

Electronic Excited States of Organic Sulfides

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Abstract: SCF and CI molecular wave functions are derived for the ground and first few excited states of the ethylene sulfide, propylene sulfide, dimethyl sulfide, and hydrogen sulfide. The optical activity of (*R*)-(+)-propylene sulfide is also considered. From the theoretical results, assignments of the transitions of saturated organic sulfides in the region 38,000–51,000 cm⁻¹ are proposed.

Several analyses of the first few electronic transitions in organic sulfides have been reported.^{2–6} Since the absorptions of these molecules in the region 38,000–51,000 cm⁻¹ are not discrete, definite conclusions cannot be reached about the nature of the excited states from the analysis of the uv spectra, and the assignments rely mainly on the comparison of experimental and theoretical energies, intensities, and optical activities.

Let 3s and 3p be atomic orbitals of sulfur and h₁ and h₂ sp³ hybrids on carbon, directed toward the sulfur atom. With reference to the coordinates listed in Table I, the occupied molecular orbitals of higher energies in molecules containing the chromophore C–S–C may be written down as in (1) where a₁ and b₁

$$\begin{aligned} a_1 &= a(3s) + b(3p_y) + c(h_1 + h_2) \\ b_1 &= d(3p_x) + e(h_1 - h_2) \\ b_2 &= (3p_z) \end{aligned} \quad (1)$$

are σ bonding orbitals and b₂, the lone pair of the sulfur atom, may be classified as a nonbonding orbital with π symmetry. The sequence of virtual molecular orbitals available to electronic excitations is far less clear. It is generally assumed that antibonding molecular orbitals and Rydberg-type orbitals must be considered to interpret the spectra of organic sulfides in the region 35,000–51,000 cm⁻¹, Rydberg orbitals being approximately represented by the "excited" atomic orbitals 3d and 4s of the sulfur atom. SCF–MO theory provides a simple model to assess how 3d and 4s orbitals of sulfur contribute to the description of the ground and of the low-lying excited states of these molecules. So far, the attention has been mainly concentrated on the 3d orbitals of sulfur. Thompson, *et al.*,^{2b} performed a semiempirical computation, where both 3d and 4s orbitals are considered. Even if their results indicate that the 4s orbital of sulfur is the lowest virtual orbital of sulfides, they interpreted the two lowest singlet–singlet transitions of (CH₃)₂S as promotions to essentially 3d orbitals of the sulfur atom.

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We have obtained nonempirical, approximate wave functions for the ground state and several excited states of the following molecules: dimethyl sulfide, ethylene sulfide, and propylene sulfide, the latter in the *R*(+) absolute configuration. The first two molecules are the simplest examples of saturated sulfides, while the third exhibits optical activity. Its CD spectrum is known⁷ and provides interesting information about the nature of the electronic states of this molecule. As expected, 3d and 4s orbitals were not found to be important in the description of the ground states of these molecules. On the other hand, the inclusion of the 4s orbital modifies the sequence of virtual orbitals.

In this paper we present an analysis of the uv absorptions of sulfides. In sections I and II of the paper we report details and results of our computations; in section III a consistent interpretation of the spectra is presented.

I. Details of Computation and Transition Energies

Nonempirical LCAO–SCF wave functions were obtained for the three molecules for the geometries listed in Table I. For comparison, the case of H₂S was also considered. The calculations have been performed using bases of contracted Gaussian-type orbitals (CGTO). Each CGTO is a short expansion⁸ of a Slater-type orbital (STO) with the best atomic exponent.⁹ The number of primitive Gaussians (GTO) used to expand each STO is the following: four for sulfur 1s, three for sulfur 2s and 2p and carbon 1s, and two for the remaining atomic orbitals. The two-term expansion of the 4s orbital was obtained by using the variational treatment described in ref 10.

For the 3d and 4s orbitals of sulfur the exponents 1.5 and 0.93 were adopted, respectively.^{11,12} Total electronic energies and orbital energies for the occupied and the low-lying virtual orbitals of ethylene and dimethyl sulfide are given in Table II. The computed total electronic energy for propylene sulfide is –511.6558 au, the sequence of molecular orbitals being very similar to that observed in ethylene sulfide. The chromophore C–S–C in its ground state is described essentially by the occupied MO's given in eq 1.

