

the e_g level increases in energy from the fourth to the outermost position, if the d orbital component is omitted, while the t_{2g} level remains relatively stable. The changes in the other levels are not significant. (However, it should be pointed out that the e_g and t_{2g} levels, which belong to the same representations as the added basis, are lowered but all the other levels raised by including a d component on the central atom.⁵¹) From their charge distributions the t_{1g} , t_{1u} , and t_{2u} levels have been characterized as nonbonding levels. Therefore, it seems natural that they are not sensitive to whether or not the d orbital component is included on the sulfur atom. The assignment of these levels as the nonbonding orbitals is therefore reasonable. Then the e_g level should be assigned as the one below these orbitals.

The only way of having the e_g level not in the top-most position is to include the d orbital component. Thus we have to conclude that the d orbital participation is important as far as the assignment of the SF_6 photoelectron spectrum is concerned.

Let us consider this problem from another viewpoint. The charge distributions and ΔQ value are not very much affected through an omission of the d orbital component (see Table I). Without the d component electronic charge is slightly more drained from the central atom to the ligands. Considering the unchanged general level structure and charge distribution, one

(51) This behavior seems to be general. It has been shown⁵² that the inclusion of the polarization functions raises most of the molecular orbital energies except for a few which strongly mix with the added functions. We note that a strong mixing should come from those levels which belong to the same representations as the added basis.⁴⁹

(52) (a) J. I. Musher, *J. Amer. Chem. Soc.*, **94**, 1370 (1972); (b) H. Nakatsuji and J. I. Musher, *Chem. Phys. Lett.*, **24**, 77 (1974).

might be able to explain the formation of the MF_6 molecules even without invoking the d orbital participation.⁵³

Another point we can make from Figure 3 is that the e_g level is higher than the t_{2g} level regardless of the S-F bond length and of the overlapping sulfur and fluorine atomic spheres. One of many reasons given by La-Villa¹⁷ in assigning the 19.69-eV peak as e_g is that the overlap of the sulfur d orbital with the fluorine 2p orbitals is greater in the e_g than in the t_{2g} orbital. Our calculation with overlapping spheres may be considered as a test for this question as it should increase the interaction of the sulfur d orbital and the t_{2g} and e_g levels of the F_6 lattice. However, there is hardly a change in the character of these levels and their relative positions is unaltered.

The bonding of other hypervalent sulfur fluorine compounds shall be examined in a forthcoming paper.⁵⁴

Acknowledgment. We wish to thank Professor K. H. Johnson for his kindness in furnishing the computer programs used in this study and for much helpful advice (to N. R.) on the use of the SCF-X α -SW method. We also express our gratitude to the Deutsche Forschungsgemeinschaft for a stipend to N. R. and to the National Research Council for a fellowship to M. H. W. and an operating grant to V. H. S.

(53) The importance of d orbital participation is usually judged by considering the magnitude of a d orbital population, which depends significantly on the number of s and p basis orbitals used. For a systematic study on this topic, see R. S. Mulliken and B. Liu, *J. Amer. Chem. Soc.*, **93**, 6738 (1971). They also expressed an interesting opinion that d orbital participation in molecules, small or large, may be called a chemical effect when absent in free atoms.

(54) M. H. Whangbo, V. H. Smith, Jr., and N. Rösch, to be submitted for publication.

Ab Initio Calculations on Large Molecules Using Molecular Fragments. Characterization of Unsaturated Sulfur-Containing Molecules

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Abstract: An *ab initio* procedure for the investigation of large molecules is applied to a series of unsaturated sulfur-containing molecules. Prototype molecules used to characterize the procedure include thioformaldehyde, carbon disulfide, and carbonyl sulfide. For each molecule studied, the equilibrium geometry, molecular orbital ordering, various one-electron properties, and population analyses were determined and compared to experimental findings and other theoretical calculations where possible. In general, accuracies for geometric properties were found to be comparable to that observed in molecules containing first-row atoms only. Also, molecular orbital ordering for valence orbitals was found to be in excellent agreement with more extensive basis set calculations. Other one-electron properties were also calculated, and the adequacy of the basis was assessed.

This study is the second of a series done on sulfur-containing molecules using the molecular fragment procedure. The first study¹ was concerned with mole-

cules in which the sulfur could be considered to be either in an "sp³" or "sp²" hybridized state. This study concerns sulfur-containing molecules in which the sulfur can be considered to be in an "sp" hybridized state.

Since the details of the molecular fragment procedure puters in Chemical Research and Education, Ljubljana, Yugoslavia, 1973, in press.

