct excitations.<sup>3</sup> If the sample gas consists of a small fraction of the precursor molecules seeded in an unreactive carrier gas, such as a rare gas, secondary reactions of the photoproducts can be minimized. In principle, the distortion of primary photoproduct branching ratios due to secondary processes can be examined by varying the precursor gas to rare gas ratio.

The ultraviolet (UV) photochemistry of thiophene has been the subject of many previous studies.<sup>7-19</sup> Photoproducts resulting from the irradiation of thiophene in the gas phase at 2139, 2288, and 2537 Å have been examined by Wiebe and Heichlen.<sup>10</sup> Due to the very weak absorption of thiophene at wavelengths > 2475 Å, direct photolysis of thiophene at 2537 Å is found to be negligible. For all these photodissociation wavelengths, the products are found to be C<sub>2</sub>H<sub>2</sub>, CH<sub>2</sub>=C=CH<sub>2</sub>, CH<sub>3</sub>C=CH, CS<sub>2</sub>, CH<sub>2</sub>=CH-C=CH, and polymers. On the basis of photolysis experiments in the presence of olefins, these authors conclude that sulfur atoms are not formed as a primary photodissociation product.

Studies of photoisomerizations in aryl- and alkyl-substituted thiophene in solution<sup>19-26</sup> reveal permutations of ring atoms, a photochemical behavior observed for other heterocyclic organic compounds.<sup>14,27,28</sup> In a thiophene photolysis experiment at 2290 Å in an argon-matrix, Rendall *et al.* have identified CH<sub>2</sub>=C=CHCH=S, C=C-CHS, and Dewar thiophene, in addition to CH<sub>2</sub>=CH-C=CH, C<sub>2</sub>H<sub>2</sub>, CS<sub>2</sub>, and CH<sub>3</sub>C=CH, which have also been observed in gas phase studies.<sup>10</sup> Three reaction mechanisms, namely, the ring contraction-ring expansion,<sup>22-24</sup> internal cyclization,<sup>25,26</sup> and zwitterion-tricyclic mechanisms, <sup>19-21</sup> have been proposed to account for these experimental observations. The zwitterion-tricyclic mechanism invokes an expanded valence of sulfur atom involving d orbital participation.<sup>29</sup>

The photoproducts induced by infrared multiphoton dissociation (IRMPD) of thiophene have also been examined.<sup>18</sup> Under various precursor pressures and infrared laser energies,  $C_2H_2$ ,  $CH_3C=CH$ , and  $CS_2$  are found to be the major products. Since IRMPD processes are expected to proceed via vibrational excitations of the ground electronic state, the IRMD dynamics should be different from those of UV photodissociations, where electronic excited states are involved.

The first direct examination of primary photoproducts of thiophene at 193 nm has been made in a recent photofragmentation time-of-flight (TOF) mass spectrometric experiment.<sup>30</sup> In

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this experiment, six product channels have been identified, as summarized by processes 1-6 in decreasing order of importance.

 $C_4H_4S$  (thiophene) +  $h\nu$  (193 nm)  $\rightarrow C_4H_4 + S$  (1)

$$\rightarrow C_2 H_2 S + C_2 H_2 \quad (2)$$

$$\rightarrow \text{HCS} + \text{C}_3\text{H}_3 \qquad (3)$$

$$\rightarrow CS + C_3 H_4 \qquad (4)$$

$$\rightarrow \text{HS} + \text{C}_4\text{H}_3 \qquad (5)$$

$$\rightarrow H_2 + C_4 H_2 S \qquad (6)$$

The relative dissociation yields for processes 1-6 are estimated to be  $29 \pm 10\%$ ,  $23 \pm 8\%$ ,  $20 \pm 7\%$ ,  $14 \pm 5\%$ ,  $9 \pm 3\%$ , and  $5 \pm 2\%$ . In a laser photofragmentation TOF mass spectrometric experiment, the product channel identifications are achieved by matching the kinetic energy release distributions derived from the TOF spectra of product pairs (such as  $C_2H_2S$  and  $C_2H_2$  in process 2). The matching process is often complicated by ion fragmentations of polyatomic species occurring in the electron impact ionizer and by the unknown energetics for a product photodissociation channel.

We have adopted the photodissociation-photoionization (PD-PI) experimental scheme described above to identify the primary photoproducts of thiophene at 193 nm. This experiment provides insight into the isomeric structures for C<sub>4</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>S, and C<sub>2</sub>H<sub>2</sub> produced in processes 1 and 2. The S(<sup>3</sup>P<sub>2,1,0</sub>, <sup>2</sup>D<sub>2</sub>) state distributions formed in process 1 have been determined using 2 + 1 resonance-enhanced multiphoton (REMPI) ionization detection schemes.<sup>31-34</sup> Ab initio multiconfiguration self-consistent-field (MCSCF) calculations of the ground and excited electronic potential energy surfaces have also been made to rationalize the experimental observations.

#### **II. Experimental and Theoretical Methods**

A. Experiment. (a) Vacuum Ultraviolet PIE Measurements. The VUV photoionization sampling of 193 nm photofragments from thiophene has been performed using the molecular beam photoionization mass spectrometer.<sup>2,3,35,36</sup> The experimental procedures used are similar to those described in the recent photoionization studies of CS, SO, CH<sub>3</sub>S, CH<sub>3</sub>CH<sub>2</sub>S, CH<sub>2</sub>Br, and CH<sub>3</sub>SS.<sup>2-6</sup>

The pulsed jet of thiophene (C<sub>4</sub>H<sub>4</sub>S) (99% pure, vapor pressure  $\approx$  160 Torr at 310 K) seeded in Ar is produced by expansion through a pulsed valve with a nozzle diameter of 0.5 mm and a total stagnation pressure of 1200 Torr. The pulsed valve is operated at 40 Hz. In this experiment, the photodissociation ArF excimer laser beam is mildly focused and intersects the Ar-thiophene free jet at 90° and  $\approx$ 2 mm from the nozzle tip. The triggering pulse for firing the excimer laser is delayed by 500  $\mu$ s with respect to the trigger pulse for opening the pulse valve. The excimer laser pulse energies used vary in the range 30-80 mJ. The internal excitations of the primary photoproducts acquired in the photodissociation process are expected to relax efficiently as the radicals entrained in the carrier gas expand further into the vacuum.

