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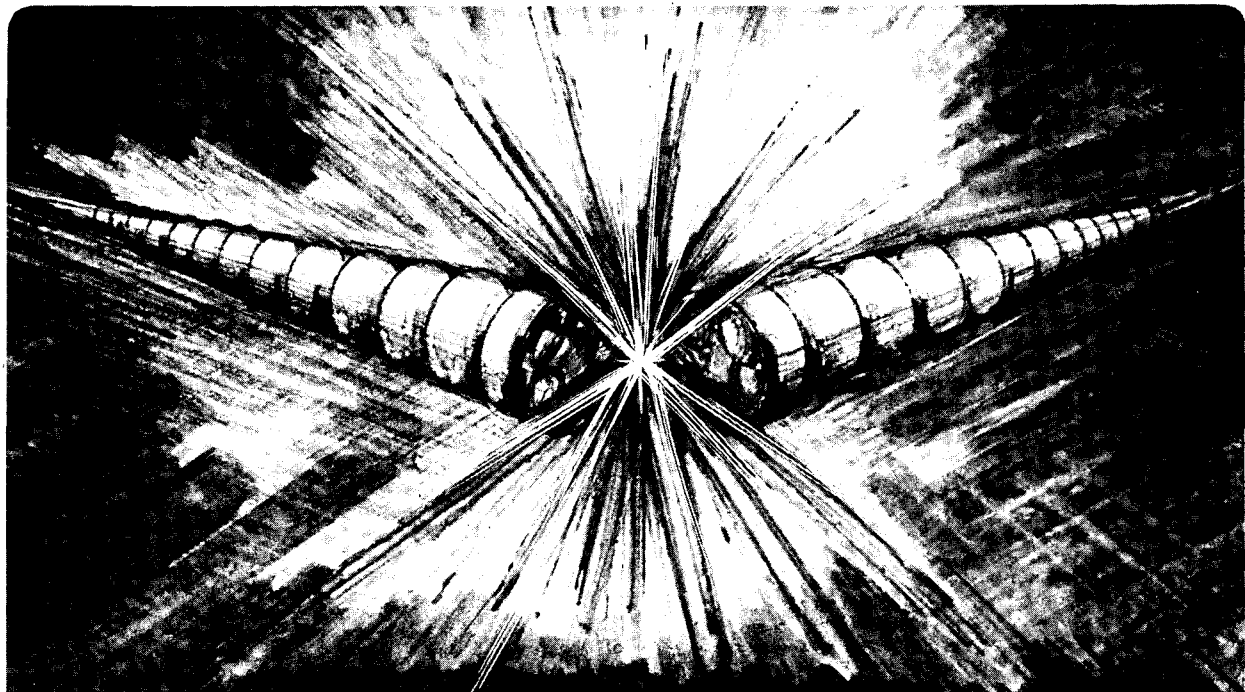
MOLECULAR X-RAY SPECTRA: S-K $\beta$  EMISSION AND  
K ABSORPTION SPECTRA OF THIOPHENE

R.C.C. Perera and R.E. LaVilla

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MOLECULAR X-RAY SPECTRA: S-K $\beta$   
•  
EMISSION  
AND K ABSORPTION SPECTRA OF THIOPHENE

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## ABSTRACT

The high resolution sulfur  $K\beta$  emission in fluorescence and sulfur K absorption of thiophene ( $C_4H_4S$ ) were measured with a double crystal spectrometer. The sulfur  $K\beta$  emission spectrum was analyzed by comparison with complementary spectral data and with MNDO and ab initio (STO-3G) MO calculations. A tentative assignment of the prominent features in the absorption spectrum was made using MO calculations as a guide. In addition the sulfur  $L_{II,III}$  emission spectrum was reinterpreted. The sulfur 1s binding energy of thiophene was estimated as 2477.4 eV.

## I. INTRODUCTION

Thiophene ( $C_4H_4S$ ) is unique in being the simplest molecule containing a sulfur atom as one member of a five-member ring structure. Because of this uniqueness, the molecular orbital (MO) electronic structure has been studied both theoretically and experimentally. The ultraviolet photoelectron spectrum (UPS) using HeI (21 eV) photon excitation of gaseous thiophene was measured by Eland<sup>1</sup> who obtained ionization potentials to about 18 eV. Derrick, et al.<sup>2</sup> extended the range of measured ionization potentials to 25 eV using HeII (40 eV) photon excitation. The x-ray excited photoelectron spectrum (XPS) was measured by Gelius et al.<sup>3</sup> in the vapor phase using Mg-K $\alpha$  x-ray excitation. They adjusted the peak positions of their XPS spectrum to agree with the inner levels of the UPS spectrum by Derrick et al.<sup>2</sup> and interpreted the results with the aid of ab initio MO calculations<sup>4</sup> performed with an extended set of contracted Gaussian basis wave functions.

X-ray spectra complement photoelectron spectra since x-ray transitions are governed by selection rules. Hence, x-ray emission provides an effective method to study the valence (outer) MO structure by probing with different inner shell vacancies of the molecular atoms. For electric dipole transitions<sup>5</sup>, the S-K $\beta$  emission profile from a sulfur containing molecule is proportional to the outer MO's with sulfur 3p character<sup>5</sup>, whereas, the S-L<sub>II,III</sub> emission is related to the outer MO's with [3s + (2/5) 3d] character<sup>6</sup> computed to be present multiplied by the cube of photon energy for

the particular MO. To date, reports of x-ray emission from vapor phase thiophene have been limited to the S-K $\beta$  measurement by Phillips and Andermann<sup>7</sup> and to the S-L<sub>II,III</sub> measurement by Taniguchi and Henke<sup>6</sup>. The purpose of this report is to present high resolution S-K $\beta$  emission and S-K absorption spectra of vapor phase thiophene and to interpret our spectra and previous measurements in terms of our present MO calculations.

