Theoretical Studies on the Electronic Structure of the H_2S Anion Radical

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The electronic structure of the H_2S anion radical has been investigated by means of the non-empirical unrestricted Hartree-Fock method. The most stable conformation of this radical has been obtained at bond length R(S–H)= 1.550 Å and bond angle θ (<HSH)=160°. These values are relatively larger in comparison with observed values of the neutral molecule (R=1.335 Å and θ=92.2°). ESR hyperfine coupling constants and excitation energies have also been examined through analyses of the electronic structure of the most stable conformation of this radical. Furthermore, the dissociation process, $H_2S \rightarrow H_2+S^-$ or HS^-+H, has been discussed.

There have been a number of studies on the electronic structure of sulfur compounds from both theoretical and experimental aspects.[1] Most of the theoretical investigations on simple molecules such as H_2S have been done employing the *ab initio* SCF method and discussed the role of the vacant 3d-orbitals of sulfur.[2] Previous studies[2] seem to have led to the conclusion that the 3d-orbitals of sulfur with normal valences do not greatly contribute to the molecular properties in the ground state. This has, however, led to an improvement in the quality of the calculation. Recently, Schwenzer and Schaefer[3] also came to similar conclusions for the ground electronic state of the hypervalent molecules, SH_4 and SH_6, although they pointed out that the contribution of the 3d-orbitals is larger for SH_6 and SH_4 than SH_2. However, the contribution of the 3d-orbitals cannot be neglected in the ground state as well as the excited one as indicated from the theoretical studies of Hillier *et al.*[2b] and Bendazzoli *et al.*[2c]

Experimental studies on the H_2S anion radical have been few compared to H_2S or H_2S^+,[4] since it is difficult to produce the H_2S anion radical. For example, the radiation method[5] showed that H_2S reacts with an e^- at a higher rate ($k=1.35\times10^{10}$ M^{-1} s^{-1}) and produces predominantly H and HS^- with minor fractions H_2 and S^-. In 1966, Bennett *et al.*[6] reported the ESR spectrum of the H_2S anion radical in the reaction between an alkali-metal atom and H_2S or D_2S at 77 K. Theoretical studies on the H_2S anion radical followed: Cook *et al.*[7] performed the non-empirical calculation using the mixed basis method with d-orbitals and found poor agreement between the theoretical and experimental values of ESR hyperfine coupling constants of sulfur nuclei. Claxton *et al.*[8] carried out the *ab initio* UHF calculation on the same molecule with minimal Gaussian basis set and expressed considerable doubt on the interpretation of the ESR spectrum assigned to the H_2S anion radical by Bennett *et al.*[6] An inexplicable discrepancy between their calculation[8] and Cook's result[7] was reported.

In the present paper, the *ab initio* UHF calculation on the H_2S anion radical has been performed in the LCAO MO approximation with spin annihilation to obtain the pure doublet spin state. SCF atomic orbitals used for this calculation are the minimal basis set of Csizmadia *et al.*,[9] minimal STO-3G basis,[10] and larger basis of "double ζ" quality (4-31 G).[11] The primary purposes of this work are (1) to determine the stable conformation of the H_2S anion radical in both the $^2B_2$ and the $^2A_1$ states, taking the correlation of the Walsh diagram into consideration; (2) to calculate and examine the molecular properties of ESR hyperfine coupling constants and excitation energies; (3) to investigate the formation of solvated electrons in the system of H_2S and electrons as experimentally observed in H_2O, or the dissociation towards $H+HS^-$ or H_2+S^- of the H_2S anion radical.

Method of Calculation

The UHF calculations have been performed based on the minimal Gaussian-type orbitals (MGTO) by Csizmadia *et al.*,[9] STO-3G,[10] and 4-31 G[11] basis sets. The exponent values of the STO's, ζ, are the same as reported previously.[9,10] In the STO-3G expansion, the values of the exponents (α_m) and coefficients (d_m) of the GTO's were taken from Stewart[12] (χ_r=STO(ζ)= $\sum_{m=1} d_m$ GTO(α_m)). For the 4-31 G basis set the bases for the valence shells were split into inner and outer parts over the smaller minimal set, and the standard scale factors presented by Hehre *et al.*[11] were used. Consideration of the total energies, orbital energies, charge densities, and spin densities was made with the results obtained after the single annihilation.[13]