The gas beam is skimmed by a conical skimmer before entering the photoionization region of a quadrupole mass spectrometer. Photoionization sampling of the photoproducts takes place  $\approx 8$  cm from the nozzle tip. Similar to previous observations,<sup>2-6</sup> the C<sub>2</sub>H<sub>2</sub><sup>+</sup>, C<sub>2</sub>H<sub>2</sub>S<sup>+</sup>, and C<sub>4</sub>H<sub>4</sub><sup>+</sup> ion beam pulses resulting from the photoionization of photoproducts C<sub>2</sub>H<sub>2</sub>,  $C_2H_2S$ , and  $C_4H_4$  have a full-width-at-half-maximum (fwhm) of  $\approx 800 \ \mu s$ . The photoion counts are measured by gating the multichannel scaler within the temporal range 0.9-2.9 ms with respect to the triggering pulse for opening the pulse valve. In order to obtain a better background correction, the laser beam is operated at 20 Hz, i.e., half the repetition rate of the pulsed molecular beam. The ion counts arising from the photoionization of laser photofragments are taken to be the difference between the ion counts observed when the laser is on and when the laser is off.

In previous studies of the ionic fragmentation pattern of thiophene by VUV photoionization,<sup>37</sup> electron impact ionization,<sup>38</sup> and charge transfer<sup>39</sup> techniques,  $C_4H_3S^+$ ,  $C_3HS^+$ ,  $C_3H_3^+$ ,  $C_2H_2S^+$ , and HCS<sup>+</sup> have been identified as fragment ions with appearance energies (AE) of approximately 12.9, 13.0, 13.1, 12.1, and 13.2 eV,<sup>37</sup> respectively. Fortunately, the IEs for  $C_3H_3$ ,  $C_2H_2S$ , and HCS are expected to be significantly lower than 12 eV. Thus, the search for  $C_3H_3$ ,  $C_2H_2S$ , and HCS can be conducted at photoionization energies well below 12 eV, avoiding the problem of background ions arising from the dissociative ionization of thiophene.

The photoionization wavelength resolution used in this experiment  $\approx 2$  Å fwhm. Efforts were made to search for photoions produced from HS, CS, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>S, C<sub>3</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>3</sub>, and C<sub>4</sub>H<sub>4</sub>. Within the sensitivity of this experiment,<sup>40</sup> we have positively identified the formation of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>S, and C<sub>4</sub>H<sub>4</sub> as the major products of the 193 nm photodissociation of thiophene. The C<sub>4</sub>H<sub>4</sub><sup>+</sup> intensity is observed to be higher than that for C<sub>2</sub>H<sub>2</sub><sup>+</sup> and C<sub>2</sub>H<sub>2</sub>S<sup>+</sup>. This may be due to the higher photoionization cross sections and higher VUV light intensities near the ionization threshold for C<sub>4</sub>H<sub>4</sub>. For ion-counting times of 30 min at each photoionization wavelength, we have found that ion signals attributable to HS, CS, C<sub>3</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>4</sub>, and C<sub>4</sub>H<sub>3</sub> are negligible.

(b) 2 + 1 REMPI of  $S({}^{3}P_{2,1,0}, {}^{1}D_2)$ . The detailed experimental setup and procedures used to measure the electronic  $S({}^{3}P_{2,1,0}, {}^{1}D_2)$  state distribution formed in the 193 nm photodissociation of organosulfur species have been described previously.<sup>32-34</sup> Briefly, a pulsed molecular beam of neat thiophene is produced by supersonic expansion through a pulsed valve (nozzle diameter = 0.5 mm, temperature  $\approx 298$  K, stagnation pressure = 90 Torr). The molecular beam is skimmed by a conical skimmer and intersects at 90° with both the dissociation and ionization lasers 15.3 cm downstream from the pulsed nozzle. The pulsed valve is operated at a repetition rate of 17 Hz.

The ArF photodissociation laser (Questek 2460) is operated in the constant pulse energy mode. The ArF laser energies used are in the range 160–1000  $\mu$ J/pulse. The ionization of S(<sup>3</sup>P<sub>2,1,0</sub>, <sup>1</sup>D<sub>2</sub>) is accomplished with an excimer laser (Lambda Physik EMG 201 MSC) pumped dye laser (FL 3002) system. The pulse energy of the dye laser is typically 200  $\mu$ J/pulse.

The firing of the dissociation excimer laser is delayed by 570  $\mu$ s with respect to the triggering pulse for opening the pulsed valve. A delay of 50 ns between the two laser pulses is set for all the experiments. The firing sequence of the pulsed valve and the two lasers is controlled by two digital delay units (Stanford Research, Model DG 535). A home-built TOF mass spectrometer of the two-stage Wiley-McLaren design is used to detect S<sup>+</sup> ions. The ion signal observed at the microchannel plate and the excimer laser signal from the pyroelectric detector feed into two identical boxcar integrators (Stanford Research, SR-250), which are interfaced to an IBM AT computer.