The molecular orbital energies of H₂S are approxi-

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Table I. Atomic Coordinate (au) for Dimethyl Sulfide, Ethylene, Propylene Sulfides, and Hydrogen Sulfide Referred to Sulfur as Origin^a

Ethylene sulfide			Propylene sulfide				
C ₁	1.410188	3.134883	0.0	C	-2.840331	3.970227	-2.344537
C ₂	-1.410188	3.134883	0.0	H ₁	-4.407661	2.678844	-2.689096
H ₁	2.360593	3.646087	1.727829	H ₂	-3.569947	5.875541	-2.061102
H ₂	2.360593	3.646087	-1.727829	H ₃	-1.569408	3.955586	-3.965475
H ₃	-2.360593	3.646087	1.727829				
H ₄	-2.360593	3.646087	-1.727829				

Dimethyl sulfide			Hydrogen sulfide				
C ₁	2.586925	2.214523	0.0	H ₁	-1.858655	0.0	1.703143
C ₂	-2.586925	2.214523	0.0	H ₂	1.858655	0.0	1.703143
H ₁	1.845460	4.136274	0.0				
H ₂	3.739888	1.923272	1.681888				
H ₃	3.739888	1.923272	-1.681888				
H ₄	-3.739888	1.923272	1.681888				
H ₅	-1.845460	4.136274	0.0				
H ₆	-3.739888	1.923272	-1.681888				

^a For propylene sulfide only the coordinates of the atoms in the methyl group are given. The other coordinates are the same as in the ethylene sulfide.

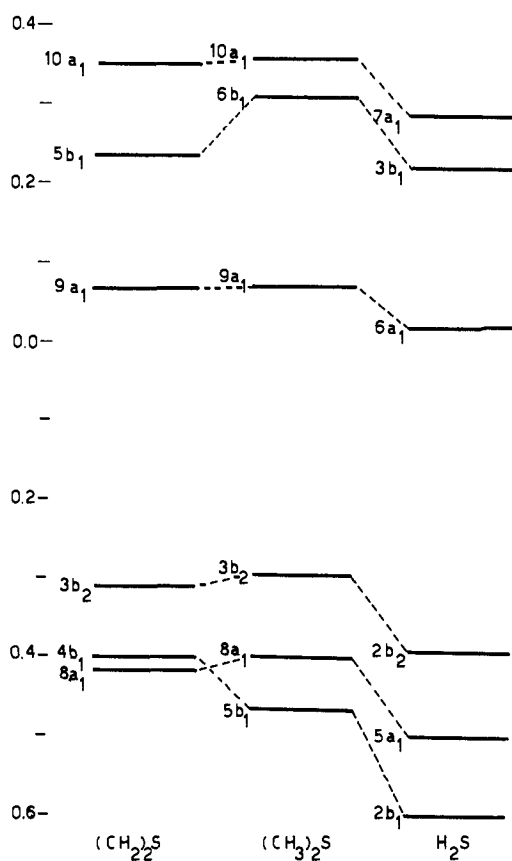


Figure 1. Orbital energies for the highest occupied and lowest virtual molecular orbitals in $(\text{CH}_2)_2\text{S}$, $(\text{CH}_3)_2\text{S}$, and H_2S .

mately 0.1 au lower than those in $(\text{CH}_3)_2\text{S}$. This has a counterpart in the experimental values of the ionization potentials of the two molecules. The ionization limit of $(\text{CH}_3)_2\text{S}$ is in fact 1.8 eV lower¹³ than that observed for H_2S . The lowest virtual molecular orbitals are $9a_1$, $5b_1$, and $10a_1$ for $(\text{CH}_2)_2\text{S}$ and $9a_1$, $6b_1$, and $10a_1$ for $(\text{CH}_3)_2\text{S}$ and correspond in sequence to the lowest virtual orbitals of H_2S . MO's $5b_1$ and $10a_1$ in $(\text{CH}_2)_2\text{S}$ and $6b_1$ and $10a_1$ in $(\text{CH}_3)_2\text{S}$ have a definite antibonding

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Table II. Total Electronic Energies (au) and Orbital Energies for Ethylene and Dimethyl Sulfide and Hydrogen Sulfide^a

Ethylene sulfide		Dimethyl sulfide		Hydrogen sulfide	
1a ₁	-91.8075	1a ₁	-91.8205	1a ₁	-91.9830
1b ₁	-11.3649	2a ₁	-11.3317	2a ₁	-8.9696
2a ₁	-11.3635	1b ₁	-11.3316	1b ₁	-6.6601
3a ₁	-8.7183	3a ₁	-8.7248	3a ₁	-6.6589
4a ₁	-6.4130	2b ₁	-6.4195	1b ₂	-6.6561
2b ₁	-6.4077	4a ₁	-6.4169	4a ₁	-0.9895
1b ₂	-6.4042	1b ₂	-6.4120	2b ₁	-0.6002
5a ₁	-1.1279	5a ₁	-1.0428	5a ₁	-0.5003
3b ₁	-0.8342	3b ₁	-0.9401	2b ₂	-0.3924
6a ₁	-0.7990	6a ₁	-0.7780	6a ₁	+0.0193
2b ₂	-0.6531	7a ₁	-0.5956	3b ₁	+0.2216
7a ₁	-0.5791	2b ₂	-0.5746	7a ₁	+0.2861
1a ₂	-0.5219	1a ₂	-0.5473		
8a ₁	-0.4140	4b ₁	-0.5396	Total energy =	
4b ₁	-0.3982	5b ₁	-0.4646		-398.6774
3b ₂	-0.3102	8a ₁	-0.3987		
9a ₁	+0.0683	3b ₂	+0.2952		
5b ₁	+0.2350	9a ₁	+0.0700		
10a ₁	+0.3515	6b ₁	+0.3118		
Total energy =	-473.0269	10a ₁	+0.3574	Total energy =	
		Total energy =	-474.1983		