Excitation energies of the H_2S anion radical were calculated from the following equations[14] using values of ε, J, and K obtained from the calculation of H_2S equivalent with the geometry of the H_2S anion radical:

$$\Delta E_{p\rightarrow k} = \varepsilon_k - \varepsilon_p,$$

$$\Delta E_{i\rightarrow p} = \varepsilon_p - \varepsilon_i - 2J_{pi} + K_{pi} + J_{pp},$$

$$\Delta E_{i\rightarrow k}(1) = \varepsilon_k - \varepsilon_i - (J_{pi}-K_{pi}/2) - (J_{ki}-2K_{ki}) + (J_{pk}-K_{pk}/2),$$

$$\Delta E_{i\rightarrow k}(2) = \varepsilon_k - \varepsilon_i - (J_{pi}-K_{pi}/2) - J_{ki} + (J_{kp}+K_{kp}/2),$$

where, i, p, and k denote the doubly occupied, singly occupied, and virtual orbitals, respectively.

Results and Discussion

(I) The calculations of the H_2S anion radical were performed with MGTO,[9] STO-3G,[10] and 4-31 G[11] basis sets, varying the angle θ (<HSH) from 92.2

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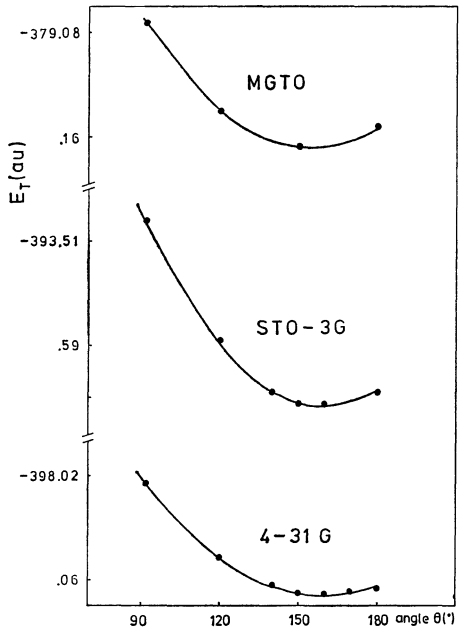

Fig. 1. Total energies of H_2S anion radical, with the angle variation, calculated by MGTO, STO-3G, and 4-31 G basis.

(experimentally determined for H_2S)[15] to 180°, fixing the bond distance at 1.335 Å.[15] The results obtained are shown in Fig. 1, and demonstrate the superiority of the STO-3G and 4-31 G basis sets in comparison with the MGTO basis. Consequently the results obtained from the STO-3G and 4-31G basis will be discussed later. It is worth noting that the H_2S anion radical is most stable at $\theta=160°$ in these basis sets. Here, it should be remembered that the calculations of this anion radical reported previously[7,8] were conducted using the same geometry as H_2S (92.2°).

The ground and lowest excited states of the H_2S anion radical are the $^2B_2$ and $^2A_1$ states, respectively. The $^2B_2$ and $^2A_1$ states are equivalent with the entrance of one electron into the $3b_2$ orbital (lowest unoccupied

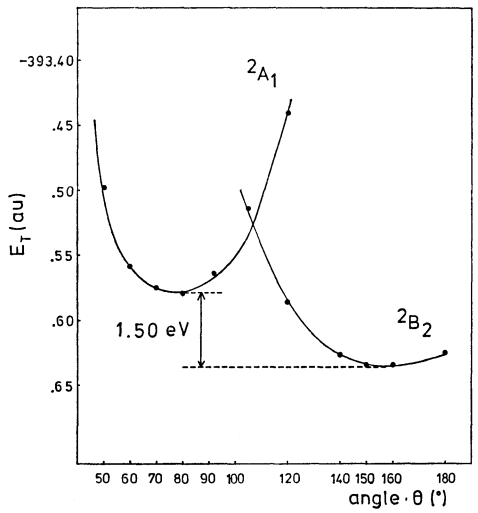

Fig. 2. Total energies of $^2B_2$ and $^2A_1$ states with the variation of angle θ.