(1) R. E. Christoffersen and L. E. Nitzsche, "Ab Initio Calculations on Large Molecules Using Molecular Fragments. Development of an Analytical Tool and Extension to Molecules Containing Second Row Atoms," Proceedings of the 1973 International Conference on Com-

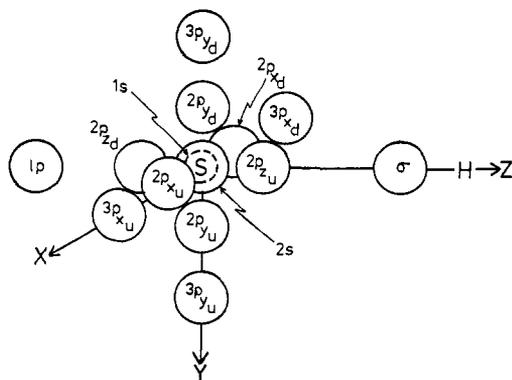


Figure 1. Depiction of the $\cdot\text{SH}$ fragment.

can be found elsewhere,²⁻⁵ they will not be repeated here. The basis functions used are floating spherical Gaussian orbitals (FSGO) and are defined as

$$G_i(r) = (2/\pi\rho_i^2)^{3/4} \exp\{-(r - \mathbf{R}_i)^2/\rho_i^2\} \quad (1)$$

where ρ_i is the "orbital radius," and \mathbf{R}_i is the location of the FSGO relative to some origin. In the case of p-type orbitals, a linear combination of two FSGO is used, each placed on opposite sides of the particular nucleus, and is defined as

$$G_p(r) = (G_u - G_d)/[2(1 - \Delta_{ud})]^{1/2} \quad (2)$$

where G_u corresponds to the positive lobe and G_d corresponds to the negative lobe of the p orbital and Δ_{ud} is the overlap integral between the two FSGO.

The calculations carried out in this study used the "split inner shell" description¹ of the 1s electrons in sulfur; *i.e.*, a linear combination of two FSGO was used to describe the 1s electrons in sulfur. In this case, both the linear and nonlinear parameters are determined in the fragment optimization. The primary reason behind the slight generalization of the "non-split" FSGO basis is that preliminary studies using a single FSGO to describe the 1s electrons in sulfur failed to predict a stable sulfur-sulfur internuclear distance in hydrogen persulfide.¹

For this study, the HS \cdot moiety was used as the fragment (see Figure 1), and the optimized basis functions from this fragment would be suitable for a "sp" hybridized sulfur. The adequacy of the basis functions was assessed *via* calculations on the prototype molecules thioformaldehyde (H_2CS), carbon disulfide (CS_2), and carbonyl sulfide (OCS). The molecules studied and the coordinate systems used are depicted in Figure 2. Hydrogen persulfide (HSSH) and thiophene ($\text{C}_4\text{H}_4\text{S}$), which were studied earlier¹ but are included in the discussions in this study, are also included in Figure 2. For each molecule studied, the equilibrium geometry, molecular orbital ordering, various one-electron properties, and population analyses were determined and compared to experimental findings, and other theoretical calculations where possible.

Fragment Calculations

Three fragments were used to describe the molecules

(2) R. E. Christoffersen and G. M. Maggiora, *Chem. Phys. Lett.*, **3**, 419 (1969).

(3) R. E. Christoffersen, D. W. Genson, and G. M. Maggiora, *J. Chem. Phys.*, **54**, 239 (1971).

(4) R. E. Christoffersen, *Advan. Quantum Chem.*, **6**, 333 (1972).

(5) R. E. Christoffersen, D. Spangler, G. G. Hall, and G. M. Maggiora, *J. Amer. Chem. Soc.*, **95**, 8526 (1973).

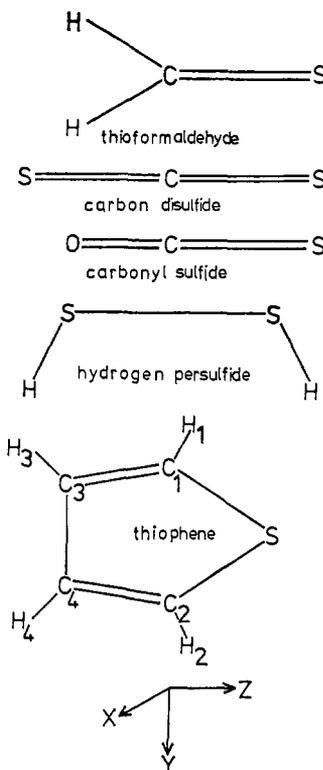


Figure 2. Coordinate system and atomic numbering for the molecules studied.

in this study: namely, the $\cdot\text{SH}$, $\cdot\text{CH}_3$, and $\cdot\text{OH}$ fragments. The $\cdot\text{SH}$ fragment was optimized as part of this study, and the $\cdot\text{CH}_3$ and $\cdot\text{OH}$ fragments were characterized earlier.^{6,7} The optimized parameters for the $\cdot\text{SH}$ fragment are given in Table I. The parameters for