^a For the latter molecule the total energies and orbital energies were obtained with a near-Hartree-Fock orbital basis.

character. With respect to the plane of the C-S-C chromophore, they can be classified as σ^* MO's. Relevant contributions to these two molecular orbitals come from the 3d orbitals of sulfur. On the other hand, if d orbitals are not included in the orbital basis, shapes and energies of the excited orbitals of b_1 and a_1 symmetry are not drastically changed. We conclude that 3d orbitals, although mathematically important, are not essential to the understanding of the spectra of saturated organic sulfides. The lowest virtual orbital ($9a_1$) has a predominant 4s character. In sulfides, the 4s orbital is slightly mixed with the 2s orbital of carbon to give a molecular orbital with a moderate antibonding character with respect to the S-C bonds. In H_2S the corresponding MO ($6a_1$) is essentially an atomic orbital. Since the presence of this orbital is dependent on the inclusion in the orbital bases of the 4s orbital of sulfur, it is important to assess the stability of the $9a_1$ orbital with respect to changes in the orbital bases and in the

occupation numbers of molecular orbitals. In the last column of Table II, the energies of near-Hartree-Fock molecular orbitals of H₂S are reported. They were obtained with an orbital basis of double- ζ quality,¹⁴ augmented with 3d and 4s orbitals on sulfur and p orbitals on hydrogens. The sequence of occupied and of the lowest virtual orbitals is identical with that found with the smaller basis, and the orbital energies are similar.

Csizmadia, *et al.*,¹⁵ performed recently an SCF computation on ethylene sulfide, using a large orbital basis not including the 4s orbital of sulfur. They did not obtain the 9a₁ molecular orbital, while the energies of the other low-lying virtual molecular orbitals are similar to the values given in Table II.

At last the stability of the 9a₁ orbital was tested by performing separate open-shell SCF computations on the excited states.

It was found that the 9a₁, 5b₁, and 10a₁ MO's in (CH₂)₂S and the 9a₁, 6b₁, and 10a₁ MO's in (CH₃)₂S are not substantially modified when electrons are promoted to those orbitals. For example, molecular orbitals for the 1¹B₂, 1¹A₂, and 2¹B₂ states of (CH₂)₂S corresponding to electronic configurations ... (8a₁)²(4b₁)²(3b₂)(9a₁), ... (8a₁)²(4b₁)²(3b₂)(5b₁), and ... (8a₁)²(4b₁)²(3b₂)(10a₁), respectively, are found to be

$$\begin{aligned} (9a_1)^{1^1B_2} = & -0.00000(1a_1)^{1^1A_1} - 0.00005(2a_1)^{1^1A_1} - \\ & 0.00004(3a_1)^{1^1A_1} + 0.00004(4a_1)^{1^1A_1} + \\ & 0.00743(5a_1)^{1^1A_1} - 0.01680(6a_1)^{1^1A_1} - \\ & 0.02886(7a_1)^{1^1A_1} - 0.02453(8a_1)^{1^1A_1} + \\ & 0.99810(9a_1)^{1^1A_1} - 0.01567(10a_1)^{1^1A_1} + \\ & 0.02376(11a_1)^{1^1A_1} + 0.00645(12a_1)^{1^1A_1} - \\ & 0.02790(13a_1)^{1^1A_1} + 0.01999(14a_1)^{1^1A_1} \quad (2) \end{aligned}$$

$$\begin{aligned} (5b_1)^{1^1A_2} = & +0.00011(1b_1)^{1^1A_1} - 0.00061(2b_1)^{1^1A_1} - \\ & 0.02220(3b_1)^{1^1A_1} - 0.14250(4b_1)^{1^1A_1} + \\ & 0.98858(5b_1)^{1^1A_1} - 0.03757(6b_1)^{1^1A_1} - \\ & 0.01629(7b_1)^{1^1A_1} + 0.01519(8b_1)^{1^1A_1} \end{aligned}$$

$$\begin{aligned} (10a_1)^{2^1B_2} = & +0.00000(1a_1)^{1^1A_1} - 0.00009(2a_1)^{1^1A_1} - \\ & 0.00043(3a_1)^{1^1A_1} - 0.00010(4a_1)^{1^1A_1} - \\ & 0.03682(5a_1)^{1^1A_1} + 0.06163(6a_1)^{1^1A_1} + \\ & 0.00804(7a_1)^{1^1A_1} - 0.02710(8a_1)^{1^1A_1} + \\ & 0.03324(9a_1)^{1^1A_1} + 0.98886(10a_1)^{1^1A_1} - \\ & 0.05633(11a_1)^{1^1A_1} + 0.07789(12a_1)^{1^1A_1} + \\ & 0.07591(13a_1)^{1^1A_1} + 0.00993(14a_1)^{1^1A_1} \end{aligned}$$

