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Excited Orbitals of Sulphur in Aliphatic and Unsaturated Sulphides

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The energies of some electron configurations of sulphur in organic sulphides involving *3d* and *4s* orbitals have been derived by simulating the radial and angular perturbation of the molecular environment on sulphur valence orbitals, with electrostatic potentials. In order to discuss the relevance of the electron configurations in the molecular valence state and the role of the excited orbitals *4s* and *3d* to bonding, the energies were minimized in respect of size and orientation of sulphur valence orbitals. Interatomic exchange terms were included and the importance of interatomic exchange terms involving the electrons on carbons is discussed. The results are indicative for a negligible participation of *3d* and *4s* orbitals of sulphur to the ground state of aliphatic and unsaturated sulphides.

Die Energien einiger Elektronenkonfigurationen mit *3d*- und *4s*-Bahnfunktionen des Schwefels in organischen Sulphiden wurden berechnet, wobei die radiale und winkelabhängige Störung der Valenzorbitale durch die molekulare Umgebung mit Hilfe von elektrostatischen Potentialen berücksichtigt wurde. Um die Bedeutung der betrachteten Elektronenkonfigurationen in dem molekularen Valenzzustand und die Rolle der angeregten Orbitale *4s* and *3d* für die Bindung zu diskutieren, wurden die Energien bezüglich der Größe und Orientierung der Schwefel-Valenz-Orbitale minimisiert. Zwischenatomare Austausch-Terme wurden mit einbezogen, und die Wichtigkeit der zwischenatomaren Austausch-Terme, die die Elektronen am Kohlenstoff betreffen, wird diskutiert. Die Resultate zeigen, daß die *3d* und *4s* Orbitale für den Grundzustand des Schwefels in aliphatischen und ungesättigten Sulfiden vernachlässigt werden können.

Les énergies de certaines configurations électroniques du soufre dans les sulfures organiques mettant en jeu les orbitales *3d* et *4s* ont été obtenues en simulant à l'aide de potentiels électrostatiques la perturbation radiale et angulaire subie par les orbitales de valance du soufre sous l'influence de l'environnement moléculaire. Afin de discuter du rôle des configurations considérées dans l'état de valence moléculaire ainsi que du rôle des orbitales excitées *4s* et *3d* dans la liaison, les énergies ont été minimisées par rapport à l'extension et à l'orientation des orbitales de valence du soufre. Les termes d'échange interatomiques ont été introduits et l'importance de ceux impliquant les électrons des atomes de carbone est discutée. Les résultats indiquent une participation négligeable des orbitales *3d* et *4s* du soufre à l'état fondamental des sulfures aliphatiques et non saturés.

The difficulties involved in a quantitative theoretical description of molecules containing second row atoms are well known. One has in fact to deal with a large number of electrons. Also, there are experimental indications that a satisfactory description of the charge distribution around the second row element in some molecular species requires participation of excited atomic orbitals *3d* and *4s* [1, 2]. In the free atom these orbitals extend in regions of space far from the nucleus [3–7], and, in principle, one should expect that the fraction of charge described by excited orbitals is particularly sensitive to the molecular environment [8]. From a theoretical point of view this means the molecular wave function ought to be chosen as flexible as possible. In particular the variation of a large number of parameters should be allowed and the inclusion of many electron configurations is likely to be essential. These are the main reasons why in dealing with complex systems such as sulphides we shall limit ourselves to a qualitative description in terms of local charge distribution around the heavy element. No attempt will be made to derive molecular wave function. Only the energies of some electron configurations of sulphur in the field of the ligands will be derived.