Table I. HS \cdot Fragment Description^a

Nuclear geometry	
R_{SH}	2.36172
Parameters ^b	
ρ_{1s}	0.05283276
c_{1s}	14.80080
ρ_{1s}'	0.13664980
c_{1s}'	11.83021
$R_{1s,2s}^d$	0.00000735
ρ_{2s}	0.54292773
ρ_{2p}	0.40105
R_{2p}^c	0.1
ρ_{σ}	1.67584
R_{σ}	1.43492
ρ_{1p}	1.90485
R_{1p}^c	0.55045
ρ_{3p} (doubly occupied)	1.78070
ρ_{3p}' (singly occupied)	1.74176
R_{3p}^c	0.55045871
Total energy (unscaled)	-376.27265930
Scale factor	1.0031039

^a Unless otherwise specified, hartree atomic units are employed for distances and energies. The sulfur nucleus is taken as the origin. ^b The c 's are the linear coefficients of the FSGO in the split inner shell description. ^c Parameter not varied in calculation. See ref 1. ^d Both the 1s and 2s FSGO were located at the same point.

(6) L. J. Weimann and R. E. Christoffersen, *J. Amer. Chem. Soc.*, **95**, 2074 (1973).

(7) H. G. Cohen, private communication.

Table II. Optimized Split Inner Shell Data for Methyl Radical and Hydroxyl Radical Fragments

Parameter	Value
$\cdot\text{CH}_3(D_{3h})$ Fragment ^a ($R_{\text{CH}} = 2.06414059$)	
ρ_{1s}	0.38822192
c_{1s}	2.44787
ρ_{1s}'	0.14768823
c_{1s}'	3.33585
ρ_{σ}	1.64673
R_{σ}	1.24820
ρ_{π}	1.78057
R_{π}	0.1
$\cdot\text{OH}(\text{sp})$ Fragment ^b ($R_{\text{OH}} = 1.54774058$)	
ρ_{1s}	0.28390625
c_{1s}	3.92786
ρ_{1s}'	0.10870971
c_{1s}'	5.17986
R_{1s}	0.00022919
ρ_{σ}	1.23731
R_{σ}	0.76678
ρ_{1p}	1.29001
R_{1p}	0.21805
ρ_{π} (doubly occupied)	1.18972
ρ_{π}' (singly occupied)	1.11572
R_{π}	0.1

^a See ref 7. ^b See ref 6.

the $\cdot\text{CH}_3$ and $\cdot\text{OH}$ fragments that were used from other studies are summarized in Table II.

In the fragment optimization procedure, certain parameters must be fixed to preserve mathematical stability of the procedure. The values for the parameters fixed in the $\cdot\text{SH}$ fragment optimization (see Table I) were determined in an earlier study¹ on sulfur-containing molecules.

Also, in the previous study¹ on sulfur-containing molecules, two different descriptions of the L-shell electrons in sulfur were used. The description using a 2s FSGO and three orthogonal 2p functions gave the best results in that study; therefore, only this description of the L shell was used here.

For the special case of molecules having cylindrical symmetry (CS_2 , OCS), the fragments had to be modified to assure the appearance of molecular orbitals consistent with cylindrical symmetry in the SCF calculations. In the $\cdot\text{CH}_3$ fragment, one of the three σ FSGO was deleted, and the remaining two σ FSGO were made collinear with the carbon nucleus and other heavy atoms, one on each side of the carbon atom. In addition, another singly occupied p-type function was added perpendicular to the other p-type function and the σ FSGO. This would correspond to a $:\text{CH}_2$ fragment where each carbon p orbital was singly occupied. For the $\cdot\text{SH}$ and $\cdot\text{OH}$ fragments, to assure the correct symmetries of the molecular orbitals, a choice had to be made as to whether to use the singly or doubly occupied ρ value for the p-type functions in the SCF calculations. In earlier calculations on CO_2 ,⁶ it was found that the use of the doubly occupied ρ value gave results more consistent with experimental determinations of the molecular orbital ordering. Thus, for the calculations on the linear molecules studied here, the doubly occupied ρ value was used for the p-type functions.

The Thioformaldehyde Molecule

Although there are no other calculations on this molecule, it has been sufficiently characterized experimentally

that it served as a suitable test for the $\cdot\text{SH}$ basis functions. The $\cdot\text{CH}_3$ and $\cdot\text{SH}$ fragments were used for the calculations on this molecule. The molecular orbital ordering and the molecular properties were calculated at the experimental geometry.⁸

Concerning the molecular orbital ordering, Kroto and Suffolk⁹ have characterized the two highest filled molecular orbitals experimentally and inferred the ordering of the remaining valence orbitals from the ordering in formaldehyde. The ordering from this calculation and that of Kroto and Suffolk is given in Table III. It is

Table III. Molecular Orbital Ordering and Energies in Thioformaldehyde

This calculation		Kroto and Suffolk ^a	
Orbital symmetry	Orbital energy	Ionization energies	
$8a_1$	0.6366		
$3b_1(\pi)$	0.2556		
$3b_2$	-0.1865	$3b_2$	0.3429
$2b_1(\pi)$	-0.2515	$2b_1$	0.4381
$7a_1$	-0.3798	$7a_1$	
$2b_2$	-0.4832	$2b_2$	
$6a_1$	-0.7484	$6a_1$	
$5a_1$	-1.0332	$5a_1$	
$1b_2$	-4.5852		
$1b_1$	-4.5923		
$4a_1$	-4.6054		
$3a_1$	-8.9026		
$2a_1$	-11.1619		
$1a_1$	-90.5724		
E_{total}	-413.4488		