where the upper index refers to the electronic states of the molecule (CH₂)₂S. Similar results were obtained for several states of the three molecules studied. The above arguments, and the fact that the 4s orbital in the free sulfur atom is the lowest virtual orbital, lead to the conclusion that the lowest virtual orbital 9a₁ for episulfide and dimethyl sulfide is not a spurious by-product of the SCF treatment and the 4s orbital of sulfur should be considered when interpreting the uv absorption of saturated sulfides.

Going from ethylene sulfide to dimethyl sulfide, the

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(15) O. P. Strausz, R. K. Gosavi, A. S. Denes, and I. G. Csizmadia, *Theor. Chim. Acta*, **26**, 367 (1972).

greatest changes in orbital energies are observed for the 4b₁ orbital. The "bonding power" of this orbital is increased (see Figure 1), as expected for bonding orbitals of B₁ symmetry, since the angle C-S-C increases approximately by 30° on going from episulfide to dimethyl sulfide. Also this is the MO which changes the most when carbon is replaced by hydrogen. As a consequence, the sequence of MO's 5b₁ and 8a₁ in (CH₃)₂S is inverted with respect to the corresponding molecular orbitals in (CH₂)₂S. The "antibonding power" of 5b₁ molecular orbitals in (CH₂)₂S increases when going to dimethyl sulfide, but the sequence of virtual orbital energies is not modified.

Following Cooper-McWeeny,¹⁶ approximate wave functions for the excited states were constructed using occupied and virtual orbitals obtained by the SCF treatment of the ground state. Equation 3 gives an ap-

$$\Phi_{kl}^{mn} = \alpha \left\{ \phi_1(r_1)\phi_1(r_2) \dots \phi_k(\dots)\phi_l(\dots)\phi_m(\dots)\phi_n(\dots) \times \prod_{i,j \text{ (all pairs)}} 2^{-1/2} [\alpha(i)\beta(j) - \alpha(i)\beta(j)] \right\} \quad (3)$$

proximate wave function for a singlet state corresponding to the excited configuration, obtained by promoting two electrons from the *k*th and *l*th occupied molecular orbitals to the *m*th and *n*th virtual orbitals. General rules were given¹⁶ to obtain the expectation values of the energy for functions of Φ 's, once molecular integrals over ϕ orbitals were known. Transition energies computed in this way are reported in the first column of Table III.

Table III. Transition Energies (au) to Low-Lying Electronic States for Ethylene Sulfide, Propylene Sulfide, Dimethyl Sulfide, and Hydrogen Sulfide

Molecule	State	Wave function	<i>a</i>	<i>b</i>	<i>c</i>
(CH ₂) ₂ S	1 ¹ B ₂	$\Phi_{3b_2}^{9a_1}$	0.2159	0.2211	0.1811
	1 ¹ A ₂	$\Phi_{3b_2}^{5b_1}$	0.2147	0.2234	0.1979
	1 ¹ B ₁	$\Phi_{4b_1}^{9a_1}$	0.3104	0.3298	0.2861
	2 ¹ A ₁	$\Phi_{8a_1}^{9a_1}$	0.3286	0.3461	
	2 ¹ B ₂	$\Phi_{3b_2}^{10a_1}$	0.3448	0.3535	0.3228
Propylene sulfide ^d	1 ¹ B ₂		0.2179	0.2221	0.1960
	1 ¹ A ₂		0.2168	0.2256	
	1 ¹ B ₁		0.3050	0.3238	
	2 ¹ A ₁		0.3243	0.3411	
	2 ¹ B ₂		0.3459	0.3549	
(CH ₃) ₂ S	1 ¹ B ₂	$\Phi_{3b_2}^{9a_1}$	0.2028	0.2062	0.1883
	1 ¹ A ₂	$\Phi_{3b_2}^{6b_1}$	0.2651	0.2755	0.2588
	2 ¹ A ₁	$\Phi_{8a_1}^{9a_1}$	0.3166	0.3191	
	2 ¹ B ₂	$\Phi_{3b_2}^{10a_1}$	0.3674	0.3716	0.3536
	1 ¹ B ₁	$\Phi_{5b_1}^{9a_1}$	0.3816	0.3881	0.3738
H ₂ S	1 ¹ B ₂	$\Phi_{2b_2}^{8a_1}$	0.2790	0.2752	
	1 ¹ A ₂	$\Phi_{2b_2}^{3b_1}$	0.2777	0.2863	
	2 ¹ A ₁	$\Phi_{5a_1}^{8a_1}$	0.3875	0.3835	
	2 ¹ B ₂	$\Phi_{2b_2}^{7a_1}$	0.3886	0.3945	
	1 ¹ B ₁	$\Phi_{5a_1}^{3b_1}$	0.4662	0.4501	

^a The excited state wave function is a single configuration constructed from the ground state SCF orbitals. ^b CI wave functions for the ground and excited states. ^c Separate SCF calculations for ground and excited states. ^d For the (*R*)-(+)-propylene sulfide only the approximate symmetry of the electronic state is reported.

