X-Ray Transitions in Compounds of Sulphur: Relativistic Corrections and K_β-, L-Spectra

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Relativistic corrections to K_α transition energies in compounds of sulphur, where the latter has a formal charge between -2 and $+6$ are derived. The results indicate that relativistic corrections do not depend on the number of electrons in the valence shell of the atom, thus confirming a correlating function previously derived between experimental shifts of K_α doublets and net charges on sulphur. In the monocentric approximation theoretical energies for K_β and L transitions in elemental sulphur and for K_β transitions in sulphides and sulphates are obtained. The results agree fairly well with experimental data and a tentative attribution of K_β lines is given.

Les corrections relativistes aux énergies des transitions K_α dans des composés du soufre, où ce dernier a une charge formelle entre -2 et $+6$, sont établies. Les résultats indiquent que les corrections relativistes ne dépendent pas du nombre d'électrons dans la couche de valence de l'atome, confirmant ainsi une fonction, précédemment obtenue, corrélant les déplacements expérimentaux des doublets K_α et les charges nettes sur le soufre. On obtient dans l'approximation monocentrique les énergies théoriques pour les transitions K_β et L de l'atome de soufre isolés, et les transitions K_β dans les sulfures et les sulfates. Les résultats sont en bon accord avec les données expérimentales et l'on tente une attribution des raies K_β.

Es wird gezeigt, daß die relativistischen Korrekturen für K_α-Übergangsenergien in Schwefelverbindungen nicht von der Zahl der Valenzelektronen abhängen. Eine früher angegebene Beziehung zwischen den gemessenen Verschiebungen der K_α-Dubletts und der Ladung des Schwefels wird so bestätigt. Unter Benutzung einer einzentrischen Näherung werden theoretische Werte für K_β und L Übergangsenergien für elementaren Schwefel, für K_β Übergangsenergien bei Sulfiden und Sulfaten in guter Übereinstimmung mit experimentellen Daten erhalten. Eine Zuordnung der K_β-Linien wird vorgeschlagen.

An investigation was recently published concerning a theoretical correlation between experimental shifts δE of K_α-doublets in compounds of sulphur and net charges q in the valence shell of sulphur [1]. By adopting a monocentric model, to say by considering explicitly only sulphur with a variable number of electrons in the M-shell, and a basis set of orthonormal orbitals, function (1) was obtained:

$$\delta E \cong q(q + 3)/8 . \tag{1}$$

Calculations were performed with one variational parameter, exponential factor K_M for the valence orbitals. From experimental shifts δE, one obtains, through Eq. (1), q-values which fit reasonably well with the chemical evidence available for various classes of sulphur derivatives. An energy of 2310.42 eV was derived for the transition in elemental sulphur, to be compared with the experimental value 2307.07 eV (baricenter of doublet). Later, the calculations were repeated by

Table 1. *Variation in K_α-transition energies in sulphides, sulphites and sulphates*

Class of derivatives	Mean value (eV) of upper component of K_α-doublet [3]	Range of variability (mean square deviation)
Inorganic sulphides	2317.32	0.01
Sulphites	2308.43	0.03
Sulphates	2308.67	0.02

using a greater number of variational parameters, one for each class of orthonormal orbitals with equal n [2]. As expected, it was found that the energies of upper and lower states involved in the transition increase in absolute value: an estimate of transition intensities was made and a value of 2309.60 eV obtained for the transition in elemental sulphur. Correlating function (1) remained however very much the same. One thus feels that any further improvement on type and flexibility of atomic orbitals will lead to better absolute transition energies, but will influence little function (1).

Although the preceeding results, on the whole, are rather encouraging, further points concerning a theoretical treatment of X-ray transitions in molecules need to be discussed and investigated, such as: 1. the adoption of an approximate hamiltonian operator which neglects relativistic terms; 2. the extension of the calculations to other types of X-ray transitions such as K_β and L, and 3. the limits of the monocentric approach and the neglect of ligands.

Apart from other implications, approximation 3. means that the transition is considered perpendicular in respect of q: to say, variations in the valence shell charge distribution when going from higher to lower state are neglected [2]. In order to clarify this point, extensive calculations in model compounds are called for. From the other hand, variations in experimental K_α-transition energies within a class of derivatives are rather small as Tab. 1 indicates: thus the ligand perturbation may perhaps be considered a second order effect.

In the present paper, points 1. and 2. are dealt with: as far as relativistic corrections are concerned, since high energy orbitals are involved in X-ray transitions, it is expected that the contribution of relativistic terms to the energy of the states involved will not be negligible. It is thus of relevance to investigate wether the relativistic correction will affect appreciably also correlating function (1). K_β and L transitions involving valence shell electrons, present many interesting features.

Relativistic corrections to transition energies

In order to evaluate relativistic corrections to transition energies, we have adopted the many-electron functions obtained previously by a limited variational scheme, starting from an orthonormal set of Slater orbitals [2]. The problem of their reliability for relativistic calculations shall be discussed later.