## II. Experimental

The fluorescent sulfur K $\beta$  emission and sulfur K absorption spectra in the present work were obtained with a double crystal spectrometer,<sup>8</sup> using calcite crystals ( $2d = 6.0717 \text{ \AA}$ ). These crystals have a nominal resolving power of about 10,000 in the 4-5  $\text{\AA}$  region which limits the instrumental broadening to about 0.2 eV. The monochromatized radiation was detected with a gas flow proportional counter filled with P-10 (90 vol % argon, 10 vol % methane) to 50.7 k Pascal (0.5 atm). Primary radiation was obtained from a gold plated copper anode<sup>8</sup> operating at 16 kV, 120 mA. All spectra were recorded by stepscanning the spectrometer. The pressure of the flowing gas sample in the fluorescent cell<sup>9</sup> was maintained at 5.25 k Pascal for the emission spectra and in a 5 cm long cell at 3.54 k Pascal for the absorption spectra. The sample vapor was contained in both cells by 6  $\mu\text{m}$  thick beryllium windows. Commercially obtained reagent grade thiophene was used with no further purification.

The measured sulfur  $K\beta$  emission and K absorption spectra of thiophene are shown in Fig. 1, and the energies of the indicated features are given in Table 1. All of the spectra presented in this work are the average of two different scans with individual scans reproducible to within statistical deviations. The energy scale in Fig. 1 was established relative to the sulfur K absorption<sup>10</sup> of  $SF_6$  which in turn had been set relative to vanadium  $K\alpha_1$  in second order<sup>11</sup>.

## II. Results and Discussion

### A. MO Calculations

The semi-empirical MNDO method<sup>12</sup> and ab initio (STO-3G) method<sup>13</sup> with complete geometry optimization were performed as described in Appendix I. A good estimate of the orbital composition was obtained directly from the eigenvectors of the MO calculations listed in tables 2 and 3. The calculated sulfur  $K\beta$  and  $L_{II,III}$  radiative yield values for both MO methods are also presented in tables 2 and 3. The single vacancy S- $K\beta$  spectrum was synthesized<sup>14</sup> from the calculated S- $K\beta$  radiative yield values and the XPS/UPS experimental binding energies<sup>2</sup>, and was smeared with a Lorentzian function of 1.0 eV FWHM. The synthesized emission profiles are compared in fig. 2 with the measured sulfur  $K\beta$  emission spectrum.

In table 4 is a comparison of MO energies from the previous ab initio calculations of Gelius et al.<sup>4</sup> using an extended set of contracted Gaussian



basis functions, the many body approach of Niessen et al.<sup>15</sup> that includes the effects of electron correlation and reorganization beyond the Hartree-Fock approximation, and the present MO calculations. Note that, the calculated orbital energies vary with MO method employed which would be expected in view of the different approximations used in the procedures. The orbital energies of the "deep lying"  $1a_1$  and  $1b_2$  valence MO's calculated by the MNDO method differs relatively more from the other calculations. This is not surprising for a valence basis set MO calculation, since the contribution of the core electrons are more important for this MO energy region and are not as well represented in the MNDO MO method. The order of orbitals resulting from the MNDO method agrees well with the results of a more sophisticated ab initio<sup>4,15</sup> method, whereas, the minimum basis set ab initio (STO-3G) method does not. In previous works, the MNDO method has been shown to be successful in calculating the order of orbitals, especially for unsaturated hydrocarbon ring structures<sup>16</sup>. The order of MO levels calculated with the CNDO/2 MO method<sup>17</sup> does not compare very well with the other MO methods. This is not surprising since extensive approximations are made in the CNDO/2 method to simplify the calculations.

#### B. Emission Spectrum

The overall structure and relative peak positions in sulfur  $K\beta$  emission spectrum of thiophene in fig. 1 agree with the previous measurement of Phillips and Andermann<sup>7</sup>, but spectral lines in fig. 1 are narrower.

The assignment of prominent features in the experimental S-K $\beta$  emission spectrum was made by comparison with the calculated synthesized spectrum in fig. 2. As seen in fig. 2 the calculated spectrum based on the semi-empirical MNDO MO method<sup>12</sup> gives the best overall agreement with the experimental data.

The emission peaks A, B and C are assigned as the dipole allowed transitions of the initial 1s vacancy of the molecular sulfur atoms to the 2b<sub>1</sub>, 6a<sub>1</sub> + 1b<sub>1</sub> and 4b<sub>2</sub> valence MO's respectively. The broad features D and E in S-K $\beta$  emission spectrum are identified as single vacancy transitions to 2b<sub>2</sub> + 4a<sub>1</sub> and 2a<sub>1</sub> + 1b<sub>2</sub> valence MO's, respectively. It is suggested that A' is a high energy satellite complex to the parent A line resulting from transitions between multiple vacancy states. Similar but more prominent high energy satellite peaks were observed in other S-K $\beta$  molecular emission spectra<sup>14,18</sup> and in Cl-K $\beta$  emission spectrum.<sup>19</sup>