Configuration mixing among wave function Φ 's corresponding to the lowest energies was next admitted.

(16) R. McWeeny and I. Cooper, *J. Chem. Phys.*, **45**, 226, 3484 (1966).

Table IV. Oscillator and Rotational Strengths ($\times 10^{-40}$ cgs)

Molecule	Transition	Oscillator strengths		Rotational strengths	
		a	b	a	b
Propylene sulfide	$1^1B_2 \leftarrow 1^1A_1$	0.0049	0.0043	eq 5 -0.0882	-1.4045
				eq 6 -0.6365	-4.0930
	$1^1A_2 \leftarrow 1^1A_1$	0.0013	0.0003	eq 5 -13.3239	-4.0930
				eq 6 -18.0156	-14.1210
	$1^1B_1 \leftarrow 1^1A_1$	0.0108	0.0111	eq 5 -6.3844	-4.3970
			eq 6 -13.6251	-12.1593	
	$2^1A_1 \leftarrow 1^1A_1$	0.0091	0.0245	eq 5 -1.5720	-7.8218
			eq 6 6.5668	5.0434	
	$2^1B_2 \leftarrow 1^1A_1$	0.0835	0.0706	eq 5 5.0400	5.0620
			eq 6 4.2170	-0.0325	
$(CH_3)_2S$	$1^1B_2 \leftarrow 1^1A_1$	0.0019	0.0023		
	$1^1A_2 \leftarrow 1^1A_1$	0	0		
	$2^1A_1 \leftarrow 1^1A_1$	0.0035	0.0070		
	$2^1B_2 \leftarrow 1^1A_1$	0.0904	0.0670		
	$1^1B_1 \leftarrow 1^1A_1$	0.0001	0.0014		

^a Single configuration wave function. ^b Many configurational wave functions.

Practically all singlet states arising from single and double excitations from MO's, $4b_1$, $8a_1$, and $3b_2$ to MO's $9a_1$, $5b_1$, and $10a_1$ in $(CH_2)_2S$ (altogether 54 singlet states) were considered. The equivalent configurations were considered for the other molecules. Configuration interaction (CI) wave functions were constructed from the basis functions of the type in eq 3 by solving the corresponding secular equation. The different transition densities among wave functions expressed as linear combinations of functions in eq 3 were evaluated. In the *second column* of Table III, we report transition energies computed in this way. Substantial agreement exists between the two sets of values. The only significant difference is the inversion of the nearly degenerate 1^1B_2 and 1^1A_2 states for $(CH_2)_2S$ and H_2S . This limited configuration interaction treatment proved to be more effective on the ground state energy; therefore, the net result is a general increase of transition energies.

More important are the effects on transition densities, since one-particle excitations are not negligibly mixed by configuration interaction. The relevant contributions to the transition densities are given, as examples, in eq 4 for the low-lying transitions of $(CH_3)_2S$ in terms of MO products.

$$\begin{aligned}
 P_1(r)_{1^1A_1, 1^1B_2} &= (1.3947)3b_2(r)[9a_1(r)] + \\
 &\quad (0.0345)3b_2(r)[10a_1(r)] \\
 P_1(r)_{1^1A_1, 1^1A_2} &= (1.3799)3b_2(r)[6b_1(r)] \\
 P_1(r)_{1^1A_1, 2^1A_1} &= (0.0496)5b_1(r)[6b_1(r)] + (1.3926) \times \\
 &\quad 8a_1(r)[9a_1(r)] - (0.0326)8a_1(r)[10a_1(r)] \\
 P_1(r)_{1^1A_1, 2^1B_2} &= (0.0108)3b_2(r)[8a_1(r)] - (0.0306) \times \\
 &\quad 3b_2(r)[9a_1(r)] + (1.3230)3b_2(r)[10a_1(r)]
 \end{aligned} \quad (4)$$

In the *third column* of Table III, we report transition energies obtained as differences between ground and excited state SCF energies. A disadvantage of performing separate SCF calculations for the excited states is that functions for states with the same symmetry are only approximately orthogonal. On the other hand, the procedure gives a more realistic picture of virtual orbitals. Transition energies obtained with the latter method compare favorably with experimental values.