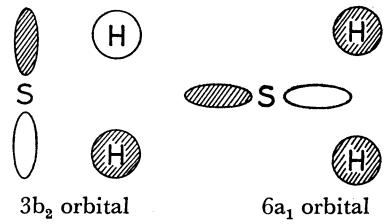

Fig. 3. Orbital shapes of $3b_2$ and $6a_1$ orbitals of H_2S molecule (angle θ(<HSH)=92.2°).

molecular orbital (LUMO)) and the $6a_1$ orbital (LUMO +1), respectively. Energy changes for both states as a function of the angle θ are shown in Fig. 2, which were obtained from the calculation of STO-3G basis. The $^2B_2$ state is energetically more stable compared to the $^2A_1$ state by 1.50 eV. Interestingly, the angle θ has become larger for the former and smaller for the latter than that of the H_2S molecule (92.2°). Examination of the extension of $3b_2$ and $6a_1$ orbitals and the relationship of the chemical bonds of H_2S (see Fig. 3) showed that the $3b_2$ and $6a_1$ orbitals are antisymmetric and symmetric on the plane bisecting the angle θ (<HSH), respectively. Accordingly excess electrons of H_2S^- entering into the $3b_2$ and $6a_1$ orbitals may decrease the electronic repulsion between the hydrogen atoms and form a bond between them, respectively. Such considerations are consistent with the calculated results of the most stable conformation of $^2B_2$ and $^2A_1$ states of the H_2S anion radical.

It is interesting and important to consider the correlation between the total energies and orbital energies from the Walsh diagram[16] of both states. Figure 4 shows the one-electron orbital energy changes of H_2S as a function of the angle θ. This figure demonstrates that the electron occupancy into the $3b_2$ orbital makes the angle θ larger, while in the case of the $6a_1$ orbital the reverse is indicated, *i.e.*, the angle θ becomes smaller. The present qualitative consideration is in good agree-

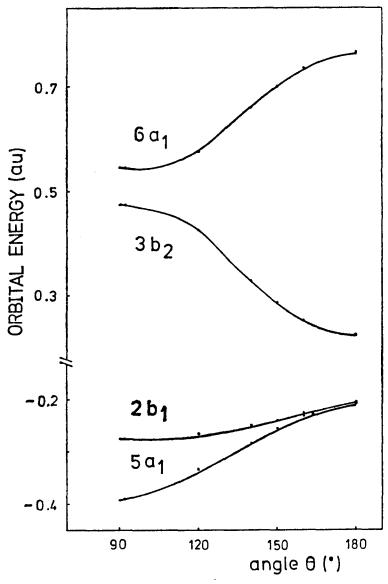

Fig. 4. Orbital energy diagram of H_2S from 90 to 180° calculated by STO-3G basis set.

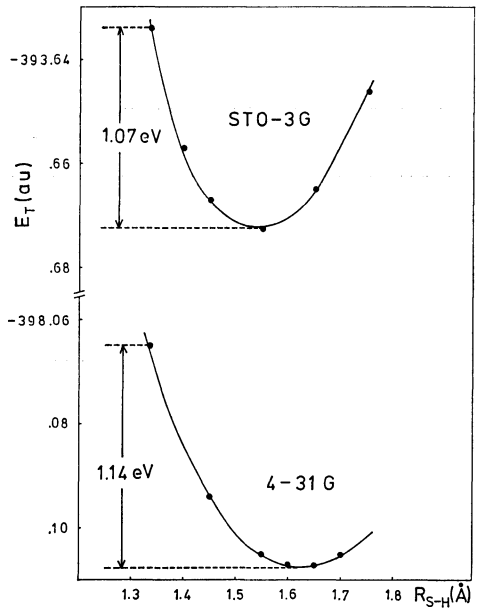

Fig. 5. Total energies of H_2S anion radical (angle θ(<HSH)=160°) with the variation of R(S–H).

ment with the changes of total energies (Fig. 2) and also appears to be interpretable for the H_2S cation radical which has been treated in a previous paper,[4] that is, the $^2B_1$ and $^2A_1$ states of the H_2S cation radical are most stable for θ=92.9 and 127° in accord with the observed values obtained from the emission spectra,[17] respectively.

Subsequently the changes in the total energy of the H_2S anion radical for the variation of R(S–H) were examined, since the excess electron on H_2S may lead to molecular deformation caused by decreasing the electronic repulsion between hydrogen and hydrogen or sulfur atoms. As expected, Fig. 5 clearly shows the minimum energy of the anion radical at R(S–H)=1.650 Å from the calculation of 4-31 G basis and 1.550 Å from STO-3G basis, respectively. Namely, the total energy decreases *ca.* 1.14 and 1.07 eV by the lengthening of the S–H bond, 0.315 and 0.215 Å, in comparison with R(S–H)=1.335 Å of H_2S, respectively.