The line widths of peaks in emission spectrum indicate the bonding nature of the MO for the allowed dipole transitions. Very sharp lines would be attributed to transitions from non-bonding valence MO's which are the outermost easily ionized MO's. Transition from the outermost bonding MO's will have an additional width due to the vibrational structure associated with these bonding MO's. This is clearly evident in the C-K emission spectrum<sup>20</sup> of CO<sub>2</sub> and in the envelope of the S-K $\beta$  spectrum in H<sub>2</sub>S.<sup>18</sup> The transitions from deeper lying valence MO's which are most atomic-like would be expected to be sharp, but these transitions are broadened by the competing Coster-Kronig decay of the final states. Some of these distinctions in line width can be

observed in the S-K $\beta$  emission of thiophene in figs. 1 and 2. An estimate of the natural line width can be obtained from peak A, the transition from the non bonding 2b<sub>1</sub> valence MO, which has a minimum of overlapping in the spectrum. The FWHM (full width half maximum) of peak A is 1.0 eV. Since the instrumental broadening is about 0.2 eV, the natural line width is approximately 0.8 eV, assuming Lorentzian line shapes. This is in accord with previously estimated widths of valence MO's for thiophene molecule.<sup>6</sup>

### C. Absorption Spectrum

The sulfur K absorption spectrum of thiophene, shown in Fig. 1, has not been reported to date. The sulfur 1s electron binding energy and hence the 1s threshold in the K absorption spectrum can be estimated by adding the binding energy of the final states from photoelectron spectra to the energy positions of the relevantly assigned K $\beta$  emission lines. The sulfur K shell binding energy of thiophene is estimated to be 2477.6 eV and is indicated in fig. 1. This estimate was made using the sharpest emission line A, assigned to 2b<sub>1</sub>  $\rightarrow$  1s and the 2b<sub>1</sub> MO binding energy<sup>2</sup> from UPS data. The estimated binding energy is 1 eV lower than the sulfur 1s of H<sub>2</sub>S and may reflect an increase of screening from the valence electrons of the ring structure.

The immediate unoccupied ground state valence MO's of thiophene are 3b<sub>1</sub>, 2a<sub>2</sub> and 5b<sub>2</sub> + 7a<sub>1</sub>, in that order. The sharp peaks, F and G, in the absorption spectrum of thiophene shown in Fig. 1 are suggested to be transitions of the

sulfur 1s electron to the unoccupied  $3b_1$  and  $2a_2$  MO's, respectively. Feature H is suggested to be due to overlapping transitions to unoccupied  $5b_2$  and  $7a_1$  valence MO's. The broad structure observed above the 1s threshold, is tentatively attributed to a shape resonance structure. Similar suprathreshold structures were observed and identified<sup>19</sup> in Cl-K emission and absorption spectra of  $\text{CH}_3\text{Cl}$ .

#### D. Comparison with S-L<sub>II,III</sub> Emission

To facilitate the comparison with the S-L<sub>II,III</sub> spectrum of thiophene<sup>6</sup>, the ab initio calculations of Gelius et al.<sup>4</sup> and the present MO calculations are presented in fig. 3 in a "stick" spectral representation in which the height of the "sticks" represent the relative radiative yield values of the respective emission line (from tables 2 and 3) positioned to indicate the principal L<sub>III</sub> component. Taniguchi and Henke<sup>6</sup> revised previous MO assignments of the S-L<sub>II,III</sub> spectrum on the basis of calculated radiative yields based upon orbital compositions from the available CNDO/2 MO method<sup>17</sup>. As seen from fig. 3, the present calculations result in an appreciably higher intensity for transitions with  $3a_1$  valence MO final state than with  $1a_1$  valence MO final state, whereas the previous CNDO/2 method gave the largest sulfur 3s character contribution to the  $4a_1$  valence MO and no significant sulphur 3s character in the  $3a_1$  valence MO. On the basis of the present MO calculations, peak 4 in fig. 3 is assigned to a transition with the  $3a_1$  valence MO final state in contrast to the earlier assignment to  $4a_1$  valence MO final state. Hence, peaks 2 and 3 are assigned to transitions from  $4b_2 + 5a_1$

and  $4a_1$  valence MO's respectively, and peak 1 is assigned to transitions from  $6a_1 + 1a_2$  orbitals. These revisions are summarized in table 5 along with the previous assignments of Taniguchi and Henke<sup>6</sup>.

Broad peaks 5 and 6 in S- $L_{II,III}$  emission spectrum of thiophene are assigned to transitions from the  $2a_1$  and  $1a_1$  valence MO's respectively, but the derived experimental intensities of these peaks are considerably higher than the calculated radiative yields presented in tables 2 and 3. This suggests that much of the intensity in these peaks may be derived from a radiative Auger process accompanying the  $L_{II,III}$  x-ray emission.<sup>21,22</sup> The calculated<sup>23</sup> approximate energies of these satellite peaks are 146.4 eV and 143.1 eV and are in good comparison with experimental position of peaks 5 and 6 at 147.8 eV and 143.2 eV, respectively. Similar low energy satellite peaks have been observed in Ar-, K- and Cl- $L_{II,III}$  emission spectra.<sup>21,23,24</sup>

The comparison of calculated and experimental sulfur  $L_{II,III}$  emission intensities presented in fig. 3 is elusive, since x-ray satellite transitions are superposed on single vacancy transitions array. In particular, the intensities of the broad peaks 5 and 6 in sulfur  $L_{II,III}$  emission spectrum should contain large contributions from the radiative Auger process. In the absence of calculated intensity contributions from the radiative Auger process, we can compare our calculated intensities with experimental by normalizing to peak 4, which should be primarily due to a single vacancy transition. The calculated intensities based upon single vacancy transitions would be expected to be smaller than the experimental intensities. The

relative intensities of peaks 4, 5 and 6 in sulfur  $L_{II,III}$  emission spectrum, normalized to peak 4, are presented in Table 6. Note, that the MNDO MO calculated relative intensities for peaks 5 and 6 are consistently less than experiment to suggest better agreement with the sulfur  $L_{II,III}$  emission spectrum.