Probing of the  $S(3^{3}P_{J})$  and  $S(3^{1}D_{2})$  atomic states is accomplished by two-photon absorption,  $S(3^{3}P_{J}) \rightarrow S(4^{3}P_{J'})$  and  $S(3^{1}D_{2}) \rightarrow S(4^{1}F_{3})$ , followed by absorption of a third photon to

TABLE 1: Theoretical and Experimental Geometries for Thiophene and Dewar Thiophene<sup>abc</sup>

	experimental <sup>d</sup> (thiophene)	MP2 <sup>e</sup> (thiophene)	MCSCF <sup>f</sup> (thiophene)	MCSCF <sup>f</sup> (Dewar thiophene)
r[S-C(2)]	1.714	1.713	1.722	1.818
r[C(2) - C(3)]	1.369	1.385	1.347	1.545
r[C(3) - C(4)]	1.423	1.423	1.445	1.329
r[C(2) - H(2)]	1.078	1.081	1.067	1.066
r[C(3) - H(3)]	1.080	1.083	1.068	1.065
r[C(2) - C(5)]				1.518
r[S-C(3)]				2.758
$\theta[C(2)-S-C(5)]$	92.1	92.3	91.3	49.3
$\theta$ [S-C(2)-C(3)	111.5	111.6	111.9	109.9
$\theta[C(2) - C(3) - C(4)]$	112.5	112.2	112.2	93.5
$\theta[C(3) - C(2) - H(2)]$	128.7	127.9	127.0	127.0
$\theta[C(2) - C(3) - H(3)]$	124.3	124.6	123.9	131.7
$\theta[S-C(2)-C(3)-C(4)]$				-62.1
$\theta[S-C(2)-C(5)-C(4)]$				113.8
$\theta[C(4) - C(3) - C(2) - H(2)]$				-134.9
$\theta$ [C(5)-C(4)-C(3)-H(3)				174.8

<sup>a</sup> The positions for the two carbon atoms adjacent to S are C(2) and C(5). The carbon atoms adjacent to C(2) and C(5) are C(3) and C(4), respectively. The H atom attached to C(i) is labeled as H(i), i = 2-4. <sup>b</sup> All bond distances (r) are in angstroms, and bond angles ( $\theta$ ) are in degrees. <sup>c</sup> All r and  $\theta$  values are for equilibrium geometry of thiophene and Dewar thiophene in the ground electronic states. <sup>d</sup> Reference 45. <sup>e</sup> Second-order Møller-Plesset perturbation theory. Reference 11. <sup>f</sup> This work.

produce S<sup>+</sup> in the <sup>4</sup>S<sup>0</sup> and <sup>2</sup>D<sup>0</sup> states, respectively.<sup>31</sup> The ionization peaks corresponding to the detection of  $S(^{3}P_{21,0})$  and  $S(^{1}D_{2})$  appear in the respective wavelength region 308–311 nm and at 288.19 nm.

The branching ratio  $S(^{3}P):S(^{1}D)$  and the fine-structure distribution  $S({}^{3}P_{2}):S({}^{3}P_{1}):S({}^{3}P_{0})$  resulting from the 193 nm photodissociation of CS<sub>2</sub> have been determined previously by VUV laser-induced fluorescence<sup>41</sup> and TOF mass spectrometric<sup>42</sup> experiments. The fine-structure distribution of  $S(3^{3}P_{2,1,0})$ is measured by summation over the peak intensities corresponding to transitions to the upper  $S(4^{3}P_{2,1,0})$  fine-structure levels.<sup>31</sup> The calibration of the  $S(^{3}P)$  and  $S(^{1}D)$  signals observed from thiophene to those observed from CS<sub>2</sub> at sufficiently low 193 nm photodissociation laser fluences allows determinations of the S(<sup>3</sup>P):S(<sup>1</sup>D) branching ratio and the absolute photodissociation cross section for the formation of S(3P, 1D) resulting from the 193 nm photodissociation of thiophene. We find that the fine-structure distribution for  $S(^{3}P_{2,10})$  from the 193 nm photodissociation of  $CS_2$  determined here using the 2 + 1 REMPI detection schemes is in excellent agreement with that obtained previously using the VUV laser-induced fluorescence technique.<sup>41</sup> The CS<sub>2</sub> samples (99% purity) used were obtained from Aldrich.

**B.** Theoretical Calculations. All calculations on the electronic structures of thiophene are performed using the GAMESS program.<sup>37</sup> The calculations are based on the MCSCF and the first-order configuration interaction (FOCI) methods.

We have optimized the structures of thiophene and Dewar thiophene using the 3-21G\* basis set.<sup>44</sup> The optimized geometric parameters (i.e., bond lengths (r) and bond angles ( $\theta$ )) of thiophene and Dewar thiophene obtained here are in good agreement with the experimental<sup>45</sup> and previous theoretical results (Table 1).<sup>11,46</sup> Thiophene is a sulfur-containing fivemembered heterocyclic planar molecule. The six  $\pi$  electrons (four  $\pi$  electrons from the conjugate diene and two  $\pi$  electrons from S) render thiophene an aromatic-like stability. The positions of the C atoms adjacent to S are labeled C(2) and C(5). The C atoms adjacent to C(2) and C(5) are C(3) and C(4), respectively. The position of the H atom attached to C(*i*) is labeled H(*i*), *i* = 2-5. For Dewar thiophene, a bond is formed between C(2) and C(5) and the S atom is located above the molecular plane containing the carbon atoms.



**Figure 1.** Schematic diagrams for the four highest occupied orbitals,  $2b_2$ ,  $11a_1$ ,  $3b_2$ , and  $1a_2$ , and the four lowest virtual orbitals,  $4b_2$ ,  $12a_1$ ,  $8b_1$ , and  $2a_2$ .

The standard 6-31G<sup>\*\*</sup> basis set<sup>44</sup> is used for all other calculations. In order to properly describe the excited states of thiophene, we have extended the basis set to include the Rydberg functions with  $\alpha_{4s} = 0.023$ ,  $\alpha_{4p} = 0.020$ , and  $\alpha_{3d} = 0.015$  for the sulfur atom and  $\alpha_{3s} = \alpha_{3p} = 0.040$  for the carbon atom.

