An MO Theoretical Investigations of the Electronic Spectra of Divalent Sulfur Compounds

Hideki SAKAI, Tokio YAMABE, Hiroshi KATO*, Shinichi NAGATA, and Kenichi FUKUI

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606

**College of General Education, Nagoya University, Nagoya 464*

(Received March 20, 1974)

The singlet transition energies and oscillator strengths of several divalent sulfur compounds are calculated by the semi-empirical ASMO–SCF method. It is shown that the UV absorption bands with transition energies of 5—6 eV observed in these sulfur compounds can be assigned to n-σ_1*, n-σ_2*, or σ-σ_1*, implying that the 3d orbitals of the sulfur atom do not play an important role in these electronic transitions or may contribute absorption bands with higher transition energies.

It is well known that a number of divalent sulfur compounds have characteristic electronic absorption bands in the near-ultraviolet region; they have often been identified as n-σ*, σ-σ*, n-3d, n-4s, *etc.* In 1965, Clark *et al.*[1] obtained satisfactory vacuum-ultraviolet spectra of several divalent sulfur compounds, *i.e.*, hydrogen sulfide, alkyl sulfides, cyclic alkyl sulfides, and thiols, and tried to give their assignments on the basis of a simple schematic molecular orbital (MO) diagram according to the Walsh rule. Subsequently, several calculations of their assignments have been carried out by semi-empirical MO methods.[2–4] The results obtained, however, show disagreement with each other in their assignments, as will be shown in this text.

In the present paper, we intend to describe some investigations concerning the singlet transition energies and the assignments of some saturated divalent sulfur compounds based on the MO calculations of the semi-empirical ASMO–SCF method.

Method

The calculations are carried out by the semi-empirical ASMO–SCF method,[5] where the approximation of the zero differential overlap is adopted for valence electron system; the contributions of the 3d atomic orbitals of the sulfur atom are also included. In parametrizing the core resonance integrals,

$$H_{rs} = -KS_{rs}(I_r+I_s)/2,$$

where the notations are the same as those in Ref. 5; we adopted a value of 0.8 for the K constant.

The compounds treated in this work are H_2S, CH_3SH, $(CH_3)_2S$, C_2H_4S, and C_3H_6S. Their geometries are shown in Table 1, where tetrahedral angles are assumed for the alkyl groups. The ultraviolet (UV) absorption spectra of these compounds observed by Clark *et al.*[1] are referred for the sake of comparison with the calculated values.

TABLE 1. MOLECULAR STRUCTURE OF SULFUR COMPOUNDS USED FOR CALCULATIONS

Compound	Bond angle RSR′ (deg)	Bond distance H–S (Å)	Bond distance C–S (Å)
H_2S	92.2	1.35	
CH_3SH	100.0	1.33	1.82
CH_3SCH_3	100.0		1.82
C_2H_4S	48.4		1.82
C_3H_6S	78.0		1.82

Results and Discussion

H_2S. The results of H_2S are presented in Fig. 1. According to the present calculations, the lowest singlet transition, $^1A_2$ (b_1—b_2*), is symmetry-forbidden and may not be detectable by UV spectroscopy, while the next one, $^1B_1$ (b_1—a_1*), with the transition energy (ΔE) of 6.54 eV and the oscillator strength (f) of 0.037 may be reasonably identified as the first absorption band of H_2S (ΔE=6.32 eV, f=0.04) observed by Clark *et al.*[1] At first they assigned it to the $^1A_1$ (a_1—a_1*) transition according to the Walsh diagram; subsequently, though, Thompson *et al.*[3] calculated the transition energy by their own semi-empirical method and predicted that the excitation must be that of an electron from the lone-pair orbital to either the 3d or the 4s orbital to be significantly atomic in nature (*i.e.*, the Rydberg state). However, their oscillator strengths are quite small ($f=4\times10^{-6}$ for the 3d and 0.006 for the 4s orbital) compared with the observed value (f=0.04), whereas our calculation gives a reasonable oscillator strength (0.037).