The experimental ionization and binding energies for valence MO's in thiophene are also summarized in table 4, where unoccupied orbitals are indicated in brackets. Note that the experimental ionization and binding energies for occupied valence MO's of thiophene are in good agreement with each other except for the S- $L_{II,III}$  binding energy for  $1a_2$  orbital. The S- $L_{II,III}$  absorption or sulfur energy spectra data for thiophene are not available to our knowledge to correlate with the sulfur K absorption features.

#### IV. CONCLUSION

The sulfur  $K\beta$  emission in fluorescence and the sulfur K absorption in the edge region for thiophene vapor have been measured with high resolution. Ground state MO calculations of thiophene using the semi-empirical MNDO and the ab initio (STO-3G) methods were performed to guide the interpretation of the spectra.

The MNDO MO calculated intensities were found to give the best overall agreement with the experimental sulfur  $K\beta$  and  $L_{II,III}$  spectra. A reinterpretation of the sulfur  $L_{II,III}$  emission spectrum was also made using

intensities obtained from the MNDO MO calculation. Computer time necessary for MNDO MO calculations is considerably less than for the other methods, thus facilitating the interpretation of valence based x-ray emissions spectra of molecular systems at a reasonable computer cost.

A tentative assignment of the resonance structure in the sulfur K absorption is given based on the MO calculations. The sulfur 1s binding energy of thiophene was estimated to be 2477.4 eV.

## ACKNOWLEDGEMENTS

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## APPENDIX I

The MNDO<sup>12</sup> and ab initio<sup>13</sup> (STO-3G) MO calculations were performed for thiophene with complete geometrical structure optimization within the constraint of C<sub>2v</sub> molecular symmetry. It is inconsistent to use the experimental molecular structure parameters that have variable uncertainties, since the procedure can lead to relatively large errors<sup>25</sup> in the calculated MO's. This is a result of the experimental molecular geometry corresponding to a completely arbitrary point in the calculated potential surface. The method for numbering of the atoms and the coordinate system used in the MO calculations for the thiophene molecule are shown in Figure 4. The calculated geometries from each MO method, presented in Table 7, are in excellent agreement with the previously reported<sup>26</sup> optimized geometries from MO calculations. As seen from Table 7, the optimized geometry from each MO method differs from the experimental structural data of Bak et al.<sup>27</sup> The geometry predicted by the MNDO MO method shows the best overall agreement with the experimental data, and in addition the MNDO MO method is about 100 times cheaper in computer time than the ab initio (STO-3G) method.

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## FIGURE CAPTIONS

- Figure 1. The experimental sulfur  $K\beta$  emission and K absorption spectra of thiophene in vapor phase. The assignments and component energies are listed in Table 1. The position of S-1s binding energy is indicated.
- Figure 2. A comparison of the experimental sulfur  $K\beta$  emission spectrum (in dots) of thiophene with the synthesized spectra based upon the orbital composition from MNDO and ab initio (STO-3G) calculations and MO binding energies from XPS/UPS data.
- Figure 3. Comparison of the experimental sulfur  $L_{II,III}$  relative intensities with the calculated radiative yield values given by MNDO and ab initio (STO-3G) MO methods. Only the positions from larger basis set ab initio (Ref. 4) are indicated as orbital compositions were not available. (Bars at the principle  $L_{III}$  component energy.)
- Figure 4. Numbering of the atoms and the coordinate system used for the MO calculations of thiophene molecule.

TABLE 1

Major components in S-K $\beta$  emission and S-K absorption spectra of molecular thiophene.

Peak	Energy (eV)	Assignment <sup>a</sup>
A'	2469.8	
A	2468.1	2b <sub>1</sub>
B	2465.5	6a <sub>1</sub> +1b <sub>1</sub>
C	2464.2	4b <sub>2</sub>
D	2459.8	2b <sub>2</sub> +4a <sub>1</sub>
E	2455.9	2a <sub>1</sub> +1b <sub>2</sub>
F	2473.0	[3b <sub>1</sub> ]
G	2475.4	[2a <sub>2</sub> ]
H	2476.9	[5b <sub>2</sub> ]+[7a <sub>1</sub> ]
S-1s	2477.6	

<sup>a</sup>Only the final state MO vacancy in the transition is tabulated. The ground state unoccupied orbitals are in brackets.

TABLE 2

Calculated orbital compositions and radiative yield values  
for thiophene by the MNDO MO method.