In FOCI calculations, valence orbitals consist of the four highest occupied orbitals,  $2b_2$ ,  $11a_1$ ,  $3b_2$ , and  $1a_2$ , and the four lowest virtual orbitals,  $4b_2$ ,  $12a_1$ ,  $8b_1$ , and  $2a_2$ . The schematic diagrams for these orbitals are shown in Figure 1.

#### **III. Results and Discussion**

A. Isomeric Structures of Photofragments C<sub>4</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>S, and  $C_2H_2$ . Parts a, b, and c of Figure 2 depict the PIE spectra for  $C_2H_2^+$ ,  $C_4H_4^+$ , and  $C_2H_2S^+$ , respectively, resulting from VUV photoionization of photoproducts formed in the 193 nm photodissociation of thiophene. The typical counting time for  $C_4H_4^+$ ,  $C_2H_2^+$ , and  $C_2H_2S^+$  at each photoionization wavelength is 5 min. Each spectrum represents the average of more than two reproducible scans. The ionization onsets for the PIE spectra of Figure 2a,b,c are sharp, yielding IEs of 11.39 eV (1089 Å), 9.57 eV (1295 Å), and 8.91 eV (1391 Å) for the photofragments C<sub>2</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>S, respectively. We have also measured the PIE spectrum for  $C_4H_4S^+$  and  $C_2H_2S^+$  from thiophene when the photodissociation ArF laser is off. The IE for thiophene (8.87  $\pm$  0.01 eV (1398  $\pm$  2 Å)) and the AE for  $C_2H_2S^+$  from thiophene (12.10 ± 0.06 eV (1025 ± 5 Å)) determined from these spectra are in excellent agreement with



Figure 2. PIE spectra near the ionization thresholds for (a)  $C_2H_2^+$  from  $C_2H_2$ , (b)  $C_4H_4^+$  from  $C_4H_4$ , and (c)  $C_2H_2S^+$  from  $C_2H_2S$  formed in the 193 nm photodissociation of thiophene.

TABLE 2:	Summary	of PD-PI ar	nd 2 + 1 RI	EMPI Results
and Company	rison of the	<b>Energetics</b> f	or Isomers	of C <sub>4</sub> H <sub>4</sub> ,
C <sub>2</sub> H <sub>2</sub> S. and	C <sub>2</sub> H <sub>2</sub>	•		

ions detected <sup>a</sup>	neutral species <sup>b</sup>	$\frac{\Delta H_{f298}}{(\text{kcal/mol})^c}$	literature IE (eV) <sup>c</sup>	this work (eV)
$\overline{C_4H_4S^+}$	C <sub>4</sub> H <sub>4</sub> S (thiophene)	27.5	8.87	8.87 (1398 Å)
$C_4H_4^+$	$CH_2 = C = C = CH_2$	83	9.15	
	CH <sub>2</sub> =CH-C=CH	73	9.58	9.57 (1295 Å)
	C=C-C=CH <sub>2</sub>	101	8.15	
$C_2H_2S^+$	CH <sub>2</sub> =C=S	39	8.77	8.91 (1391 Å)
- 2 2	c-CH=CHS	$pprox 87^d$		
	•CH=CHS•	$\approx 101^{d}$		
$C_{2}H_{2}^{+}$	CH≡CH	54.4	$11.400 \pm 0.002$	11.39 (1089 Å)

(2 + 1) REMPI Detection of S(<sup>3</sup>P<sub>2.1.0</sub>, <sup>1</sup>D<sub>2</sub>)

absolute cross section for process  $1 = (1.2 \pm 0.5) \times 10^{-18} \text{ cm}^2$ 

branching ratio  $S(^{3}P):S(^{1}D) \ge 0.96 \pm 0.05:0.04 \pm 0.05$ 

fine-structure distribution  $S({}^{3}P_{2}):S({}^{3}P_{1}):S({}^{3}P_{0}) = 0.82 \pm 0.03:0.15 \pm 0.03:0.03 \pm 0.03$ 

<sup>a</sup> Ions observed which are attributable to VUV photoionization of photofragments for thiophene at 193 nm. <sup>b</sup> Possible isomers for photoproducts of thiophene formed at 193 nm. <sup>c</sup> Heat of formation at 298 K. Values are from ref 47 unless specified. <sup>d</sup> References 12 and 30.

the literature values.<sup>37</sup> Table 2 compares the IEs of photofragments  $C_4H_4$ ,  $C_2H_2S$ , and  $C_2H_2$  observed here with the literature IEs for  $C_2H_2$  and the isomers of  $C_4H_4$  and  $C_2H_2S$ .<sup>47</sup>

As expected, the IE for  $C_2H_2$  determined here is in excellent accord with that of HC=CH (acetylene), indicating that acetylene is a major photoproduct formed in the 193 nm photodissociation of thiophene. The rapid rise of the ionization threshold observed in Figure 2a has been observed in previous PIE studies of acetylene.<sup>48</sup>

The primary photofragment accompanying the formation of HC=CH is C<sub>2</sub>H<sub>2</sub>S. The structure for C<sub>2</sub>H<sub>2</sub>S is envisioned as *c*-CH=CHS (thiirene).<sup>14</sup> The heat of formation for thiirene is estimated to be 87 kcal/mol,<sup>12</sup> which is higher than that of the most stable thioketene structure (CH<sub>2</sub>=C=S) by  $\approx$ 48 kcal/mol. If the photodissociation of thiophene involves the formation of the biradical •CH=CH-CH=CH=S• as the initial step, the rapid decomposition of this biradical may yield the biradical •CH=CH=S• biradical is estimated to lie  $\approx$ 14 kcal/mol above thiirene.<sup>12</sup> Depending on the structure of C<sub>2</sub>H<sub>2</sub>S, the energetics<sup>47</sup> for the C<sub>2</sub>H<sub>2</sub>S + C<sub>2</sub>H<sub>2</sub> channel are