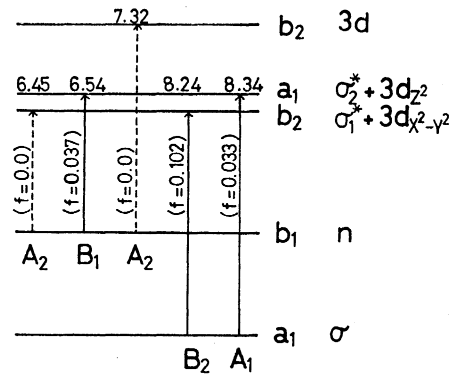

Fig. 1. Singlet transitions of H_2S. Observed values;[1] 6.32 eV (f=0.04), 7.85, 8.02.

The orbital (a_1*) to which the excitation occurs shows an antibonding character, although it includes a 33% contribution from the 3d orbital. Indeed, preliminary calculations excluding 3d orbitals show no significant change for this transition in its transition energy (0.14 eV) and its oscillator strength, implying that the 3d orbitals do not essentially change the antibonding nature of the σ^* level.

On the other hand, in their non-empirical calculations Polezzo *et al.*[6] and Hillier *et al.*[7] assigned the lowest forbidden transition, $^1A_2$, with excitation energies of 6.70 and 6.51 eV respectively, to the observed lowest transition of 6.32 eV. It may be more reasonable, however, to assign it to $^1B_1$ (b_1—a_1^*), because the $^1A_2$ transition is forbidden and, therefore, is not expected to be observed, while the oscillator strength of $^1B_1$ (f=0.037) is in good agreement with the observed one (f=0.04).

It is well known that there exists a vibrational structure in this absorption band; from their analysis of the vibrational structure, Thompson *et al.*[3] concluded that it is due to the symmetrical bending mode and that the band is the transition from the lone-pair orbital to the 3d or the 4s orbital because of a slight anharmonicity. Moreover, they have insisted that if the transition were one to the antibonding orbital, there would be more anharmonicity and other stretching modes in the vibrational structure. Such would also be expected if the transition were from the bonding orbital to the antibonding orbital. However, there is evidence that the structure of the excited H_2S molecule (H_2S^*), which corresponds approximately to the transition from the lone-pair orbital, is not altered so much as to give a considerable anharmonicity in comparison with the ground-state H_2S molecule. That is, the structure of the ground-state H_2S^+ cation radical,[8] which is probably similar to H_2S^* with respect to its molecular structure, is almost unchanged from that of H_2S, showing that a large anharmonicity in the vibrational structure is unnecessary.

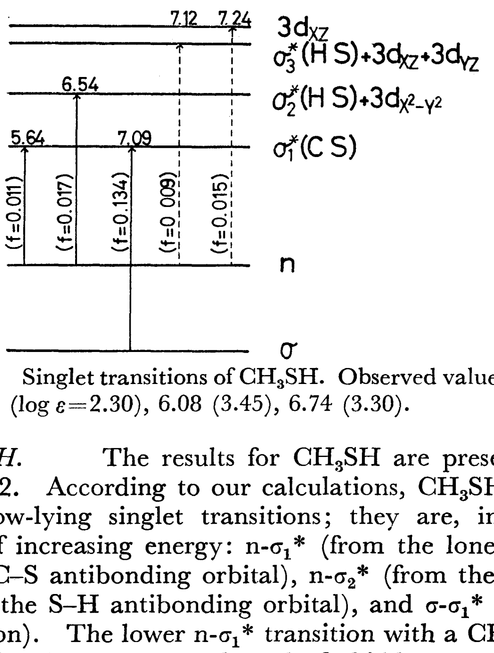

Fig. 2. Singlet transitions of CH_3SH. Observed values;[1] 5.21 (log ε=2.30), 6.08 (3.45), 6.74 (3.30).