II. Rotational Strengths of the Electronic Transitions

Oscillator strengths were obtained for the first few electronic transitions of $(CH_3)_2S$ and propylene sulfide. Also rotational strengths were computed for $(R)-(+)$ -propylene sulfide in the dipole length and in the dipole velocity representations according to the definitions in eq 5 and 6 where r , m , and ∇ are the electric dipole,

$$R_a^b = \text{Im}\langle a|r|b\rangle\langle b|m|a\rangle \quad (5)$$

$$R_a^b = \text{Im}\langle a|\nabla|b\rangle\langle b|m|a\rangle/(E_b - E_a) \quad (6)$$

the magnetic dipole, and the gradient operators, respectively, and a and b are wave functions for the electronic states a and b with energies E_a and E_b .

Since no examples, as far as we know, are reported in the literature, where rotational strengths are obtained from *ab initio* wave functions, it is of some interest to compare results obtained with (5) and (6). The values computed with single and many configurational wave functions are reported in Table IV, the reference frame being that of Table I. When approximate eigenfunctions are used, eq 5 provides rotational strengths, which depend upon the origin of the reference frame,¹⁷ while eq 6 holds only approximately. The two sets of values present significant differences but agree in sign, with the exception of the $2^1A_1 \leftarrow 1^1A_1$ transition. Configuration interaction affects considerably rotational strengths, especially those computed by eq 6, whose dependence upon the origin becomes less pronounced. In one case (transition $2^1B_2 \leftarrow 1^1A_1$), a change in sign is observed. This is illustrated in Figure 2, where rotational strengths for the transition $2^1B_2 \leftarrow 1^1A_1$, computed for different choices of the origin along the x axis, are shown before and after configuration interaction.

Rotational strengths are seen to be more sensitive than transition energies to small changes of the molecular wave functions. A nonnegligible magnetic transition moment along the y direction comes to the $3b_2 \rightarrow 9a_1$ transition by strong interaction with the $3b_2 \rightarrow 5b_1$ transition and determines the large absolute value of the rotational strength computed from CI wave functions. By a similar effect the oscillator strength for

(17) A. Moskowitz, "Modern Quantum Chemistry," 3rd ed, O. Sinanoglu, Ed., Academic Press, New York, N. Y., 1965, p 31.

Table V. Summary of the Experimental and Theoretical Results and Assignment of the Electronic Transitions^a

Molecule	Transition, eV		Assignment	f		R	
	b	c		b	c	b	c
(CH ₂) ₂ S, propylene sulfide	5.0-5.1	6.0	1 ¹ B ₂ ← 1 ¹ A ₁	1	20	-1	-1
		6.1	1 ¹ B ₂ ← 1 ¹ A ₁		1		-1
	6.2	8.8	1 ¹ B ₁ ← 1 ¹ A ₁	5	40	-5	-1
(CH ₃) ₂ S	6.5	9.3	2 ¹ A ₁ ← 1 ¹ A ₁		80	+	+
	5.0-5.6	5.6	1 ¹ B ₂ ← 1 ¹ A ₁		1		
		7.5	1 ¹ A ₂ ← 1 ¹ A ₁		0		
H ₂ S	5.7	8.7	2 ¹ A ₁ ← 1 ¹ A ₁	1	3		
	6.2	10.1	2 ¹ B ₂ ← 1 ¹ A ₁	4	30		
	5.7-7.2	7.5	1 ¹ B ₂ ← 1 ¹ A ₁				
		7.8	1 ¹ A ₂ ← 1 ¹ A ₁				
	7.8	10.4	2 ¹ A ₁ ← 1 ¹ A ₁				
	8.1	2 ¹ B ₂ ← 1 ¹ A ₁					

^a Relative intensities and rotational strengths are reported. ^b Experimental. ^c Theoretical.

the 2¹A₂ ← 1¹A₁ transition increases considerably after configuration interaction.

Unfortunately, for most of the molecules presenting optical activity, only very crude molecular wave functions are available. In this respect, it is of some interest to notice that CNDO and *ab initio* SCF-MO wave functions predict the same sign of rotational strengths for the electronic transitions, corresponding in ethylene sulfide to the 3b₂ → 5b₁, 3b₂ → 10a₁, and 4b₁ → 5b₁ one-particle excitations. Extension of the analysis to other simple molecular systems and to a larger variety of electronic transitions should be considered before definite conclusions about this point can be reached. Work along this line is in progress. On the contrary, approximations on integrals needed in the computation of (5) and (6) are clearly not allowed.¹⁸ For instance, the simplified procedure suggested by Santry,¹⁹ where two-center integrals are neglected to evaluate eq 5, leads to wrong results for all transitions considered.