Orbital	Atomic Components					Radiative Yield	
	S 3s	S 3p	C 2s	C 2p	H 1s	S-K $\beta$	S-L <sub>II,III</sub>
1a <sub>1</sub>	0.037	0.031	0.806	0.033	0.057	6	6
1b <sub>2</sub>	0.0	0.051	0.735	0.098	0.116	10	0
2a <sub>1</sub>	0.373	0.028	0.364	0.133	0.090	5	82
3a <sub>1</sub>	0.400	0.005	0.186	0.258	0.149	1	100
2b <sub>2</sub>	0.0	0.133	0.331	0.281	0.250	25	0
4a <sub>1</sub>	0.044	0.070	0.005	0.555	0.325	13	12
3b <sub>2</sub>	0.0	0.003	0.010	0.643	0.343	1	0
5a <sub>1</sub>	0.034	0.046	0.002	0.799	0.119	9	10
4b <sub>2</sub>	0.0	0.329	0.013	0.440	0.217	63	0
1b <sub>1</sub>	0.0	0.388	0.0	0.614	0.0	74	0
6a <sub>1</sub>	0.054	0.398	0.012	0.381	0.153	76	16
2b <sub>1</sub>	0.0	0.523	0.0	0.477	0.0	100	0
1a <sub>2</sub>	0.0	0.0	0.0	1.0	0.0	0	0

TABLE 3

Calculated orbital composition and radiative yield values  
for thiophene by the ab initio (STO-3G) method.

Molecular Orbital	Atomic Components										Radiative Yield	
	S 1s	S 2s	S 2p	S 3s	S 3p	C 1s	C 2s	C 2p	H 1s	S-K $\beta$	S-L <sub>II,III</sub>	
1a <sub>1</sub>	0.003	0.034	0.004	0.222	0.018	0.090	0.563	0.049	0.017	3	45	
1b <sub>2</sub>	0.0	0.0	0.0	0.0	0.020	0.098	0.763	0.072	0.067	3	0	
2a <sub>1</sub>	0.005	0.053	0.001	0.444	0.006	0.037	0.278	0.098	0.028	1	100	
3a <sub>1</sub>	0.002	0.060	0.0	0.232	0.0	0.031	0.297	0.240	0.176	0	59	
2b <sub>2</sub>	0.0	0.0	0.010	0.0	0.073	0.044	0.445	0.248	0.179	11	0	
4a <sub>1</sub>	0.001	0.011	0.004	0.138	0.034	0.002	0.021	0.522	0.268	5	36	
3b <sub>2</sub>	0.0	0.0	0.001	0.0	0.005	0.004	0.038	0.617	0.335	1	0	
5a <sub>1</sub>	0.0	0.003	0.0	0.045	0.003	0.0	0.008	0.743	0.199	0	13	
1b <sub>1</sub>	0.0	0.0	0.028	0.0	0.280	0.0	0.0	0.692	0.0	43	0	
4b <sub>2</sub>	0.0	0.0	0.037	0.0	0.312	0.0	0.013	0.450	0.188	48	0	
6a <sub>1</sub>	0.0	0.009	0.048	0.178	0.452	0.003	0.054	0.208	0.048	69	53	
1a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.00	0.0	0	0	
2b <sub>1</sub>	0.0	0.0	0.060	0.0	0.653	0.0	0.0	0.287	0.0	100	0	

TABLE 4

Calculated and experimental binding and ionization energies  
for valence molecular orbitals of thiophene.

Molecular Orbital	MO CALCULATIONS Orbital Energies (eV)				Ionization Energy UPS (eV)	EXPERIMENTAL	
	MNDO	Ab initio (STO-3G)	Ab initio (Gellius et al.)	Ab initio (Niessen et al.)		Binding Energy (eV)	
						S-K $\beta$	S-L <sub>II,III</sub>
1a <sub>1</sub>	-40.44	-30.02	-32.2	-32.09	26.1		26.7
1b <sub>2</sub>	-31.16	-25.08	-27.1	-26.99	22.3	21.7	
2a <sub>1</sub>	-27.06	-24.64	-26.8	-26.75	22.1	21.7	22.1
3a <sub>1</sub>	-20.96	-19.04	-20.8	-20.76	18.8		19.0
2b <sub>2</sub>	-20.69	-18.58	-20.5	-20.49	17.8	17.8	
4a <sub>1</sub>	-17.37	-17.32	-19.1	-19.20	16.6	17.8	17.1
3b <sub>2</sub>	-14.39	-14.08	-15.9	-15.97	14.3		
5a <sub>1</sub>	-13.88	-12.80	-14.7	-14.90	13.9		13.8
4b <sub>2</sub>	-13.79	-12.13	-14.3	-14.43	12.7	13.4	13.8
1b <sub>1</sub>	-13.28	-12.48	-14.3	-14.34	13.3	12.1	
6a <sub>1</sub>	-12.84	-10.39	-13.0	-13.08	12.1	12.1	12.3
2b <sub>1</sub>	- 9.95	- 7.21	- 9.31	- 9.45	9.5	9.5	
1a <sub>2</sub>	- 9.51	- 7.28	- 9.06	- 9.23	8.9		12.3
(3b <sub>1</sub> )	0.07	7.52				4.6	
(2a <sub>2</sub> )	1.44	11.05				2.2	
(5b <sub>2</sub> )	2.04	12.00				} 0.7	
(7a <sub>1</sub> )	1.69	14.63					
(8a <sub>1</sub> )	4.38	16.90					



TABLE 5

Emission components and MO assignment of  
S-L<sub>II,III</sub> spectrum of thiophene.