^a See ref 9. The first two molecular orbitals were measured, while the ordering of the remaining valence orbitals was inferred from formaldehyde.

seen that the calculated ordering and that given by Kroto and Suffolk are in agreement. Additionally, this calculation characterizes the highest filled molecular orbital as a nonbonding 3p orbital ($3b_2$) localized on the sulfur atom and the next highest molecular orbital as a bonding π orbital ($2b_1$), which is the same as observed experimentally by Kroto and Suffolk.

As a further aid in assessing the adequacy of the sulfur basis orbitals, some one-electron molecular properties were calculated and are compared in Table IV to the available experimental data.^{8,10} It can be seen that the calculated properties are generally in agreement with the available experimental data. In particular, the Hellmann-Feynman electric field¹¹ at the nuclei, which should be zero for exact wave functions, is quite small and comparable in magnitude to those calculated for other molecules using the molecular fragment procedure.^{1,12} From earlier calculations on thiophene,¹ the somewhat larger value at the sulfur nucleus has been identified as being due to the fact that the FSGO representing the 2p orbitals in sulfur are placed close to the sulfur nucleus. While this choice is desirable from the point of view of other molecular properties, it

(8) D. R. Johnson, R. X. Powell, and W. H. Kirchoff, *J. Mol. Spectrosc.*, **39**, 136 (1971).

(9) H. W. Kroto and R. J. Suffolk, *Chem. Phys. Lett.*, **15**, 545 (1972).

(10) S. L. Rock and W. H. Flygare, *J. Chem. Phys.*, **56**, 4723 (1972).

(11) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

(12) G. M. Maggiora, D. W. Genson, R. E. Christoffersen, and B. V. Cheney, *Theor. Chim. Acta*, **22**, 337 (1971).

Table IV. Molecular Properties of Some Sulfur-Containing Molecules

	Thioformaldehyde		Carbon disulfide			Carbonyl sulfide		
	This calcn	Exptl	This calcn	Other calcn ^d	Exptl	This calcn	Other calcn	Exptl
Hellmann-Feynman ^a								
electric field								
E at nuclei, au								
S	0.171		0.2032			0.229		
C	0.033		0			0.001		
O						0.060		
H	0.0125							
Electric potential at nuclei, electronic component, au								
$\langle 1/r_s \rangle$	55.99		60.70			59.60		
$\langle 1/r_c \rangle$	13.93		24.77			23.03		
$\langle 1/r_o \rangle$						26.58		
$\langle 1/r_H \rangle$	0.99							
Dipole moment (D)	1.205	1.6474 ^b				+2.1765	0.99	0.71512 ^h
Second moment, electronic component, 10 ⁻¹⁶ cm ²								
$\langle z^2 \rangle$, cm	20.4	21.1 ^c	83.2	7.05		45.86	46.2 ⁱ	
$\langle y^2 \rangle$, cm	5.4	6.6 ^c	6.0	6.88		4.60	4.5 ⁱ	
$\langle x^2 \rangle$, cm	3.7	4.6 ^c	6.0	6.88		4.60	4.5 ⁱ	
Quadrupole moment, 10 ⁻²⁶ esu cm ²								
Q_{zz}	1.58	3.0 ^c	0.417	-0.818	$\{3.6 \pm 1.0^e$	0.920	-1.478 ^o	-0.786 ^h
Q_{yy}	-0.58	-2.4 ^c	-0.209		$\pm 1.8^e$	-0.460		
Q_{xx}	-1.04	-0.6 ^c	-0.209			-0.460		
Electric field gradient at nuclei, au								
	S		S	C		S	C	O
q_{zz}	-1.19		-1.36	0.05		-1.95	0.15	-0.42
q_{yy}	0.20		0.68	-0.02		0.97	-0.076	0.21
q_{xx}	-0.80		0.68	-0.02		0.97	-0.076	0.21
Total energy, au	-413.4488		-788.7207	-832.8412		-483.9127		$\{-508.40175^j$ -510.33086^o

^a See ref 11. ^b See ref 8. ^c See ref 10. ^d See ref 14. Second moments calculated from given diamagnetic susceptibilities. ^e See ref 16. ^f See ref 17. ^g See ref 22. ^h See ref 21. ⁱ See ref 20. ^j See ref 23.

does raise the Hellmann-Feynman values somewhat, as observed here. Next, the calculated dipole moment is somewhat too small compared to the experimental value,⁸ as was the case for thiophene.¹ Also, the calculated components for the second moment and the quadrupole moment are close to the experimental values,¹⁰ but the predicted ordering of the magnitude of the quadrupole moment does not agree with the experimental ordering.¹⁰ Experimentally the ordering is $|Q_{zz}| > |Q_{yy}| > |Q_{xx}|$, while the calculated ordering is $|Q_{zz}| > |Q_{xx}| > |Q_{yy}|$. This result is not surprising, however, since the quadrupole moment is calculated to be the difference between large nuclear and electronic terms.¹² Also, the dipole moment was predicted to be smaller than the experimental value, and exact agreement between the predicted and experimentally determined quadrupole and higher moment components is therefore not necessarily expected. However, while the ordering of the quadrupole moment is not correctly predicted, the signs of the components are.