This will lead to identify the configurations which ought to be relevant to a quantitative approach. Referring specially to the case of sulphur compounds with first row elements, when the valence state of the latter may be assumed to be known, this kind of approach can be summarized as follows: i) the perfect pair approximation is used as a guide to formulate the most likely electron configurations of sulphur; ii) molecular valence state energies arising from these electron configurations are derived; iii) results from ii) together with semiempirical relationships (i.e. bond energies, overlap integrals; differences in electronegativities, bond polarities) are used to attempt a qualitative description of the valence state of sulphur and of the molecular charge distribution. The mathematical formulation of i) and ii) has been previously detailed [8, 9]: here only the definition of "molecular valence state" will be outlined. The molecular wave function can be written as an antisymmetrized product of group functions [10], each group referring to different atoms:

$$\Psi = \mathscr{A}[\psi_S(x_1, \ldots, x_{N_S})\, \psi_R(x_{N_S+1}, \ldots, x_{N_S+N_R}) \ldots] \tag{1}$$

In the case under investigation, S is the sulphur atom, R is a carbon atom, ψ_S, ψ_R ... are multiconfigurational wave functions describing charge distributions around atoms, S, R ...

Our first assumption concerns the possibility of analizing separately the energies of the configurations involved in the molecular wave function (1). The mixing of configurations is thus considered a perturbation to the present zero-order treatment. Since we are mainly concerned with the possible ways of formulating a local function for sulphur, we can set up an effective hamiltonian for this group of electrons and perform a variational treatment in respect of all parameters of interest. The orbitals on different atoms being not orthogonal, the total energy of sulphur in a particular configuration[1] and molecular state can be written as in Eq. (2):

$$E_S = H_S + \sum_R J_{RS} + \text{exchange terms}. \tag{2}$$

H_S is the one center energy of sulphur, J_{RS} a coulomb interaction between groups R and S, while the third term collects all remaining terms of energy which arise from non orthogonality.

Thus energies of the electron configurations may be compared and the relative importance in wave function (1) discussed. The main features of the charge distributions associated with single configurations may also be derived. The energies pertaining to different ionic degrees in S and R can be approximately compared without difficulty if ionization potentials and electron affinities for the atoms are assumed to be known.

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[1] A random spin distribution is assumed for all valence orbitals.

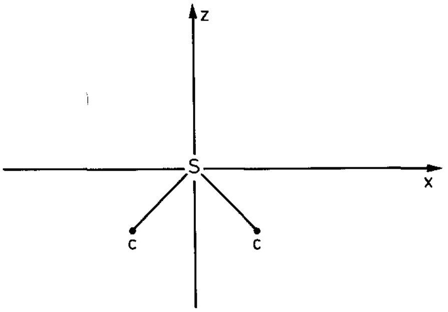

Fig. 1. Reference system for sulphides

In the present investigation computations were performed in two steps of increasing accuracy. At first an electrostatic treatment previously described [8, 9] was applied. Exponential factors of the orbitals in the valence shell of sulphur and a parameter α determining the orientation of 3*d* orbitals in respect of the nuclear framework were treated as variational parameters.

Exchange terms are expected to influence significantly the energy sequence of valence states, as well as size and orientation of excited orbitals. Thus in the second step the relevance of these terms is discussed. The reference system adopted is shown in Fig. 1. The sulphur-carbon bonding distance is taken to be 3.44 a.u. and the CSC angle 105° [11].

Saturated Sulphides

In these compounds sulphur is usually described as divalent and the discussion is limited to divalent valence states. Ionic electron configurations were not considered. With reference to Table 1 the main conclusions of the present treatment can be summarized as follows. The values of exponential parameters show that the size of 3*s* and 3*p* orbitals is practically insensitive to the molecular environment. The inclusion of intravalence exchange terms seems to affect only the 3*s* orbital and leads to a moderate contraction, as evidenced previously [7]. Excited orbitals 3*d* and 4*s* are slightly affected by the inclusion of intravalence exchange terms and, as expected, are very sensitive to the surrounding field. In particular the mean radii indicate a remarkable change from the atomic situation (see Table 2). The polarization of $3d_\sigma$ orbitals is larger than that of 4*s*-orbitals, as previously observed [12]. Qualitatively and quantitatively the stability sequence of molecular valence states does not differ much from that observed in the atom. Molecular valence state $2[s^2p^4]$ is by far the most important. Molecular valence states $2[sp^5]$, $2[s^2p^3d_{xz}]$, $2[s^2p^3d_{a1}]$ and $2[s^2p^34s]$ lie considerably higher. Thus in the molecular wave function for the ground state of saturated sulphides the participation of these last four molecular valence states is expected to be nearly negligible.