 $C_4H_4S(thiophene) +$ 

$$h\nu(193 \text{ nm}) \rightarrow CH_2 = C = S + HC = CH,$$
  
 $\Delta H^\circ_{298} = -82 \text{ kcal/mol} (7)$   
 $\rightarrow c-CH = CHS + HC = CH.$ 

$$\Delta H^{\circ}_{298} \approx -34$$
 kcal/mol (8)

→ •CHCHS• + HC=CH,  

$$\Delta H^{\circ}_{298} \approx -20 \text{ kcal/mol} (9)$$

According to the photofragmentation TOF mass spectrometric study of Myers,<sup>30</sup> the kinetic energy release for process 2 peaks at  $\approx$ 19 kcal/mol and has a kinetic energy threshold of  $\approx$ 41 kcal/ mol. The latter value is only about 50% of the exothermicity for process 7 and is close to that of process 8, after taking into account the uncertainties for the heat of formation of thiirene. This observation has been interpreted by Myers that thiirene is the dominant primary product structure formed in process 8. However, the experiment cannot rule out the formation of  $CH_2=C=S$  and •CHCHS•. The IEs for thirene and the •CH=C-S• biradical are unknown. The IE for CH<sub>2</sub>=C=S has been determined to be 8.77 eV in a photoelectron spectroscopic experiment.<sup>47,49</sup> The IE for the photofragment C<sub>2</sub>H<sub>2</sub>S from thiophene observed in this study is slightly higher than, but in reasonable agreement with, the IE of CH2=C=S. Without information about the IEs of c-CH=CHS and •CH=CH-S•, we tentatively conclude that the C2H2S photofragment from process 2 is thicketene, and the PIE spectrum of Figure 2c may be attributed to the photoionization of thioketene. The sharp ionization onset observed in the PIE spectrum of Figure 2c is consistent with similar structures for CH2=C=S and CH2=C=S<sup>+</sup>.

The photodissociation process

C<sub>4</sub>H<sub>4</sub>S(thiophene) + 
$$h\nu$$
(193 nm) →  
S(<sup>3</sup>P) + 2 HC≡CH, ΔH°<sub>298</sub> ≈ 0 kcal/mol (10)

is essentially thermoneutral. Although process 10 is energetically allowed, the yield may be small compared to the most stable channel (process 7). We note that thiophene has been observed to be a product of the reaction of  $S(^{3}P)$  and acetylene.<sup>12</sup> However, the formation of thiophene from the reaction of  $S(^{3}P)$ and acetylene most likely results from secondary collision processes. For C<sub>4</sub>H<sub>4</sub> there are three stable isomers, CH<sub>2</sub>=C=C=CH<sub>2</sub> (butatriene), CH<sub>2</sub>=CH-C=CH (vinylacetylene), and  $\overrightarrow{C=C-C}$ =CH<sub>2</sub> (3-methylenecyclopropene), with IE values of 9.15, 9.58, and 8.15 eV, respectively.<sup>47</sup> As shown in processes 11-13, the formation of these isomers is energetically feasible if the accompanying sulfur atoms are in the electronic ground S(<sup>3</sup>P) state.

 $C_4H_4S$ (thiophene) +

$$h\nu(193 \text{ nm}) \rightarrow CH_2 = CH - C = CH + S(^{3}P),$$
  
$$\Delta H^{\circ}_{298} = -36 \text{ kcal/mol} (11)$$

→ CH<sub>2</sub>=C=C=CH<sub>2</sub> + S(<sup>3</sup>P),  

$$\Delta H^{\circ}_{298} = -26 \text{ kcal/mol} (12)$$
  
→ C=C-C=CH<sub>2</sub> + S(<sup>3</sup>P),  
 $\Delta H^{\circ}_{298} = -8 \text{ kcal/mol} (13)$ 

The maximum energy release for process 1 observed in the laser photofragmentation experiment of Myers<sup>30</sup> is ≈16 kcal/mol, significantly lower than the exothermicities for processes 11 and 12. Since the first excited S(1D) state lies 27 kcal/mol above the ground  $S(^{3}P)$  state,  $S(^{1}D)$  can be also formed together with vinylacetylene. The excellent agreement of the IE for vinylacetylene (CH2=CH-C=CH) with that determined from Figure 2b indicates that the C<sub>4</sub>H<sub>4</sub> photofragments formed in process 1 are predominantly vinylacetylene. Since the IEs for  $CH_2 = C = C = CH_2$  and  $\dot{C} = C - \dot{C} = CH_2$  are lower than that for CH<sub>2</sub>=CH-C=CH, the PIEs for  $C_4H_4^+$  at photon energies below the IE of  $CH_2=CH-C=CH$  (9.56 eV (1295 Å)) can be attributed to the ionization of  $CH_2=C=C=CH_2$  and  $\dot{C}=C-\dot{C}=CH_2$ . The very small PIEs for  $C_4H_4^+$  observed at wavelengths > 1295 Å are consistent with the conclusion that formation of the isomers CH<sub>2</sub>=C=C=CH<sub>2</sub> and C=C -Ċ=CH<sub>2</sub> in process 1 is negligible.

**B.** Electronic and Fine Structure Distributions of  $S({}^{3}P_{J}, {}^{1}D_{2})$ . Due to possible relaxation of  $S({}^{1}D)$  in the supersonic jet, the PD-PI experimental scheme described in section II.A (a) is not appropriate for the determination of the nascent electronic state distribution of S atoms. The application of the 2 + 1 REMPI scheme described in section II.A (b) is essential for measuring the  $S({}^{3}P_{J}, {}^{1}D_{2})$  distribution because in the 2 + 1 REMPI experiment the nascent S atoms are probed in a collision-free regime.