Next, to see how well the ·SH fragment would predict molecular geometries, the minimum energy carbon-sulfur bond length was calculated. The calculated carbon-sulfur bond length is 3.0844 bohrs, which is 1.33% too long compared to the experimental value⁸ of 3.0440 bohrs. Thus, the predicted carbon-sulfur bond length is in excellent agreement with the experimental value.

The Carbon Disulfide Molecule

As another test of the ·SH fragment description, a

series of calculations was performed on the CS₂ molecule using the ·SH and ·CH₃ fragments, modified in the manner described earlier to assure the appearance of the proper molecular orbital symmetries. Using the experimental¹³ value of 2.937 bohrs for the carbon-sulfur internuclear distance, the molecular orbital ordering was computed. The calculated ordering for the valence molecular orbitals agrees with the ordering from the *ab initio* calculation of Fischer and Kemmey¹⁴ and the experimental determination of Turner, *et al.*¹⁵

Next, several molecular properties and the total energy were calculated, again using the experimental geometry,¹³ and compared in Table IV to those calculated by Fischer and Kemmey and to the available experimental values.^{16,17} Again, the Hellmann-Feynman electric field is quite small but is seen to be larger at the sulfur nucleus than those encountered in thioformaldehyde and thiophene.¹ This larger value in CS₂ may be due to the substantial modifications made in the CH₃ fragment.

In comparing the values for the second moments from this calculation to those obtained from the diamagnetic susceptibilities reported by Fischer and Kemmey, it can be seen that the two calculations disagree significantly. Experimental findings and other calculations of

(13) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

(14) C. R. Fischer and P. J. Kemmey, *Mol. Phys.*, **22**, 1133 (1971).

(15) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, London, 1970, p 69.

(16) S. Golub, Ph.D. Thesis, Columbia University, 1968, unpublished.

(17) D. E. Stogryn and A. P. Stogryn, *Mol. Phys.*, **11**, 371 (1966).

the second moments in thiophene,^{18,19} thioformaldehyde,¹⁰ and carbonyl sulfide²⁰ support the observation that the second moment component along the molecular axis is substantially larger than the component or components perpendicular to the molecular axis. While the current calculation supports this observed trend, the values from Fischer and Kemmey do not. The results of Fischer and Kemmey imply an approximately spherical charge distribution in CS₂, while the results of this calculation imply an ellipsoidal charge distribution. In addition, this calculation predicts a positive value for the quadrupole moment in accord with the most recent experimental determination,¹⁶ but in disagreement with the value reported by Fischer and Kemmey.

In addition to the electronic properties, the minimum energy geometry of the carbon disulfide molecule was also calculated. The bond length is predicted to be 3.07 bohrs, which is 4.8% too long when compared to the experimental value¹³ of 2.937 bohrs, and the carbon disulfide molecule is predicted to be linear, in agreement with experimental determinations.¹³

The Carbonyl Sulfide Molecule

As a final test of the ·SH basis functions, calculations were performed on the OCS molecule. Since carbonyl sulfide is used as a primary standard for calibration of Stark cells in microwave spectroscopy, there is a wealth of experimental information^{20,21} available for this molecule, allowing detailed comparisons to be made between theoretically and experimentally determined properties. In addition, there are the theoretical calculations of McLean and Yoshimine²² and Clementi²³ on carbonyl sulfide which further enhances its value in assessing the adequacy of the ·SH basis orbitals.

Using the doubly occupied ρ values for the p-type orbitals for the ·OH and ·SH fragments and treating the ·CH₃ fragment as in carbon disulfide, the molecular orbital ordering was determined using the experimental geometry and bond lengths. The calculated ordering for all the molecular orbitals agrees with the ordering from the *ab initio* calculations of Yoshimine and McLean²² and Clementi.²³ However, all of the listed theoretical calculations predict an ordering with the 2 π and 9 σ orbitals switched compared to the experimental ordering.¹⁵ Clementi, in his calculations on carbonyl sulfide, used a minimum basis set of STO, while McLean and Yoshimine used an extensive STO basis set which included 3d and 4f functions on each atom of the molecule and gives an energy within 0.003 hartree of the Hartree-Fock limit.²² The experimental¹⁵ assignment appears to be quite certain, and therefore there must be some effect operating for which Hartree-Fock theory is unable to account, *e.g.*, orbital reorganization or correlation effects.²⁴

Several molecular properties and total energy were also computed at the experimental geometry for car-

(18) U. Gelius, *Theor. Chim. Acta*, **27**, 171 (1972).