It has been suggested [13] that exchange interactions involving excited orbitals of sulphur and orbitals in the *K*-shell of ligands are of special importance. More recently, exchange interactions involving excited orbitals of sulphur and of the ligand have been studied in detail [14, 15]. For the sulphur-fluorine diatomic

Table 1. *Energy differences ΔE (eV) from $2[s^2p^4]$ for some molecular valence states (the valency is followed by the state in parenthesis), optimum exponential parameters and mean radii (Å) obtained with an electrostatic approach: a inclusive of intra-valence exchange, b inclusive of intra-atomic exchange terms. The valence state of carbon 1 is $4[sp^3]$; the principal quantum numbers for orbitals in the M-valence shell are omitted*

Sulphur	Carbon 2	ΔE		K_s		K_p		K_φ (r_φ^m)	
valence state	valence state	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$2[s^2p^4]$	$4[sp^3]$	(−274.27)	(−285.37)	2.11	2.45	1.68	1.76		
$2[sp^5]$	$4[sp^3]$	11.64	13.64	2.21	2.68	1.68	1.76		
$2[s^2p^2p_zd_{xz}]$	$4[sp^3]$	8.35	8.20	2.15	2.43	1.80	1.88	0.98 (1.88)	0.97 (1.92)
$2[s^2p_xp_y^2d_{a_1}]^a$	$4[sp^3]$	8.97	7.11	2.16	2.43	1.76	1.91	0.97 (1.91)	0.92 (2.01)
$2[s^2p_xp_y^24s]$	$4[sp^3]$	9.15	8.20	2.21	2.51	1.78	1.86	0.99 (2.47)	1.03 (2.38)
$3[s^2p^3]^+$	$3[sp^4]^-$	4.00	3.70	2.18	2.46	1.78	1.87		
$3[s^2p_xp_zd_{xy}]^+$	$3[sp^4]^-$	15.41	15.70	2.21	2.45	1.85	1.95	1.03 (1.80)	0.95 (1.95)
$3[s^2p_xp_y4s]^+$	$3[sp^4]^-$	15.63	14.97	2.25	2.50	1.89	1.96	1.06 (2.33)	1.10 (2.25)
$4[s^2p^3d_{xy}]$	$4[sp^3]$	18.96	18.97	2.18	2.46	1.78	1.87	0.64 (2.80)	0.56 (3.30)

[a] $3d_{a_1} = \sin\alpha\, 3d_{z^2} + \cos\alpha\, 3d_{x^2-y^2}$; *a* $\alpha = -17.8$, *b* $\alpha = -17.7$.

Table 2. *Energy differences ΔE (eV) from $2[s^2p^4]$, optimum exponential parameters and mean radii r^m (Å) for some atomic valence states of sulphur: a with intra-valence exchange terms and b with intra-atomic exchange terms*

Sulphur	ΔE		K_s		K_p		K_φ (r_φ^m)	
valence states	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
$2[s^2p^4]$	(−260.50)	(−272.75)	2.19	2.50	1.74	1.82		
$2[s^2p_y^2p_zd_{xz}]$	9.33	9.24	2.24	2.48	1.86	1.93	0.35 (5.22)	0.34 (5.48)
$2[s^2p_y^2p_x4s]$	7.62	7.33	2.25	2.50	1.86	1.92	0.73 (3.30)	0.77 (3.12)

system exchange interactions involving fluorine $2s$ and sulphur $3d_\sigma$ electrons have been found to be even more significant than those involving fluorine $1s$ electrons. Moreover a preliminary calculation performed with the same model showed that the size of the exchange terms involving $3d_\sigma$ and $4s$ orbitals of sulphur and valence orbitals of ligands is sensitive to $s-p$ hybridization of fluorine. By extrapolating these results to tetrahedral hybrids one expects that the stabilizing exchange interactions between bonded orbitals are balanced to a large extent by repulsive exchange terms between non bonded orbitals. Accordingly, exchange interactions between $3d_\sigma$ and $4s$ orbitals of sulphur and tetrahedral hybrids of carbons were neglected. Thus, in organic sulphides terms expressing exchange interactions of $3d_\sigma$ and $4s$ orbitals with the doubly occupied $1s$ orbital of carbon are expected to be the most significative.