Peak No.	Binding energy (eV)	Relative intensity	Previous assignment	Present work
1	12.3	16	6a <sub>1</sub> +1a <sub>2</sub>	6a <sub>1</sub> +1a <sub>2</sub>
2	13.8	8	4b <sub>2</sub>	4b <sub>2</sub> +5a <sub>1</sub>
3	17.1	20	5a <sub>1</sub>	4a <sub>1</sub>
4	19.0	64	4a <sub>1</sub>	3a <sub>1</sub>
5	22.1	100	2a <sub>1</sub>	2a <sub>1</sub> +radiative Auger
6	26.7	93	1a <sub>1</sub>	1a <sub>1</sub> +radiative Auger

TABLE 6

Comparison of normalized intensities for peaks 4, 5 and 6 of sulfur L<sub>II,III</sub> emission spectrum

Peak	<u>ab initio</u> (STO-3G)	MNDO	Experimental
4	100	100	100
5	170	82	156
6	77	6	145

TABLE 7

Comparison of theoretical and experimental  
structure parameters for thiophene

Structural Parameter	Theoretical Values		Experimental <sup>b</sup> Values
	MNDO <sup>a</sup>	Ab initio <sup>a</sup> (STO-3G)	
S-C <sub>1</sub>	1.692 A	1.732 A	1.714 A
C <sub>1</sub> -C <sub>2</sub>	1.368	1.335	1.370
C <sub>2</sub> -C <sub>3</sub>	1.457	1.454	1.424
C <sub>1</sub> -H <sub>1</sub>	1.080	1.079	1.078
C <sub>2</sub> -H <sub>2</sub>	1.083	1.081	1.081
C <sub>1</sub> SC <sub>4</sub>	93.2 deg	90.4 deg	92.2 deg
SC <sub>1</sub> C <sub>2</sub>	111.9	112.7	111.5
SC <sub>1</sub> H <sub>1</sub>	118.5	120.2	119.8
C <sub>2</sub> C <sub>3</sub> H <sub>3</sub>	122.8	123.0	124.3

a. present work

b. Reference 27

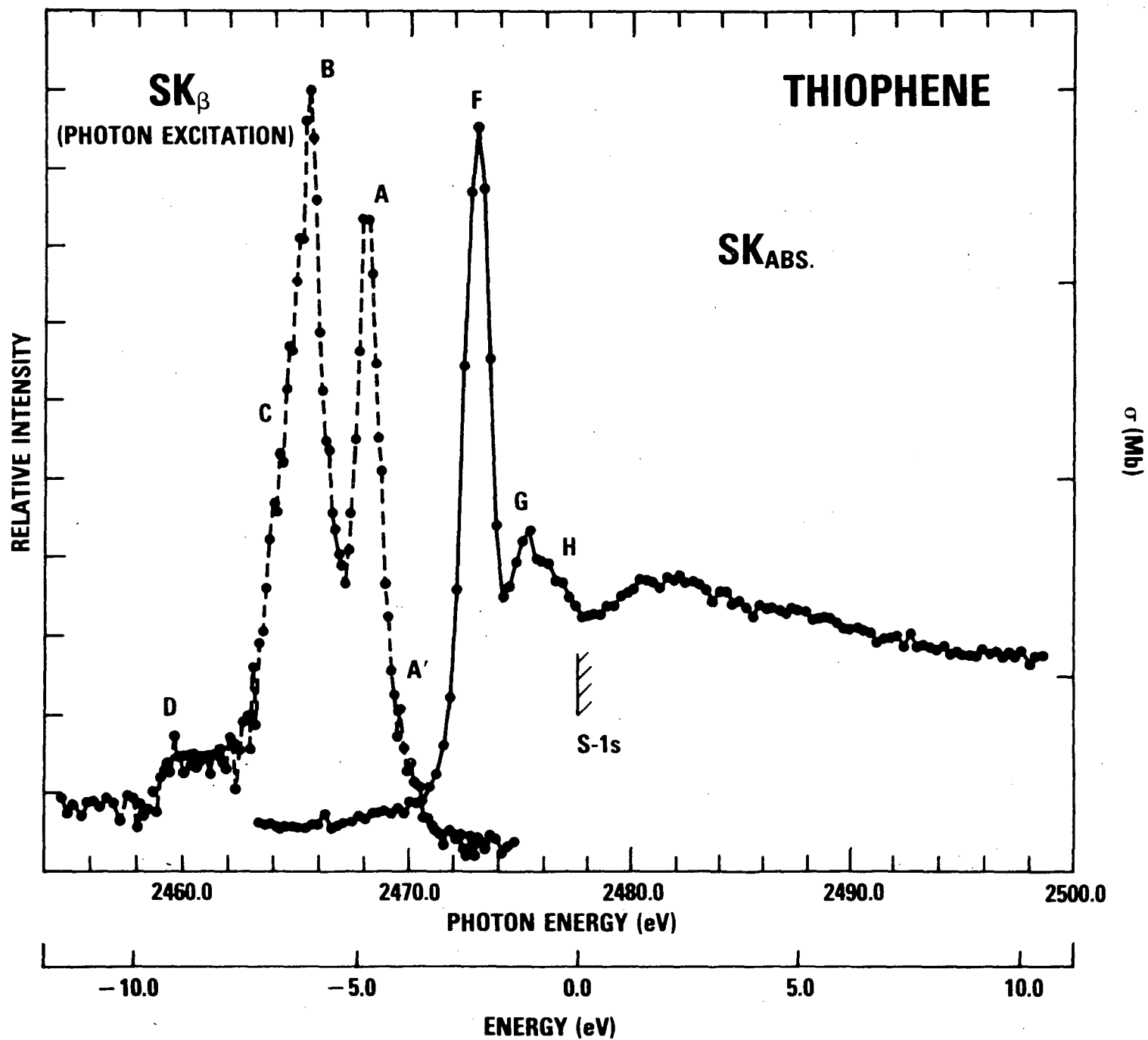


Figure 1.