As shown in Figure 3a, the S<sup>+</sup> intensity resulting from the 2 + 1 REMPI of  $S(^{3}P_{2})$  in the 193 nm photodissociation laser fluence (F) range  $(0.5-10) \times 10^{16}$  photon/cm<sup>2</sup> is linear, indicating that the formation S atoms from thiophene is the result of single-photon dissociation events. The S<sup>+</sup> intensity due to 2 + 1 REMPI of S(<sup>1</sup>D) is very low. Figure 3b depicts the 193 nm photodissociation laser F dependence for  $S^+$  from  $S(^1D)$  in the range  $\approx (5-40) \times 10^{16}$  photons/cm<sup>2</sup>. The nonlinear behavior observed in Figure 3b indicates that the formation of  $S(^{1}D)$  at high laser fluence may involve secondary photodissociation or higher order laser dissociation processes. The results obtained for the  $S(^{3}P)$ ;  $S(^{1}D)$  branching ratio and the  $S(^{3}P_{2,1,0})$  fine structure distribution resulting from process 1 are summarized in Table 2. At  $F \approx 14 \times 10^{16}$  and  $5.5 \times 110^{16}$  photons/cm<sup>2</sup>, we obtain the S(<sup>3</sup>P):S(<sup>1</sup>D) branching ratios of  $(0.92 \pm 0.05)$ :  $(0.08 \pm 0.05)$  and  $(0.96 \pm 0.05)$ : $(0.04 \pm 0.05)$ , respectively. On the basis of this observation, we conclude that S atoms resulting from process 1 are predominantly ( $\geq 96\%$ ) in the S(<sup>3</sup>P)



**Figure 3.** (a) S<sup>+</sup> ion intensity formed in the 2 + 1 REMPI of S(<sup>3</sup>P<sub>2</sub>) from THP (thiophene) plotted as a function of the 193 nm laser fluence (*F*) in the range  $(0.5-10) \times 10^{16}$  photons/cm<sup>2</sup>. (b) S<sup>+</sup> ion intensity formed in the 2 + 1 REMPI of S(<sup>1</sup>D<sub>2</sub>) from THP plotted as a function of *F* in the range  $(5-40) \times 10^{16}$  photons/cm<sup>2</sup>.

ground state. We cannot exclude the possibility that the small amount of S(<sup>1</sup>D) observed is attributable to high-order laser dissociation processes. Since the absolute 193 nm photodissociation cross section for S from CS<sub>2</sub> is known, the calibration of the 2 + 1 REMI of S from thiophene and CS<sub>2</sub> at low *F* values makes possible the measurement of the absolute cross section for process 1. The value of  $(1.2 \pm 0.5) \times 10^{-18}$  cm<sup>2</sup> for the absolute cross section of S from thiophene is similar to those for the formation of S from HS and CH<sub>3</sub>S at 193 nm estimated in previous photodissociation studies.<sup>32-34</sup>

The S( ${}^{3}P_{2,1,0}$ ) fine structure distribution is determined to be  ${}^{3}P_{2}$ : ${}^{3}P_{1}$ : ${}^{3}P_{0} = 0.82 \pm 0.03:0.15 \pm 0.03:0.03 \pm 0.03$ . This distribution is significantly colder than the statistical distribution  ${}^{3}P_{2}$ : ${}^{3}P_{1}$ : ${}^{3}P_{0} = 0.56:0.33:0.11$  and those observed previously for S atoms formed in the 193 nm photodissociation of HS and CH<sub>3</sub>S.<sup>32-34</sup> It is, however, similar to the distribution of  ${}^{3}P_{2}$ : ${}^{3}P_{1}$ : ${}^{3}P_{0} = 0.71:0.20:0.09$  for S atoms resulting from the 193 nm photodissociation of CS<sub>2</sub>.<sup>41</sup>

C. Ab Initio Calculations. According to the ab initio calculations, the ground electronic  $1^{1}A_{1}$  state for thiophene corresponds to the configuration  $(\dots 3b_2^{21}a_2^{21})$  (see orbital diagram in Figure 1). The first six singlet electronic excited states in the energy range (<7.0 eV) of this study are  $2^{1}A_{1}$ ,  $1^{1}A_{2}$ ,  $1^{1}B_{2}$ ,  $1^{1}B_{1}$ ,  $2^{1}A_{2}$ , and  $2^{1}B_{2}$ , with the main orbital configurations of  $(\dots 3b_2^{1}1a_2^{2}4b_2^{1})$ ,  $(\dots 3b_2^{2}1a_2^{1}12a_1^{1})$ ,  $(\dots 3b_2^{1} 1a_2^{2}12a_1^{1}$ , (...  $3b_2^{2}1a_2^{1}4b_2^{1}$ ), (...  $3b_2^{1}1a_2^{2}8b_1^{1}$ ), and (...  $3b_2^{2}1a_2^{1} 8b_1^{1}$ ), respectively. We note that the symmetry labels of these excited states are different from those obtained in the previous semiempirical study.<sup>29</sup> The predicted vertical excitation energies and their corresponding oscillator strengths and asymtotic adiabatic S(<sup>3</sup>P, <sup>1</sup>D) states are given in Table 3. Considering the oscillator strengths of these excited states, the  $1^{1}A_{2}$  and  $2^{1}A_{2}$ states should play little role in the photoexcitation of thiophene. According to predicted vertical excitation energies and oscillator strengths, excited thiophene is most likely formed in the  $1^{1}B_{1}$ and/or  $2^{1}B_{2}$  states by the absorption of a 193 nm photon. The  $1^{1}B_{1}$  and  $2^{1}B_{2}$  states are formed primarily by the excitation of an electron from the  $1a_2$  to the  $4b_2$  and  $8b_1$  orbitals, respectively. Thus the excitations  $1^{1}B_{1} \leftarrow 1^{1}A_{1}$  and  $2^{1}B_{2} \leftarrow 1^{1}A_{1}$  correspond to the  $\pi^* \leftarrow \pi$  and  $\sigma^* \leftarrow \pi$  transitions, respectively.