In a previous work [12] it was shown that this term of energy is reasonably well represented by Eq. (3):

$$T_{1s,\varphi} = (5/8) S_{1s\varphi}^2 E_{1s} \tag{3}$$

where $S_{1s\varphi}$ is the overlap integral between a φ orbital of sulphur ($\varphi = 3d_\sigma, 4s$) and the $1s$ orbital of carbon while E_{1s} is the $1s$ orbital energy of the ligand atom in the field of all remaining electrons and the nucleus of the ligand ($E_{1s} = 11.326$ a.u. [16]). The overall contribution due to the inclusion of exchange terms can

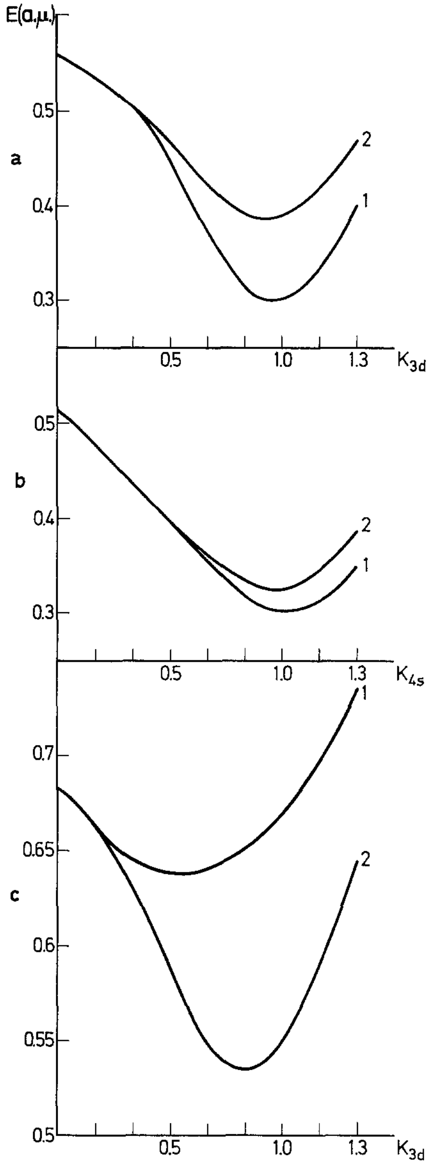

Fig. 2. a) Energy differences of molecular valence state $2[s^2p_y^2p_zd_{xz}]$ from $2[s^2p^4]$ versus K_d: (1) inclusive of intra-atomic exchange (2) inclusive of inter-atomic exchange with the $1s^2$ pair of carbon. b) Energy differences of molecular valence state $2[s^2p_y^2p_x4s]$ from $2[s^2p^4]$ versus K_{4s}: (1) inclusive of intra-atomic exchange, (2) inclusive of inter-atomic exchange with the $1s^2$ pair of carbon. c) Energy differences of molecular valence state $4[sp^3d_{xy}]$ from $2[s^2p^4]$ versus K_d: (1) inclusive of intra-atomic exchange, (2) inclusive of inter-atomic exchange. – For each $K_\varphi(\varphi = 3d, 4s)$ the energy is minimized in respect of K_s and K_p

be estimated if one supposes that those due to the two carbon atoms are approximately additive. The effect due to the inclusion of these terms is shown in Fig. 2a, 2b, where the energy differences from $2[s^2p^4]$ of molecular valence states $2[s^2p^3d_{xz}]$

Table 3. *Energy differences (eV) from* $2[s^2p^4]$ *and optimum exponential parameters for some sulphur states in sulphides obtained with an electrostatic treatment inclusive of intratomic exchange terms and of two-center exchange terms involving the* 1*s orbital of carbons*

Sulphur states	ΔE	K_φ (r_φ^m)
$2[s^2p_y^2p_xp_z]$	(−285.37)	—
$2[s^2p_y^2p_zd_{xz}]$	10.57	0.93 (1.99)
$2[s^2p_y^2p_xd_{a1}]$[a]	8.43	0.83 (2.23)
$2[s^2p_y^2p_x4s]$	8.88	0.97 (2.48)

[a] $\alpha = -24.1°$.