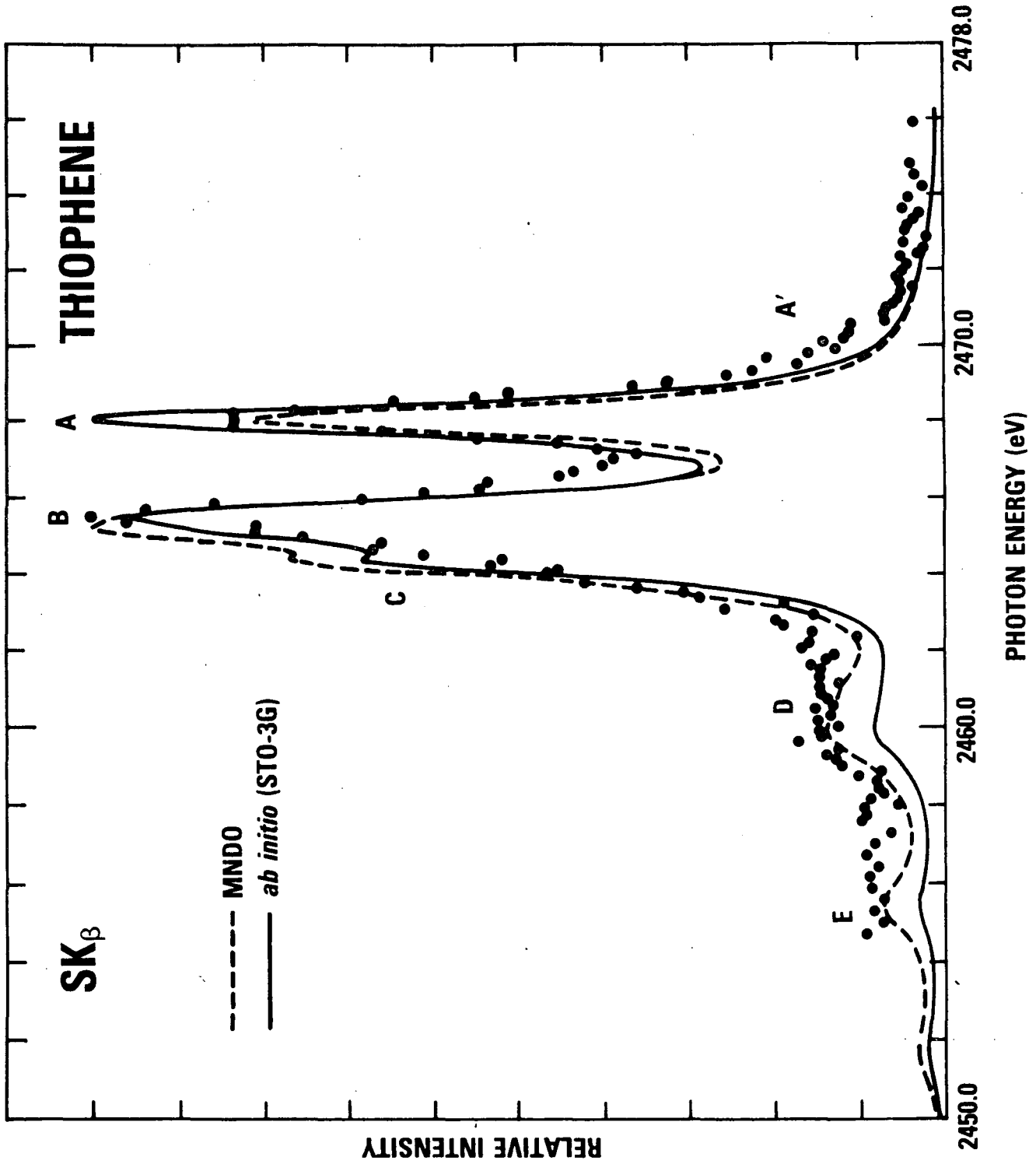


Figure 2

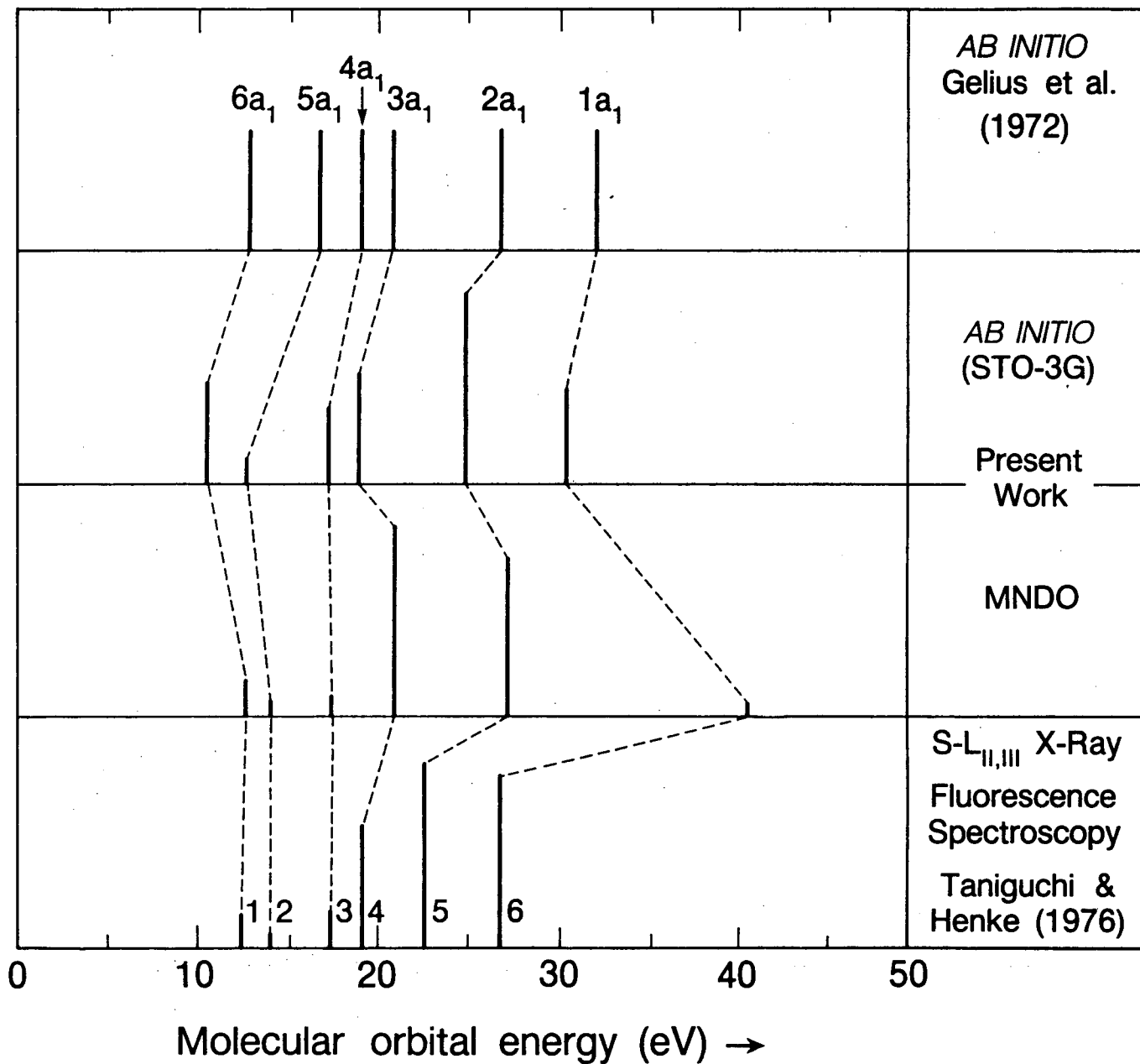


Figure 3