(19) D. H. Sutter and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 4063 (1969).

(20) W. H. Flygare, W. Hüttner, R. L. Shoemaker, and P. D. Foster, *J. Chem. Phys.*, **50**, 1714 (1969).

(21) F. H. DeLeeuw and A. Dymanus, *Chem. Phys. Lett.*, **1**, 288 (1970).

(22) A. D. McLean and M. Yoshimine, *IBM J. Res. Develop., Suppl.*, **12**, 209 (1968); M. Yoshimine and A. D. McLean, *Int. J. Quantum Chem., Symp.*, **1**, 313 (1967); A. D. McLean and M. Yoshimine, *J. Chem. Phys.*, **46**, 3682 (1967).

(23) E. Clementi, *J. Chem. Phys.*, **36**, 750 (1962).

(24) W. G. Richards, *J. Mass Spectrom. Ion Phys.*, **2**, 419 (1969).

bonyl sulfide and compared to other calculated and experimental values in Table IV. The results of these calculations indicate that there are some deficiencies in the description of the electron distribution in carbonyl sulfide. First, the Hellmann-Feynman electric field at the sulfur nucleus is larger than those observed in other sulfur-containing molecules done by the molecular fragment procedure (see ref 1 and the other molecules in this study). However, the calculated second moments agree well with the experimentally determined values.²⁰ On the other hand, the calculated dipole moment is too large, compared both to the experimentally determined value²¹ and that calculated by McLean and Yoshimine.²² Also, for the quadrupole moment, $Q_{\perp} = \frac{1}{2}Q_{\parallel}$ (where Q_{\perp} refers to the component perpendicular and Q_{\parallel} refers to the component parallel to the molecular axis), as it should²⁰ for a linear triatomic molecule, but this calculation gives the signs of the components opposite those of the experimentally determined values.

The geometric parameters of carbonyl sulfide were next calculated. The CS bond length is predicted to be 3.09 bohrs, which is 4.7% too long compared to the experimental²⁵ value of 2.949 bohrs, and carbonyl sulfide is predicted to be linear in agreement with the experimental determination.

Discussion

Though small basis sets have been used in these calculations, it has been shown that the predicted valence molecular orbital ordering agrees with the experimental ordering for thioformaldehyde and carbon disulfide. Although the ordering in carbonyl sulfide was not in agreement with the experimental ordering, the discrepancies appear to be due to the limitation of the Hartree-Fock theory.

In an effort to determine and quantify the relationship between the ordering predicted by the molecular fragment procedure and large basis set calculation, plots were constructed of valence molecular orbital energies from extensive basis set calculations *vs.* the corresponding ones from the molecular fragment procedure. When this is done, linear relationships are observed, as shown in Table V. The data in this table

Table V. Approximate Linear Relationship between Molecular Fragment and More Extensive Basis Sets

Molecule	a^a	b^a	S^b	ρ^c	Ref ^d
Thiophene	0.7955	-0.2094	0.0228	0.9955	24
CS ₂	1.1623	-0.2493	0.0514	0.9961	14
OCS	1.3471	-0.3981	0.0417	0.9981	20

^a The coefficients a and b in this table are those of eq 3 in the text. ^b S is the root-mean-square deviation from the line, *i.e.*, $S = (1/n \sum_{i=1}^n [\epsilon_i^{\text{ref}} - (b + a\epsilon_i^{\text{MF}})]^2)^{1/2}$. ^c ρ is the correlation coefficient, *i.e.*, $\rho = \sum_{i=1}^n (\epsilon_i^{\text{MF}} - \bar{\epsilon}^{\text{MF}})(\epsilon_i^{\text{ref}} - \bar{\epsilon}^{\text{ref}}) / (\sum_{i=1}^n (\epsilon_i^{\text{MF}} - \bar{\epsilon}^{\text{MF}})^2 (\sum_{i=1}^n (\epsilon_i^{\text{ref}} - \bar{\epsilon}^{\text{ref}})^2)^{1/2}$, where $\bar{\epsilon}^{\text{MF}} = \sum_{i=1}^n \epsilon_i^{\text{MF}} / n$ and $\bar{\epsilon}^{\text{ref}} = \sum_{i=1}^n \epsilon_i^{\text{ref}} / n$. ^d This is the reference to the extended basis set investigation used for comparison.

are from a least-squares fit of the points to a straight line having the form

$$\epsilon_i^{\text{ref}} = a\epsilon_i^{\text{MF}} + b \quad (3)$$

where ϵ_i^{ref} are the molecular orbital energies from the

(25) Y. Morino and C. Matsumura, *Bull. Chem. Soc. Jap.*, **40**, 1095 (1967).