Table 4. *Ionization potential and some Rydberg transitions (eV) in aliphatic sulphides*

Transition	ΔE		
	computed		exp.
	a	*b*	
$2[s^2p^4] \rightarrow 3[s^2p^3]^+$	10.27	9.90	8.7[a]
$2[s^2p^4] \rightarrow 2[s^2p^3d_{xz}]$	9.27	8.92	
$2[s^2p^4] \rightarrow 2[s^2p^34s]$	6.77	5.95	

[a] From Ref. [16].

and $2[s^2p^34s]$ are plotted as a function of K_φ. The conclusions obtained with the electrostatic treatment are practically unmodified by the inclusion of these destabilizing terms. Energy minima and optimum variational parameters for the molecular valence states of interest thus obtained are collected in Table 3. By adding these interatomic exchange terms, the energy of molecular valence states is increased of about 2 eV for states involving $3d_\sigma$ and 0.7 eV for states involving 4*s* orbitals. It is interesting to notice that parameter α, related to the orientation of sulphur $3d_{a1}$ orbital, undergoes a greater change. Table 4 collects computed values for the ionization potential and for some Rydberg transitions. One notices that the computed ionization potential compares favourably with the experimental value for $(CH_3)_2S$ [17]. This gives a feeling that the conclusions obtained with the present treatment are not grossly in error. In particular one expects that the first Rydberg transition in the near ultraviolet of aliphatic sulphides corresponds to a $3p \rightarrow 4s$ promotion and it is likely to occur in the neighbourhood of 2000 Å.

Unsaturated Sulphides

In addition to divalent states, several alternative descriptions may be in principle postulated for sulphur in unsaturated systems. Excited atomic orbitals are likely to play a more important role and charge migrations between different atoms are expected to occur to a considerable extent so that also ionic configurations must be investigated. The results concerning excited molecular valence states $3[s^2p^3]^+$, $3[s^2p^24s]^+$, $3[s^2p^2d_{xy}]^+$, and $4[s^2p^3d_{xy}]^+$ are collected in Table 1. In ionic valence states $3d_\pi$ and 4*s* orbitals are fairly compact. The $3d_\pi$ orbital is more diffuse in the covalent state $4[s^2p^3d_{xy}]$. Energy differences from the mole-

Table 5. *Energy differences ΔE (eV) from $2[s^2p^4]$ and optimum exponential parameters for some sulphur states in unsaturated sulphides: intra-atomic and inter-atomic exchange terms are included*

	ΔE	K	(r_φ^m)
$2[s^2p^4]$	(−285.37)	—	
$3[s^2p_x^2p_y4s]^+$	15.76	1.04	(2.36)
$3[s^2p_xp_zd_{xy}]^+$	12.33	0.95	(1.95)
$4[s^2p^3d_{xy}]$	16.41[a]	0.84	(2.21)

[a] See the Appendix.

cular valence state $2[s^2p^4]$ are still high, so that the contribution of electron configurations involving $3d_\pi$ and $4s$ orbitals to the ground state molecular wave function of insaturated sulphides is unlikely to be very significant. The ionic configuration of sulphur $3[s^2p^3]^+$ is expected to participate more significantly. Interatomic exchange terms involving sulphur $3d_\pi$ and carbon orbitals $2p_\pi$-orbitals can be represented approximately by Eq. (4):

$$T_{2\pi,\,3d_\pi} = -(5/3)S^2_{2\pi,\,3d_\pi}E_{2p} \tag{4}$$

where $S_{2\pi,\,3d_\pi}$ represents the overlap integral between a sulphur $3d_\pi$ and a carbon $2p_\pi$ orbital while E_{2p} is the energy of a $2p$ carbon orbital in the field of all the other electrons and nucleus of carbon ($E_{2p} = 0.433$ a.u. [16]).