TABLE 3: Predicted Spectroscopic Properties for SelectedExcited States Which May Be Involved in the 193 nmPhotodissociation of Thiophene ( $C_4H_4S$ )

electronic states $C_4H_4S (C_{2\nu})^a$	vertical transition energy (eV) <sup>b</sup>	oscillator strength <sup>c</sup>	adiabatic product S( <sup>3</sup> P, <sup>1</sup> D, <sup>1</sup> S) states
$1^{1}A_{1}(, 3b_{2}^{2}1a_{2}^{2})$			S( <sup>3</sup> P)
$2^{1}A_{1}( 3b_{2}^{1}1a_{2}^{2}4b_{2}^{1})$	5.51	0.0913	$S(^{1}D)$
$1^{1}A_{2}( 3b_{2}^{2}1a_{2}^{1}12a_{1}^{1})$	5.73	0.0000	S( <sup>3</sup> P)
$1^{1}B_{2}( 3b_{2}^{1}1a_{2}^{2}12a_{1}^{1})$	5.85	0.0231	S( <sup>3</sup> P)
$1^{1}B_{1}(, 3b_{2}^{2}1a_{2}^{1}4b_{2}^{1})$	6.09	0.0284	$S(^{1}D)$
$2^{1}A_{2}(, 3b_{2}^{1}1a_{2}^{2}8b_{1}^{1})$	6.70	0.0000	$\hat{\mathbf{S}}(\mathbf{D})$
$2^{1}B_{2}(, 3b_{2}^{2}1a_{2}^{1}8b_{1}^{1})$	6.94	0.1138	S( <sup>1</sup> D)

<sup>*a*</sup> First seven singlet electronic states for thiophene. The main orbital configurations for these states are given in parentheses. <sup>*b*</sup> Measured from the ground  $1^{1}A_{1}$  state of thiophene. <sup>*c*</sup> Oscillator strengths for photoexcitation from the ground  $1^{1}A_{1}$  state.



**Figure 4.** Potential energy curves for thiophene in  $C_{2\nu}$  symmetry plotted as a function of the distance R (=(2)<sup>1/2</sup>r[S-C(2 or 5)]) in angstroms. Note that the 1<sup>1</sup>B<sub>1</sub> potential energy curve is not labeled.

The results of these experiments and that of Myers<sup>30</sup> indicate that the sulfur atom elimination from thiophene is the dominant photodissociation channel at 193 nm. Furthermore, the 2 + 1REMPI study has also shown that S atoms are formed overwhelmingly in the ground <sup>3</sup>P state. An examination of the  $4b_2$  and  $8b_1$  orbitals reveals that the bonding between the S atom and the adjacent C(2) and C(5) carbons is antibonding in nature. suggesting that the dissociation of thiophene via these excited states favors the formation of C<sub>4</sub>H<sub>4</sub> and S. We have examined the potential energy surfaces of the  $1^{1}A_{1}$ ,  $2^{1}A_{1}$ ,  $1^{1}A_{2}$ ,  $1^{1}B_{2}$ ,  $1^{1}B_{1}$ ,  $2^{1}A_{2}$ , and  $2^{1}B_{2}$  states by symmetrically increasing r[S-C(2)]and r[S-C(5)] in the carbon-sulfur molecular plane while keeping other C-C and C-H bond lengths and angles unchanged. The potential surfaces thus obtained are shown in Figure 4,50 which reveal an avoided electronic crossing between  $1^{1}A_{2}$  and  $2^{1}A_{2}$  and between  $1^{1}B_{2}$  and  $2^{1}B_{2}$  at  $r[S-C(2 \text{ or } 5)] \approx$ 1.84 Å. If the initial 193 nm excitation involves  $2^{1}B_{2} \leftarrow 1^{1}A_{1}$ , the formation of  $C_4H_4 + S(^{3}P)$  can be rationalized by crossing from the upper  $2^{1}B_{2}$  state to the lower  $1^{1}B_{2}$  state along the dissociation coordinate via nonadiabatic couplings. The asymptotic limit for  $2^{1}B_{2}$  (i.e., for the formation of  $S(^{1}D)$ ) is predicted to be greater than the excitation energy of 6.4 eV (193 nm) shown in Figure 4. However, if the geometry for  $C_4H_4$  is allowed to relax and to rearrange to the most stable vinylacetylene structure, the formation of  $S(^{1}D)$  is energetically allowed via the  $2^{1}B_{2}$  state. The observation of vinylacetylene as the predominant C<sub>4</sub>H<sub>4</sub> isomer in this experiment clearly indicates

that rearrangement by hydrogen migration takes place as r[S-C(2)] and r[S-C(5)] are increased along the dissociation coordinate.

If the actual dissociation process of excited thiophene involves S-C bond breaking and motions of other degrees of freedom necessitated for hydrogen migration, the formation of  $C_4H_4 + S$  is probably not a concerted process. It is most likely that the initial step takes place by breaking one of the S-C bonds to form the •CHCHCHCHS• biradical, as suggested by the mechanism of van Tamalen and Whitesides.<sup>51</sup> Since hydrogen migration is fast with a relatively small activation energy of  $\approx 10$  kcal/mol, further rearrangement and dissociation of the •CHCHCHCHS• biradical can easily account for the formation of S,  $C_2H_2$ , and  $CH_2=C=S$ , and  $CH_2=CH-C=CH$ .

The antibonding character observed for the S-C(2) and S-C(5) bonds is also found in the C(3)-C(4) bond of the  $8b_1$  orbital. This indicates that the decay of thiophene via the  $2^1B_2$  state may also proceed according to process 10.