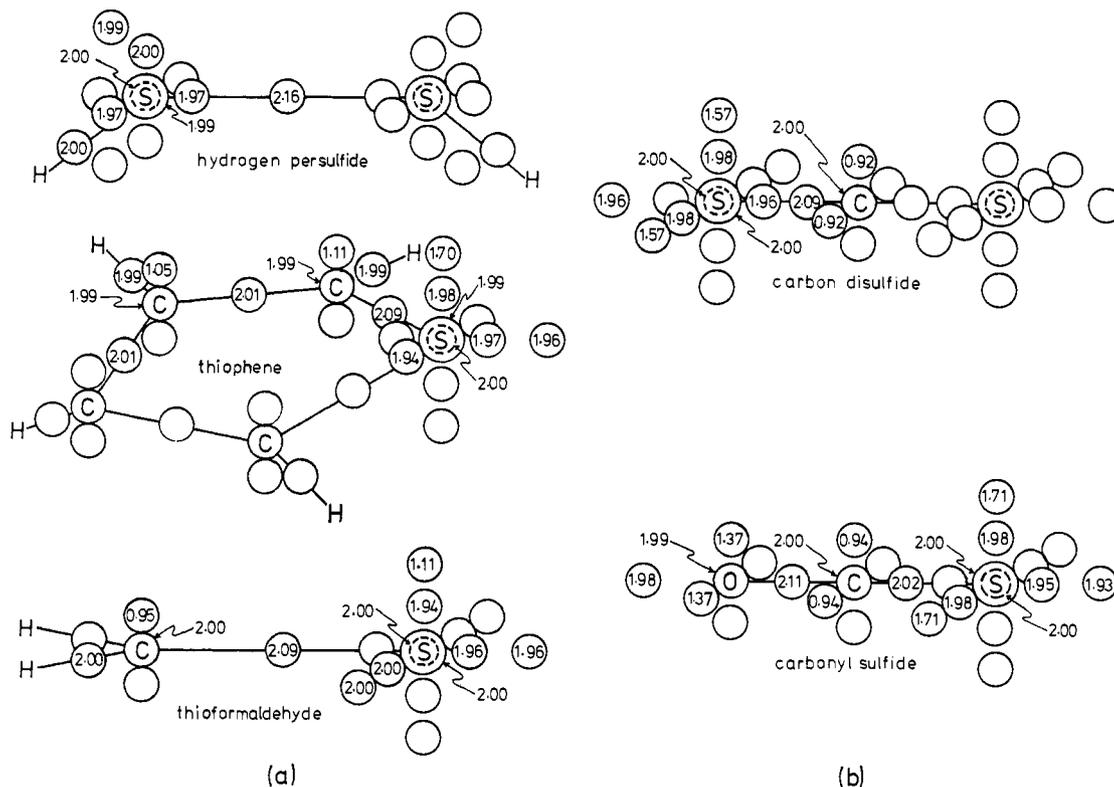


Figure 3. Orbital populations for symmetrically orthonormalized orbitals for (a) hydrogen persulfide, thiophene, and thioformaldehyde and (b) carbon disulfide and carbonyl sulfide. The population in the bonding region between "heavy" atoms is taken as the sum of the populations of the two symmetrically orthogonalized FSGO in that region.

more extensive basis set calculations, and ϵ_i^{MF} are those obtained from the molecular fragment procedure. The data for thiophene from an earlier calculation¹ have also been included. This linearity has also been observed⁵ for a wide range of other molecules containing first-row atoms. Thus, there is a quantitative, as well as qualitative, relationship between the valence molecular orbitals of the molecular fragment procedure and those of more extensive basis set calculations for molecules containing sulfur as well as those containing first-row atoms.

Also, of the molecules on which calculations have been performed using the molecular fragment procedure, the OCS and CS₂ molecules are the first instances noted where $a > 1$ in eq 3. Values of $a > 1$ correspond to the molecular orbital energies from the molecular fragment procedure having smaller spacings than those obtained in more extensive basis set studies.

As a further aid in delineating the characteristics of the molecular fragment procedure, bond order calculations and population analyses were performed for the molecules in this study, as well as for hydrogen persulfide and thiophene from an earlier study.¹ The bond orders are given in Table VI, and the population analyses are depicted in Figures 3a and 3b. Bond orders for formaldehyde⁶ and carbon dioxide⁶ are also included in Table VI for purposes of comparison. Examining these results, it can be seen that the changes in bonding that occur are primarily contained in the π bond orders and populations, while the σ bond orders and populations remain effectively constant.