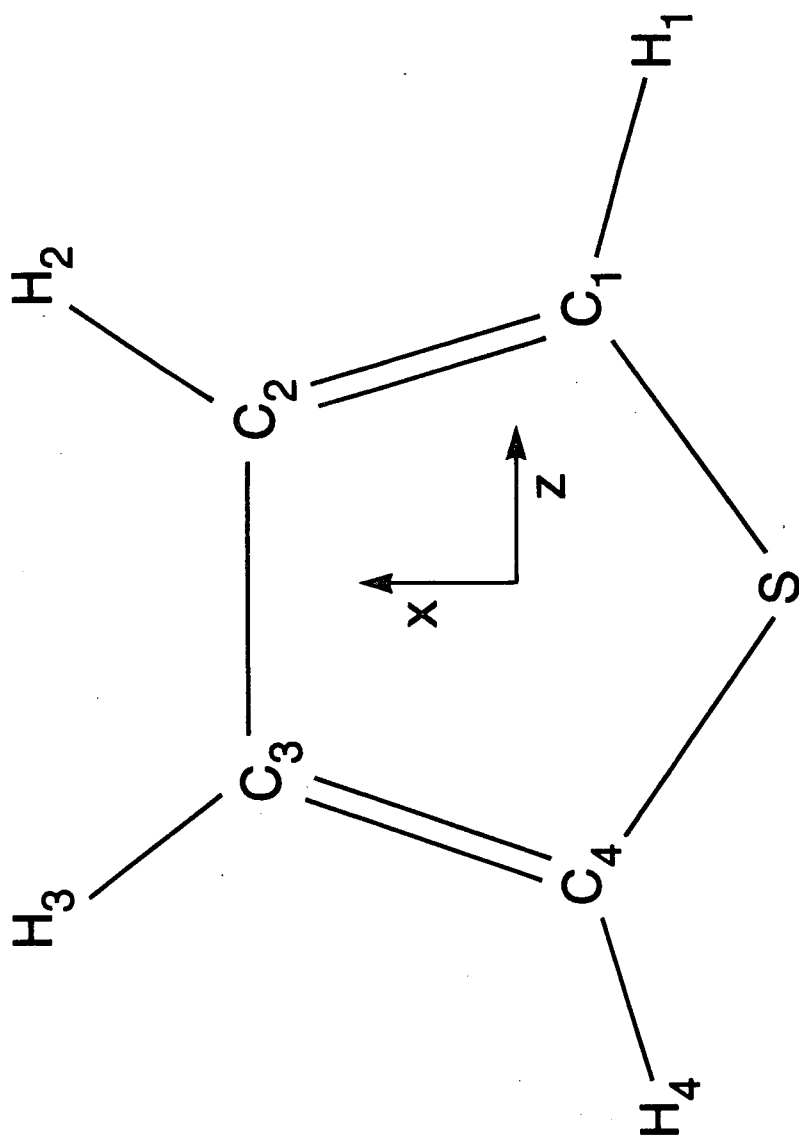


Figure 4

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