III. Experimental Data and Assignments

The ultraviolet spectra of episulfide and open-chain dialkyl sulfides have been investigated by several authors, both in the vapor phase and in solution;^{2,3} a detailed study of the optical activity of five- and six-membered ring sulfides has recently appeared;⁴ data on CD spectra of open-chain sulfides are also available.²⁰ Ethylene sulfide and propylene sulfide show distinct weak bands ($f = 0.0005$) at *ca.* 38,000 and 41,000 cm⁻¹ and stronger absorptions at *ca.* 49,000 and 51,000 cm⁻¹.^{2a} In (+)-propylene sulfide these bands are optically active, giving only a single negative Cotton effect at *ca.* 40,000 cm⁻¹ ($R = -5 \times 10^{-40}$ cgs), followed by a positive one⁷ below 50,000 cm⁻¹. Open-chain sulfides show a very weak, diffuse absorption in the region 40,000-45,000 cm⁻¹, which is detected only in solution.^{2,3,20} This absorption is enhanced in *tert*-butyl methyl sulfide.^{2b} A more intense, structured band follows at 2200 Å. Its vibronic structure has been analyzed in terms of progression and combinations of the symmetrical C-S-C stretch and methyl rock (a₁ symmetry), built on the intense 0-0 band. This transition loses its structure and is blue shifted going from vapor into solution. An intense structureless band ($f = 0.06$) is located at *ca.* 50,000 cm⁻¹. Hydro-

(18) A. Imamura, T. Hirano, C. Nagata, and T. Tsuruta, *Bull. Chem. Soc. Jap.*, **45**, 396 (1972).

(19) Y. H. Pao and D. P. Santry, *J. Amer. Chem. Soc.*, **88**, 4157 (1966).

(20) P. Salvadori, *Chem. Commun.*, 1203 (1968).

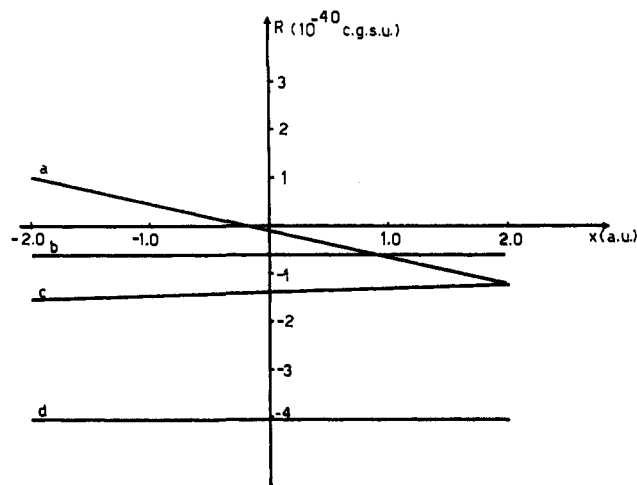


Figure 2. Rotational strengths of the 1¹B₂-1¹A₁ transition for different choices of the origin of the reference frame of the x axis: (a) and (c) eq 5 with single and many configurational wave functions, respectively; (b) and (d) eq 6 with single and many configurational wave functions, respectively.

gen sulfide has a long-wavelength diffuse absorption between 46,000 and 58,000 cm⁻¹, followed by two non-Rydberg transitions^{2,5,21} at 63,000-65,000 cm⁻¹. From the results presented in sections I and II, the assignments summarized in Table V can be suggested.

Region between 2600 and 2250 Å. In episulfides the two lower lying calculated singlet-singlet transitions are 3b₂ → 9a₁ and 3b₂ → 5b₁. The first is symmetry allowed but weak; the second is only magnetic dipole allowed in ethylene sulfide; their energy separation is very small. These transitions can be related to the first two observed bands at *ca.* 38,000 and 41,000 cm⁻¹, since the A₂ ← A₁ transition is likely to acquire some intensity through vibration, in a way similar to the $n \rightarrow \pi^*$ (A₂ → A₁) carbonyl transition.^{2a} The sequence calculated could be correct as the lower energy transition is more intense in both ethylene and propylene sulfides. This fact becomes more evident considering that the overlapping with the near-lying transitions causes an apparent intensity increase of the A₂ → A₁ transition. These assignments are further supported by the optical activity of (+)-propylene sulfide. The calculated rotational strength is dominated by the magnetic allowed 3b₂ → 5b₁ transition, which has the correct sign and order of magnitude. The rotational

(21) K. Watanabe and A. S. Jursa, *J. Chem. Phys.*, **41**, 1650 (1964).

strength calculated for the $3b_2 \rightarrow 9a_1$ transition has the same sign but is smaller. These observations, together with the limited resolving power of the dichrograph, are a satisfactory explanation for the single dichroic absorption, found experimentally for propylene sulfide.