Table 1. Calculated hyperfine coupling constants (G) of H_2S anion radical (angle (<HSH)=160°) by STO-3G and 4-31 G basis

	STO-3G	4-31 G	Exptl[a]
a_H	187.27	327.60	±7.7±0.3
a_S	159.35	−207.24	±60.0±2.0

a) Ref. 6.

(II) The molecular properties of ESR hyperfine coupling constants (a_H and a_S) of the H_2S anion radical are given in Table 1 which represents the calculated hyperfine coupling constants by both basis sets, where the following results for both a_H and a_S are indicated, *i.e.*, the calculated values are far larger than observed ones. This discrepancy between theory and experiment may be the same as that pointed out in the previous studies.[7,8] The authors obtained good agreement with the experimental values (a_H) for the H_2S cation radical[4] by the use of the same basis set as the present one. Furthermore, Claxton *et al.*[8] were also successful in the calculation of hyperfine coupling constants on many kinds of radicals except for the H_2S anion radical. Taking these results into consideration, the authors have joined Symons[18] and Claxton *et al.* in entertaining considerable doubt on the interpretation of the ESR spectrum assigned to the H_2S anion radical. This discussion will be made in a later section.

Table 2. Calculated excitation enegies (eV) of H_2S anion radical (angle θ (<HSH)=160°) by STO-3G and 4-31 G basis sets

	STO-3G	4-31 G	Exptl[a]
$\Delta E(9\rightarrow10)$[b]	6.28	1.79	1.22—1.77
$\Delta E(8\rightarrow10)$	7.81	2.81	3.10
$\Delta E(10\rightarrow11)$	11.24	9.14	
$\Delta E(9\rightarrow11)^{(1)}$	14.69	8.05	
$\Delta E(9\rightarrow11)^{(2)}$	17.68	10.52	

a) Ref. 6. b) 9, 10, and 11 denote the highest occupied, singly occupied, and lowest unoccupied molecular orbitals of H_2S anion radical, respectively.

An attempt was made to calculate the excitation energies of the H_2S anion radical, with reference to the experiments of Bennett *et al.*,[6] the details of which are given in the preceding section. The results calculated by using both basis sets are tabulated in Table 2. The absorption band found experimentally[6] at 1.22—1.77 eV may be assigned to the $2b_1\rightarrow3b_2$ transition, *i.e.*, from the lone pair electrons of sulfur to the anti-bonding orbital of the S–H bond. Such a large red shift of this band compared to H_2S is due to the fact that the σ^*_{S-H} orbital lowers, to a large extent, by the presence of an excess electron. The next band at 3.10 eV may be assigned to the $5a_1\rightarrow3b_2$ transition, that is, from the σ_{S-H} orbital to the σ^*_{S-H} one. Similarly, the red shift of this band compared to that of H_2S may be ascribed to the lowering of the σ^*_{S-H} orbital as mentioned above. Since the intensity of these absorption bands has not been experimentally determined as yet, there is no alternative except to discuss in terms of the excitation energy. In the present calculation, the $2b_1\rightarrow3b_2$ transition is theoretically forbidden (f=0.0). On the contrary, the intensity of the $5a_1\rightarrow3b_2$ band is considerably large (f=0.117, calculated) because of the symmetry allowance between both states. The excitation energies calculated by the 4-31 G basis were in good accordance with the experimental ones,[6] but those of STO-3G basis are somewhat larger, which is mainly due to the higher-energy location of virtual orbitals obtained from this basis.