CH_3SH. The results for CH_3SH are presented in Fig. 2. According to our calculations, CH_3SH has three low-lying singlet transitions; they are, in the order of increasing energy: n-σ_1^* (from the lone pair to the C–S antibonding orbital), n-σ_2^* (from the lone pair to the S–H antibonding orbital), and σ-σ_1^* (C–S excitation). The lower n-σ_1^* transition with a CH_3SH value of 5.64 eV corresponds to the forbidden transition, $^1A_2$ (b_1—b_2^*), of H_2S. Clark *et al.* assigned the observed three lowest transitions of CH_3SH, 5.21, 6.08, and 6.70 eV, to the n-σ^* type, the intramolecular charge transfer (from the C–S bonding orbital to the H–S antibonding orbital), and the C–S excitation respectively. Their assignments for the first and the third transitions are in agreement with ours. The second, however, is not in agreement; *i.e.*, our result shows that the C–T band has a higher energy (ΔE= 7.87 eV) than the C–S excitation and that in addition, another n-σ^* (H–S) transition exists (ΔE=6.54 eV) between them. On the other hand, the calculations excluding the 3d orbitals showed almost no change in the first and the third transitions, though the second one is changed in the ordering of the energy levels; the calculations show an energy shift of some extent (ΔE=7.47 eV, f=0.067). It can easily be seen from these results that the σ-σ^* transition seems not to be affected considerably by the basis set of calculations with respect to the energy and the intensity, so it may be reasonabe to assign the σ-σ_1^* and the n-σ_2^* transitions to the second or the third band of the observed spectra of CH_3SH.

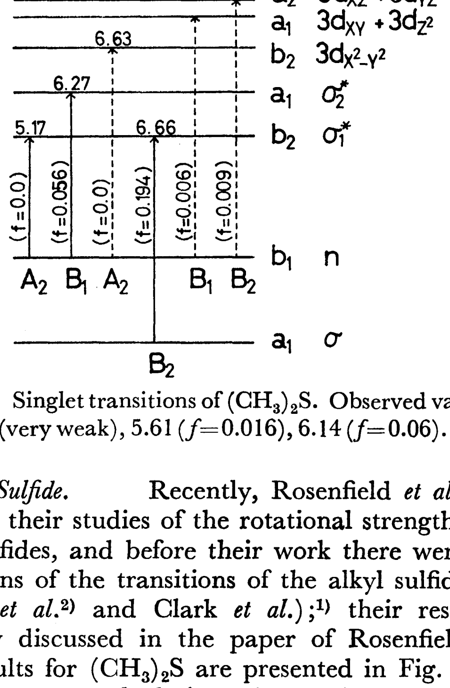

Fig. 3. Singlet transitions of $(CH_3)_2S$. Observed values;[1] 5.20 (very weak), 5.61 (f=0.016), 6.14 (f=0.06).

Alkyl Sulfide. Recently, Rosenfield *et al.*[9] have reported their studies of the rotational strengths of the alkyl sulfides, and before their work there were a few discussions of the transitions of the alkyl sulfides (*e.g.*, Carroll *et al.*[2] and Clark *et al.*);[1] their results are minutely discussed in the paper of Rosenfield *et al.* Our results for $(CH_3)_2S$ are presented in Fig. 3. According to our calculations, it can be seen that the assignments for the first two bands, which are the b_1—b_2^* (n-σ_1^*) transition and the b_1—a_1^* (n-σ_2^*) transition, are in agreement with those of Rosenfield *et al.* Furthermore, they have assigned the third band to the n-3d transition on the basis of the optical-active data and the oscillator strength. According to our results, the third is the b_1—b_2^* (n-3d) transition at 6.63 eV; this is, however, symmetry-forbidden, so the third band in the UV spectrum of this compound may be assigned to the next strong a_1—b_2^* (σ—σ_1^*) transition. Moreover, it is clear from the studies of Rosenfield *et al.* of the electric and magnetic moments of the transitions that the a_1—b_2^* transition may be optical-active when the sulfide chromophore is in a dissymmetrical field. Therefore, it seems that the observed moderately strong absorption band at 6.14 eV can reasonably be assigned to the a_1—b_2^*, but not the n—3d, transition.

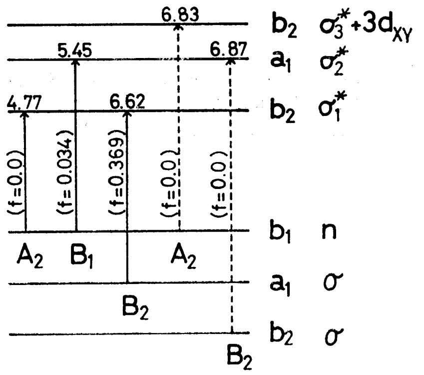

Fig. 4. Singlet transitions of C_2H_4S. Observed values;[1] 4.80 (log ε=1.30), 5.10 (1.32), 5.69 (2.30), 5.85 (3.60), 5.99 (3.60), 6.11 (3.60).