Going to dimethyl sulfide, the calculated $3b_2 \rightarrow 9a_1$ transition does not shift substantially, while its intensity is further reduced. On the contrary, the $3b_2 \rightarrow 5b_1$ transition is shifted to higher energy. Both bands are likely to be located under the broad absorption between 40,000 and 45,000 cm^{-1} . The moderately intense CD band found in open-chain and in five- and six-membered ring sulfides at *ca.* 43,000 cm^{-1} is almost certainly related to the magnetic $3b_2 \rightarrow 5b_1$ transition, while the $3b_2 \rightarrow 9a_1$ transition is difficult to locate. This absorption is strongly reminiscent of the broad band of H_2S between 58,000 and 44,000 cm^{-1} . With regards to the assignment previously given by other authors, our interpretation agrees with the work by Clark and Simpson,^{2a} Williams and Koutnik,⁶ and Rosenfeld and Moscovitz⁴ about the existence of the magnetic dipole allowed transition and its preponderant contribution to the observed optical activity.^{4,2b,22} Our interpretation has the advantage of explaining the existence of the two bands in ethylene sulfide and of the broad absorption below 43,000 cm^{-1} in open-chain sulfides.

Region between 2000 and 2200 Å. The next calculated transition in ethylene sulfide is $4b_1 \rightarrow 9a_1$; it is symmetry allowed and the theoretical intensity is moderately strong. The rotational strength of this transition is predicted to be negative in (*R*)-(+)-propylene sulfide. Experimental data²⁻⁷ show in this region a medium intensity absorption to which corresponds a negative maximum in the CD spectrum of (*R*)-(+)-propylene sulfide. Moreover, the polarization of this transition can be used to rationalize the (probable) exciton pattern observed for some phenyl episulfides.^{2,3} We do not see substantial reasons in favor of the assignment previously given in ref 2a. In dimethyl sulfide instead, the next calculated transition is $8a_1 \rightarrow 9a_1$, the theoretical intensity is smaller, and the energy is lower than for the $4b_1 \rightarrow 9a_1$ transition in ethylene sulfide, as it is indeed observed for the 2200-Å band in dimethyl sulfide.^{2a} The vibronic structure of this

(22) P. Biscarini, G. Gottarelli, B. Samori, and G. D. Nivellini, *Tetrahedron*, **28**, 4139 (1972).

(23) I. Moretti, G. Torre, and G. Gottarelli, *Tetrahedron Lett.*, 4301 (1971).

band is also consistent with an allowed transition. Previous assignments were attempted by Clark and Simpson^{2a} as a $\sigma \rightarrow \sigma^*$ transition, by Thompson, *et al.*,^{2b} as a $3p \rightarrow 3d$ transition, and by Rosenfeld and Moscovitz⁴ as a $b_2 \rightarrow a_1$ transition. All $b_2 \rightarrow a_1$ assignments reported are in principle possible as they are not in disagreement with the observed spectrum.

Region at *ca.* 2000 Å. In ethylene sulfide the next calculated transition is $8a_1 \rightarrow 3a_1$ with higher intensity than the previously discussed $4b_1 \rightarrow 9a_1$. The rotational strength calculated for the same transition in (*R*)-(+)-propylene sulfide is positive. It seems to be reasonable to identify this transition with that observed in the spectrum at *ca.* 52,000 cm^{-1} , to which probably corresponds the positive CD band beginning to appear below 50,000 cm^{-1} . Going back to dimethyl sulfide, the fourth calculated transition is $3b_2 \rightarrow 10a_1$ and is strongly allowed. This transition is likely to be responsible for the 50,000- cm^{-1} absorption band of dimethyl sulfide. Our assignment is again different from those proposed by other authors. Clark and Simpson^{2a} are in favor of a $\sigma \rightarrow \sigma^*$ B_1 allowed transition; Thompson, *et al.*,^{2b} support a $3p_z \rightarrow 4s$ promotion; Moscovitz and Rosenfeld⁴ support a $3p \rightarrow 3d$ transition, where 3d is a linear combination of sulfur 3d orbitals, the particular combination being dependent on the compound. In the light of the calculations reported, it seems to be unlikely to find the $3p \rightarrow 4s$ transition in this spectral region. The other assignments²⁻⁴ are in principle possible.

Hydrogen Sulfide. The assignments we propose for H_2S are strictly analogous to those given above for dimethyl sulfide. The broad low-intensity absorption between 58,000 and 46,000 cm^{-1} is likely to contain both the $9a_1 \rightarrow 3b_2$ and the $3b_2 \rightarrow 5b_1$ transitions; obviously the allowed transition should dominate the intensity.

The following transitions at 63,000 and 65,000 cm^{-1} are assigned to $5a_1 \rightarrow 6a_1$ and $2b_2 \rightarrow 7a_1$. Previous works^{2b,21,24} are in favor of the assignment $3p \rightarrow 4s$ for the low-energy transition. The bands at 63,000 and 65,000 cm^{-1} are known to be non-Rydberg,^{2a,5,21} but no definite assignments were previously attempted.

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(24) R. S. Mulliken, *J. Chem. Phys.*, **3**, 500 (1935).