A simple additive scheme for the contributions to interatomic exchange energies by the two carbon atoms was followed and the effects due to the inclusion of exchange terms (4) are shown in Fig. 2c, for the molecular valence state $4[s^2p^3d_{xy}]$. Curve 1 refers to the energy of $4[s^2p^3d_{xy}]$ computed with intratomic exchange terms, curve 2 to that inclusive of interatomic exchange effects. One observes a substantial stabilizing effect and a considerable contraction of the $3d_\pi$ orbital. Energy minima and optimum exponential parameters for ionic and tetravalent molecular valence states, when the interatomic exchange terms (4) are added, are collected in Table 5. Although the $4s$ and $3d_\pi$ radial functions in all the molecular valence states investigated are strongly perturbed by the ligand field, the energy differences of the excited valence states from $[2s^2p^4]$ are still very high.

The most interesting results of the present investigation can be summarized as follows: i) as expected, in saturated sulphides the most relevant molecular valence states is $2[s^2p^4]$. For unsaturated sulphides valence states $2[s^2p^4]$ and $3[s^2p^3]^+$ are expected to give the largest contributions to the ground state wave function and participation of $3d$ and $4s$ orbitals to this function appears to be negligible; ii) exchange terms of energy involving $3d$ and $4s$ orbitals of sulphur and orbitals on carbon atoms although significative, are not critical energy terms.

Appendix

Values of monocentric integrals involving $3d$-orbitals of sulphur were taken from Ref. [8]. The remaining one and two-center integrals were computed by numerical integration [18]. Exponential factors of $1s$, $2s$ and $2p$ sulphur orbitals were taken from Ref. [8]. Those of $1s$, $2s$ and $2p$ carbon orbitals from Ref. [19].

Energies of ionic and tetracovalent molecular valence states involve ionization potentials and electron affinities of unsaturated groups bonded to sulphur. The values employed here refer to benzene [20, 21].

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References

1. See, e.g. Mangini, A.: The valence state of sulphur in Organic Compounds in: Kharash, N.: Organic sulphur compounds, Symposium Publications Division, vol. IV, 19. Oxford: Pergamon Press.
2. Craig, D. P., Maccol, A., Nyholm, R. S., Orgel, L. E., Sutton, L. E.: J. chem. Soc. (London) **1954**, 332.
3. Cruickshank, D. W., Webster, B. C., Mayers, D. F.: J. chem. Physics **40**, 3733 (1964).
4. Bendazzoli, G. L., Zauli, C.: J. chem. Soc. (London) **1965**, 6827.
5. Craig, D. P., Thirunamachandran, T.: J. chem. Physics **43**, 4183 (1965).
6. Palmieri, P., Zauli, C.: J. chem. Soc. (London) **1967**, 813.
7. Bernardi, F., Zauli, C.: J. chem. Soc. (London) A **1968**, 2633.
8. Craig, D. P., Zauli, C.: J. chem. Physics **37**, 601 (1962).
9. Bendazzoli, G. L., Bernardi, F., Palmieri, P., Zauli, C.: J. chem. Soc. (London) A **1968**, 2186.
10. Klessinger, M., McWeeny, R.: J. chem. Physics **42**, 3343 (1965).
11. Tables of interatomic distances and configurations in molecules and ions. Chem. Soc. Special Publication, 1968.
12. Bernardi, F., Zauli, C.: J. chem. Soc. (London) A **1969**, 867.
13. Cruickshank, D. W., Webster, B. C., Spinnler, M. A.: Int. J. quant. Chem. **1** S, 225 (1967).
14. Bendazzoli, G. L., Bernardi, F., Palmieri, P., Zauli, C.: in elaboration.
15. Mitchell, K.A.R.: J. chem. Soc. (London) A **1968**, 2676; Canad. J. Chem. **46**, 3499 (1968).
16. Clementi, E.: I.B.M. Journal of Research and Development **9**, 2 (1965).
17. Teegan, J. P., Walsh, A. D.: Proc. Roy. Soc. (London) **201** A, 600 (1950).
18. Magnusson, F. A., Zauli, C.: Proc. physic. Soc. **78**, 53 (1961).
19. Clementi, E., Raimondi, D. L.: J. chem. Physics **38**, 2686 (1963).
20. Kumii, T. L., Kuzoda, H.: Theoret. chim. Acta (Berl.) **11**, 97 (1968).
21. Watanabe, K.: J. chem. Physics **22**, 1564 (1954).

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