Cyclic Sulfides. The results of C_2H_4S are presented in Fig. 4. The calculated lowest singlet transition energies are 4.77, 5.45, and 6.62 eV, which correspond to the b_1—b_2^* (n—σ_1^*), b_1—a_1^* (n—σ_2^*), and a_1—b_2^* (σ—σ_1^*) transitions respectively. Those σ^* levels (b_2^* and a_1^*) at which the transitions occur bear little d-character. The calculated transitions can reasonably be assigned to the absorption spectrum of C_2H_4S; *i.e.*, the first band, which is characterized by the transition energy of 5.1 eV with a very weak intensity (log ε_{max}=1.3) in solution, may be assigned to the b_1—b_2^* (n—σ_1^*) transition, because, although the transition is apparently symmetry-forbidden, the ring distortion, which may occur as a result of excitation in such a strained molecule, has little effect on the oscillator strength. According to our additional MO calculations, in which the CSC ring is distorted by changing the length of one S–C bond only, the oscillator strength of the n—σ_1^* transition is about 10^{-4}; this value does not change greatly with the extent of distortion. The vapor-phase UV spectrum of this transition band, however, shows two broad peaks at 4.80 and 5.10 eV, while in the solution spectrum[14] only one is observed in the same region. For these two peaks, Williams *et al.*[4] have assigned two different transitions based on their CNDO/2 calculation including 3d orbitals. However, it is obvious from the CD and ORD spectra of the optical-active steroidal episulfides[12,13] that there is only one electronic transition band in this region. The splitting of this band in the vapor-phase UV spectrum is probably due to the non-vertical transition, as was recently pointed out by Strausz *et al.*[10] based on the non-empirical MO calculations. The second lowest transition, b_1—a_1^* (n—σ_2^*), may be easily assigned to the observed absorption of 5.69 eV. The third transition, a_1—b_2^* (σ—σ_1^*), might be assigned to the three observed peaks, 5.85, 5.99, and 6.11 eV, which are probably the vibrational splittings corresponding to the CH_2 bending (1120 cm^{-1} in the Raman spectrum[11]) or the ring deformation (1040 cm^{-1} in the Raman spectrum).

The results for C_3H_6S are presented in Fig. 5. The two lowest observed absorption bands, 4.46 and 4.71 eV, can also be assigned to the symmetry-forbidden b_1—b_2^* (n—σ_1^*) transition of 4.07 eV, while the other transitions may be assigned to the b_1—a_1^* (n—σ_2^*),

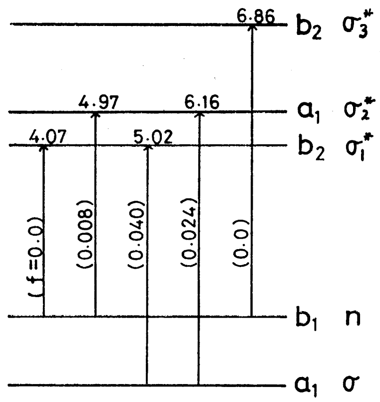

Fig. 5. Singlet transitions of C_3H_6S. Observed values;[1] 4.46 (log ε=1.00), 4.71 (1.11), 5.58 (3.30), 5.83 (3.11), 6.20 (3.45).

a_1—b_2^* (σ—σ_1^*), and a_1—a_1^* (σ—σ_2^*) transitions in the order of increasing energy. The σ^* levels (b_1^* and a_1^*) at which these transitions occur have little d-character. For this compound, Williams *et al.*[4] have also given assignments which are different from the situation with C_2H_4S; *i.e.*, they assigned the first two absorption bands as one electronic transition. Their result for the first transition is equivalent to ours, but they seem to overestimate the role of the 3d orbitals; *i.e.*, their result for the lowest vacant orbital shows 30% of the 3d orbital contribution. The discrepancy is due to the difference in the parametrizations adopted for the MO calculations.

Conclusion

It has been shown that the saturated divalent sulfur compounds have similar electronic transitions in the lower-energy region. They are usually the n—σ_1^*, the n—σ_2^*, and the σ—σ_1^* transitions, although there are a few exceptions caused by the substituents on the sulfur atom or the molecular symmetries. The 3d orbitals of the sulfur atom may not play an important role in the lower-energy transitions.

The authors are indebted to the Data Processing Center of Kyoto University, where the numerical calculations have been performed.

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