The 4b<sub>2</sub> orbital exhibits antibonding character between C(2) and C(3) and between C(4) and C(5). Breakage of the C(2)– C(3) and C(4)–C(5) bonds, together with cyclization between C(2) and C(5) of excited thiophene in the 1<sup>1</sup>B<sub>1</sub> state, would give CH=CH and *c*-CH=CHS. The formation of CH<sub>2</sub>=C=S can be realized if the internal energy content of *c*-CH=CHS is higher than the rearrangement barrier between *c*-CH=CHS and CH<sub>2</sub>=C=S. The 1<sup>1</sup>B<sub>1</sub> state may play an important role in UV photochemistry of thiophene at wave lengths > 193 nm.

Previous photochemical studies of thiophene at lower photon energies suggest that the dissociation mechanism for thiophene may involve an intermediate with a Dewar thiophene structure (see geometrical parameters in Table 1). The Dewar thiophene structure is formed by internal cyclization forming a bond between C(2) and C(5) with concomitant deformation of the S atom out of the molecular plane. We have examined the potential surfaces for the 1<sup>1</sup>A<sub>1</sub>, 2<sup>1</sup>A<sub>1</sub>, 1<sup>1</sup>A<sub>2</sub>, 1<sup>1</sup>B<sub>2</sub>, and 1<sup>1</sup>B<sub>1</sub> states by deforming the planar thiophene structure to the Dewar thiophene structure. This reveals an avoided electronic crossing between the  $1^{1}A_{1}$  and  $2^{1}A_{1}$  surfaces, suggesting that, with sufficiently high internal excitations, thiophene in the ground  $1^{1}A_{1}$  state may rearrange to a stable Dewar thiophene structure. This conclusion is in accord with the previous semiempirical calculation.<sup>29</sup> The Dewar thiophene should play a role in ultraviolet photochemistry of thiophene in condensed phases, where internal relaxation is rapid. This is consistent with the observation of Dewar thiophene in a photochemical study of thiophene in an Ar-matrix.<sup>16</sup>

The thiopheme to argon seeding ratio used in the PD-PI experiment described in section II.A(a) is  $\approx 13\%$ . Although the  $C_4H_4$ ,  $C_2H_2S$ , and  $C_2H_2$  observed in the PD-PI experiment are believed to be comprised mainly of primary photodissociation products, at this seeding ratio and the relative high partial stagnation pressure ( $\approx$ 140 Torr) of thiophene used, the effects of secondary reactions cannot be eliminated. Due to the low sensitivity of this experiment, it is not possible to measure accurately the PIE spectra for  $C_4H_4^+$ ,  $C_2H_2S^+$ , and  $C_2H_2^+$  at a partial stagnation pressure of thiophene significantly lower than 140 Torr. Furthermore, since the photodissociation of thiophene is initiated in the high-pressure region of the supersonic jet, the dissociation of long-lived internally excited intermediates may be quenched by collisions with the bath Ar atoms. Because of this, the branching ratios for product channels measured in the PD-PI experiment described may be modified. It is possible to study the collision-quenching effect by examining the PIE spectra of photofragments as a function of the distance between the laser photodissociation region and the nozzle tip. Again,

this study was not performed because of the low sensitivity of the PD-PI experiment. The fact that processes 3-6 are not identified in this study may be partly the result of collision quenching and/or the low sensitivity of the PD-PI experiment. It also possible that the ArF laser energies of 30-80 mJ used in this experiment are sufficiently high to induce secondary photochemical processes,<sup>30</sup> which may complicate the product branching ratio measurements.

The sensitivity of the PD-PI experiment can be improved by increasing the repetition rates of the 193 nm photodissociation laser and the pulsed nozzle valve. The VUV photon intensities obtainable from the conventional discharge light sources used in this experiment are estimated to be  $\approx 10^{10} - 10^{11}$  photons/s at the bandwidth of  $\approx 2$  Å fwhm. Third-generation sychrotron radiation sources, such as the Advanced Light Source at the Lawrence Berkeley Laboratory, using the proper undulator design are expected to provide up to  $10^{15}-10^{16}$  photons/s at a 0.1% bandwidth in the photon energy range 5-30 eV.<sup>51</sup> Future PD-PI experiments utilizing this synchrotron source for VUV photoionization detection are very promising for detailed structure identification of primary photofragments formed in photochemical processes which have significantly lower photodissociation cross sections than that for thiophene.

Excited potential energy curves of higher multiplicities may also be involved in the UV photochemistry of thiophene. The detailed examination of the UV photodissociation dynamics of thiophene in the future will require a higher level theoretical study.

#### **IV.** Conclusion

Using the PD-PI and 2 + 1 REMPI experimental schemes, we have examined the isomeric structures of photofragments formed in the 193 nm photodissociation of thiophene. The major product channels are found to be CH=CH-C=CH +  $S(^{3}P)$  and  $CH = CH + CH_{2} = C = S$ .

Ab initio calculations reveal that the excited electronic  $1^{1}B_{1}$ and 21B2 states are most likely involved in the 193 nm photodissociation of thiophene. These states have a main configuration corresponding to excitation to an excited molecular orbital with significant antibonding between S and its adjacent C atoms, favoring the elimination of S. The potential energy surface for the first seven electronic states of thiophene have been examined along the dissociation coordinate for the elimination of S. An avoided crossing between the  $1^{1}B_{2}$  and  $2^{1}B_{2}$  has been found. Since the  $1^{1}B_{2}$  state dissociates adiabatically to form  $S(^{3}P)$ , the observation of  $S(^{3}P)$  in this experiment is rationalized by transition from  $2^{1}B_{2}$  to  $1^{1}B_{2}$  by nonadiabatic couplings along the dissociation coordinate.

With significant increase in available VUV light intensity from third-generation synchrotron sources, the PD-PI experimental scheme is very promising for structural identification of photochemical processes involving polyatomic species.

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