(III) In the preceding section, the electronic structures and molecular properties of the H_2S anion radical were discussed. It is interesting to consider this anion radical as a reaction product of H_2S+e^- and the starting molecule for dissociation into $H+HS^-$. At the outset, it is supposed that the electron outside H_2S is describable by placing the diffuse s-type orbital outside

TABLE 3. CALCULATED HYPERFINE COUPLING CONSTANTS (G) AND CHARGE DENSITIES OF H_2S ANION RADICAL (angle θ ($<$HSH) = 160 AND 92.2°) WITH OUTER 2s-TYPE ORBITAL ($\xi_{2s}=0.1$)[a]

Distance (Å)[b]	H_2S^- (160°)				H_2S^- (92.2°)			
	E_T(au)	a_H	a_S	ρ (outer orbital)	E_T(au)	a_H	a_S	ρ (outer orbital)
0.5	−393.6641	189.18	165.37	0.273				
1.0	−393.7134	229.07	82.44	0.349				
1.5	−393.7349	192.34	50.00	0.780	−393.8049	−18.86	16.54	0.942
2.5	−393.7653	52.32	8.83	0.931	−393.8744	−6.95	1.94	0.982
3.5	−393.7790	5.37	0.42	1.001	−393.8957	−0.48	0.35	0.992
5.0	−393.7747	1.51	−0.01	1.000	−393.8935	0.58	−0.07	0.999

a) Calculations were carried out using STO-3G basis set. b) Between sulfur atom of H_2S and diffuse 2s-type orbital on the line bisecting the angle θ($<$HSH).

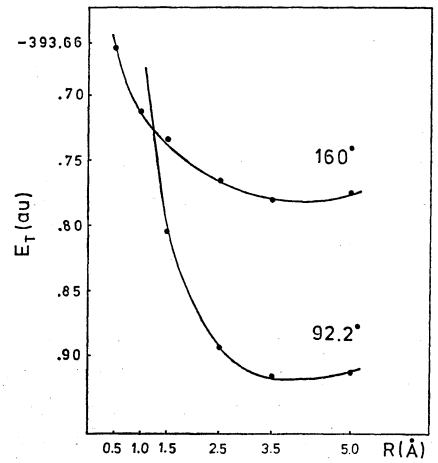

Fig. 6. Total energies of H_2S anion radical (angle θ($<$HSH) = 92.2 and 160°) in the condition of locating the diffuse 2s-type orbital.

t, that is, on the bisector of the angle θ and the opposite side of the pσ orbital of sulfur on the H_2S plane. The calculated results for two kinds of angle ($<$HSH), 92.2 and 160°, are shown in Fig. 6 and Table 3, which were obtained from the calculation consisting of both STO-3G basis and diffuse 2s type orbital. From these, it can be rationalized that the H_2S+e^- system is impelled to destabilize as the e^- approaches H_2S. At the same time, one can easily recognize that in the distant region (>1.5 Å) between H_2S and e^- this system retains the original form of H_2S (92.2°) and separated electron, but that the approach of the e^- to H_2S in the region less than 1.5 Å tends to make the angle θ open (see the point of intersection of Fig. 6). As a consequence, the H_2S+e^- system is inclined to form the H_2S anion radical in the region less than 1.5 Å. Such a tendency may also be explained from the change of charge densities on the outer orbital (Table 3), *i.e.*, the excess electron of the H_2S anion radical may be regarded as flowing into the diffuse orbital placed outside the region over 1.5 Å, and delocalizing by the orbital hybridization in the region less than 1.5 Å, respectively.

Here, it should be remembered that the minimum energy was found at *ca.* 4 Å in both cases of 92.2 and 160°, implying that the H_2S anion radical is highly reactive and that H_2S forms a kind of solvated electron in this region as observed in the case of H_2O.[5] Hyperfine coupling constants and charge densities calculated by the addition of outer orbitals are given in Table 3, from which the remarkable decrement of a_H and a_S values with the separation of e^- are seen. The hyperfine coupling constants of H_2S anion radical are far larger than the experimental ones[6] and hence the possibility of the formation of a solvated electron or trapped electron for the H_2S+e^- system cannot be neglected.

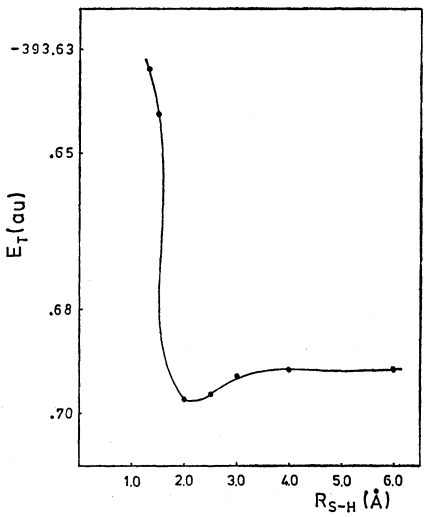

Fig. 7. Total energies accompanied with the dissociation reaction of $H_2S^- \rightarrow HS^- + H$.