It is interesting to note that the bond orders for thioformaldehyde and carbon disulfide are less than those for their oxygen-containing counterparts. Also, the CS

Table VI. Bond Orders of Some Sulfur- and Oxygen-Containing Molecules^a

Molecule	Bond	Bond orders		
		σ	π	Total
HSSH ^b	S—S	0.92		0.92
Thiophene ^b	S—C ₁	0.95	0.43	1.38
	C ₁ —C ₃	0.99	0.82	1.81
	C ₃ —C ₄	0.99	0.50	1.49
	C ₂ —C ₅	0.95	0.97	1.92
H ₂ CS	C=S	0.95	1.00	1.95
H ₂ CO ^c	C=O	0.94	1.37	2.31
CS ₂	C=S	0.93	1.42	2.35
CO ₂ ^c	C=O	0.89	1.02	1.91
OCS	C=S	0.89	1.63	2.52
	C=O			

^a Atomic numbering is shown in Figure 2. ^b See ref 1. The value reported for HSSH was calculated at a dihedral angle of 0°. ^c See ref 6.

bond order in OCS is less than the corresponding value in CS₂, and the CO bond order in OCS is greater than the corresponding value in CO₂. Hence, in agreement with chemical intuition, the CO "double bond" is found to be stronger than the CS "double bond."

In Figure 4, the total energy of CO₂ (taken from an earlier study⁶) as a function of the OCO angle (θ) relative to the total energy at $\theta = 180^\circ$ is plotted with the corresponding values for OCS and CS₂. Since the measured bending force constant for CO₂ is larger than the corresponding values for OCS and CS₂,²⁶ the ordering shown in Figure 4 is incorrect. The relative energy for CO₂ should be larger than the corresponding values of OCS and CS₂ for any value of θ .

In an effort to determine which calculation was

(26) G. Herzberg, "Molecular Structure and Molecular Structure," D. Van Nostrand, Princeton, N. J., 1966, pp 173 and 174.

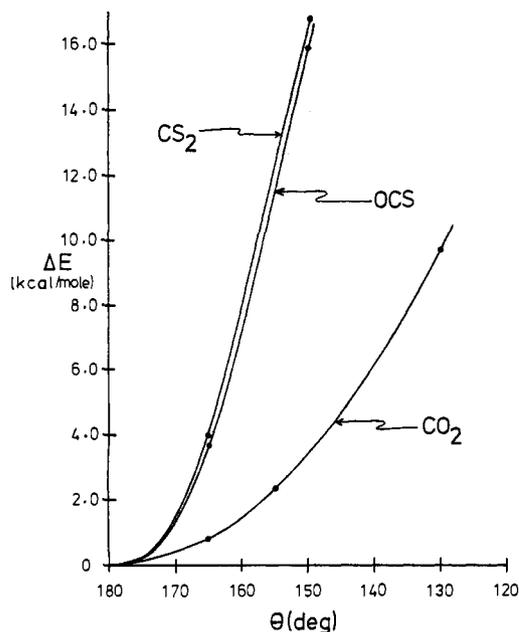


Figure 4. Total energy of CO_2 , OCS , and CS_2 as a function of the XCX angle (θ) relative to the total energy at $\theta = 180^\circ$. The data for CO_2 were taken from ref 6.

responsible for the incorrect ordering, the data for each molecule from Figure 4 were fitted to a parabola and the bending force constants (k_θ/l_1l_2) calculated from the second derivative of the total energy with respect to the angle θ . The results of these calculations and the observed²⁶ bending force constants are summarized in Table VII. It can be seen that the value of the bending force constant for CS_2 is in excellent agreement with the observed value, while the corresponding value for CO_2 is much smaller than the observed value. Since the same $\cdot\text{CH}_3$ fragment was used in the CS_2 and the CO_2 calculations, this suggests that the $\cdot\text{OH}$ fragment is perhaps describing the CO_2 molecule inadequately. Also, since the same oxygen fragment is used in the OCS and the CO_2 molecules, this indicates that the oxygen fragment may be at least partly responsible for the incorrect electron distribution in OCS .

Table VII. Bending Force Constants for the CO_2 , OCS , and CS_2 Molecules

Molecule	$k_\theta/l_1l_2, \times 10^6 \text{ dyn/cm}^2$	
	Calcd	Obsd ^b
CO_2^c	0.066	0.57
OCS	0.29	0.37
CS_2	0.223	0.234

^a k_θ is the force constant for the bending motion and l_1 and l_2 are bond lengths. For CO_2 and CS_2 $l_1 = l_2$. ^b See ref 26. ^c Data for CO_2 were taken from ref 6.

In further examining the incorrect prediction of some of the molecular properties in OCS , Gelius has shown¹⁸ that functions representing sulfur 3d orbitals had to be added to the basis set to describe some of the molecular properties in thiophene properly. He has also shown that these orbitals acted primarily as polarization functions. Although functions representing d orbitals were not explicitly added to the basis set used in these calculations, it has been shown^{1,5} that FSGO (which are not usually centered on nuclei) contain fixed amounts of s, p, d, . . . atomic character, where the amount of contribution from any particular component depends upon the FSGO nonlinear parameters. Thus, d and higher orbital character is implicitly built into the basis set, allowing some polarization to occur. Evidently, oxygen-containing molecules, and OCS in particular, represent cases where the basis set may not have enough flexibility to allow for the polarization necessary to describe the electron distribution properly. Further investigations designed to increase the flexibility of the FSGO basis in these respects are currently underway.

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