Finally the dissociation process of the H_2S anion radical to HS^-+H will be discussed. Figure 7 suggests that the H_2S anion radical tends to separate such as HS^-+H through weak bonding at R(S–H) = 2.2 Å.[20] Taking these results into account, the process may be as follows; the separated system of H_2S+e^-, which is originally stable, begins to interact to form a quasi-stable anion radical which dissociates into $H+HS^-$, probably because of an excess electron entered into the antibonding orbital of the S–H bond of the b_2 symmetry. The process leading to the formation of H_2+S^- may be explained in terms of the dissociation through the $^2A_1$ state due to an excess electron in the $6a_1$ orbital, since the bonding nature between the hydrogen atoms is indicated from the analysis of the charge density contour maps.

Conclusion

The present calculation on the H_2S anion radical indicates that the most stable conformation is the $^2B_2$ state with $\theta=160°$ and that the bond length of R(S–H) increases a little compared with that of H_2S. These results on the bond angle and bond length seem to be reasonable from the Walsh diagram and chemical reasoning. The H_2S anion radical itself, however, is very unstable and tends to dissociate as discussed. Consequently, more accurate experiments will make more detailed discussion on the H_2S anion radical possible, as Bennett *et al.*[6] obtained the ESR spectrum assigned to this anion radical. Moreover, the possibility of the formation of a solvated electron for the H_2S+e^- system should be examined from both theoretical and experimental aspects.

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References

1) A. Senning, "Sulfur in Organic and Inorganic Chemistry," Marcel Dekker, Inc. (1972), Vols. 1—3.

2) (a) F. P. Boer and W. N. Lipscomb, *J. Chem. Phys.*, **50**, 989 (1969); (b) I. H. Hillier and V. R. Saunders, *Chem. Phys. Lett.*, **5**, 384 (1970); (c) S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Am. Chem. Soc.*, **92**, 3243 (1970); (d) J. R. Sabin, *ibid.*, **93**, 3613 (1971); (e) G. L. Bendazzoli, G. Gottarelli, and P. Palmieri, *ibid.*, **96**, 11 (1974).

3) G. M. Schwenzer and H. F. Schaefer, *J. Am. Chem. Soc.*, **97**, 1393 (1975). See also, for comparison, V. B. Koutecky and J. I. Musher, *Theor. Chim. Acta (Berl.)*, **33**, 227 (1974).

4) H. Sakai, S. Yamabe, T. Yamabe, K. Fukui, and H. Kato, *Chem. Phys. Lett.*, **25**, 541 (1974) and references cited therein.

5) E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York (1970), p. 113.

6) J. E. Bennett, B. Mili, and A. Thomas, *Chem. Commun.*, **1966**, 182.

7) D. B. Cook, A. Hinchliffe, and P. Palmieri, *Chem. Phys. Lett.*, **3**, 223 (1969).

8) T. A. Claxton, D. McWilliams, and N. A. Smith, *Chem. Phys. Lett.*, **4**, 505 (1970).

9) I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theor. Chim. Acta (Berl.)*, **6**, 191 (1966); A. Rauk and I. G. Csizmadia, *Can. J. Chem.*, **46**, 1205 (1966).

10) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

11) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); W. J. Hehre and W. A. Lathan, *ibid.*, **56**, 5255 (1972).

12) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

13) T. Amos and L. C. Snyder, *J. Chem. Phys.*, **41**, 1773 (1964).

14) A. Ishitani and S. Nagakura, *Theor. Chim. Acta (Berl.)*, **4**, 236 (1956).

15) H. C. Allen, Jr., and E. K. Plyer, *J. Chem. Phys.*, **25**, 1132 (1956).

16) A. D. Walsh, *J. Chem. Soc.*, **1953**, 2260.

17) G. Duxbury, M. Horani, and J. Rostas, *Proc. R. Soc. London, Ser. A*, **331**, 109 (1972).

18) M. C. R. Symons, *Adv. Chem. Ser.*, **82**, 1 (1968).

19) D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **44**, 1865 (1966).

20) R(S–H) indicates the distance between sulfur of HS^- and hydrogen atoms separated accompanied with the progress of reaction.