The relativistic energy for an N electron system can be obtained by employing an hamiltonian operator extrapolated [4, 5, 7] from BREIT's bielectronic hamiltonian. By adopting the usual notations [4] this relativistic hamiltonian H_r, inclusive of terms in α^2, is written $H_r = \sum_{i=1}^{5} H_i$ where spin-orbits interactions (H_3)

and part of spin-spins interactions (H_5) are the terms removing the J-degeneracy of levels belonging to an atomic multiplet. As the experimental separation of the K_α-doublet is constant (~ 1.2 eV) for all sulphur derivatives and since we are interested here only in the shift δE of the baricenter of the doublet, these operators are ignored. Orbit-orbits interactions are also neglected on the basis of the results obtained by FROMAN and PEKERIS [5, 6, 8, 9]. H_r then takes the simpler form (2):

$$H_r = H_1 + H_4 + H_5' \qquad (2)$$

where operators H_1, H_4, H_5' have the following expected values:

$$\langle H_1 \rangle = - (\alpha^2/8) \sum_{i=1}^{N} \int |\, p_i\, \varphi_i\,|^2\, d\tau \qquad (3)$$

$$\langle H_2 \rangle = + (\alpha^2/8) \sum_{i=1}^{N} \langle \operatorname{div} \varepsilon_i \rangle \qquad (4)$$

$$\langle H_5' \rangle = - (8\pi\alpha^2/3) \sum_{i>j} \langle S_i\, S_j\, \delta^3(r_{ij}) \rangle \qquad (5)$$

φ_i is here the orbital occupied by the i-th electron inclusive of the spin function, S_i the corresponding spin momentum operator and ε_i the electric field generated by the nucleus, by the remaining electrons and by any external field acting on the i-th electron. H_r is considered as a perturbation. Its expected value was derived from upper and lower states of K_α-transitions involving a sulphur atom with net charges $q = -2, 0, +6$. Relativistic corrections were evaluated also for $S^+(K^2L^83s^23p^5)\star$ which represents the lower state for some K_β and L transitions. The results are collected in Tab. 2, where are given the net charge on sulphur valence shell (column 1), electron configurations and optimum exponential parameters of atomic orbitals in K-, L- and M-shell for upper and lower states of the transition (columns 2, 3, 5, 6), expected values for operators H_1, H_4, H_5', and relativistic correction to energies for upper and lower states (columns 4, 7), relativistic corrections to K_α and K_β transition energies (column 8).

Relativistic energies are seen to depend essentially on $\langle H_1 \rangle$ which accounts for variation of electronic masses with velocity and $\langle H_4 \rangle$ which does not have a classic analogue. These operators are defined as sums of monoelectronic contributions and it is found that those due to $1s$- and $2s$-electrons are by far the most important. Moreover $\langle H_4 \rangle$ is very sensitive to the value of these functions at the nucleus. Therefore the accuracy of relativistic calculations depend largely on the radial behaviour of s-type functions, particularly near to the origin.

For these reasons, the relativistic perturbation ought to be evaluated with fully correlated atomic functions: however it has been shown [7, 10] that reasonably accurate values are presumably obtained by using S.C.F. analytical functions. Thus a check on the reliability of the functions employed for the present calculations can be made by comparing them with the corresponding S.C.F. analytical orbitals. This is shown in Fig. 1 for $V_1S^{4+}(K^2L^83s)$ and for $1s$- and $2s$-orbitals. One can see that, while $1s$ functions are practically the same, $2s$ functions diverge substantially near to the nucleus. This means that the computed value of the

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* In this case the many-electron function employed is less accurate since optimum values of variational parameters were extrapolated.

Table 2. *Calculated relativistic corrections (eV) to K_α- and K_β-transitions*

q charge on sulphur atom	Upper States			Lower States			Relativistic correction to transition energies
	Configuration[a]	Exponential parameters	$\langle H_{i,r}\rangle$	Configuration[a]	Exponential parameters	$\langle H_{i,r}\rangle$	
$+6$	$[1s^{-1}]$	$K_K = 15.548$ $K_L = 6.174$	$\langle H_1\rangle = -78.599$ $\langle H_4\rangle = 56.293$ $\langle H_5\rangle = 0.404$ $\langle H_r\rangle = -21.90$	$[2p_{0\pm}^{-1}]$	$K_K = 15.464$ $K_L = 5.907$	$\langle H_1\rangle = -125.060$ $\langle H_4\rangle = 96.022$ $\langle H_5\rangle = 1.801$ $\langle H_r\rangle = 27.24$	$\Delta E(K_\alpha) = 5.34$
0	$[1s^{-1},3s^23p_0^23p_+3p_-]$	$K_K = 15.523$ $K_L = 6.164$ $K_M = 2.246$	$\langle H_1\rangle = -79.819$ $\langle H_4\rangle = 56.866$ $\langle H_5\rangle = 0.431$ $\langle H_r\rangle = -22.52$	$[2p_{0\pm}^{-1},3s^23p_0^23p_+3p_-]$ $[3s^23p_0 3p_+3p_-]$	$K_K = 15.441$ $K_L = 5.887$ $K_M = 2.211$ $K_K = 15.468$ $K_L = 5.763$ $K_M = 2.047$	$\langle H_1\rangle = -126.154$ $\langle H_4\rangle = 96.650$ $\langle H_5'\rangle = 1.833$ $\langle H_r\rangle = 27.76$ $\langle H_1\rangle = -125.093$ $\langle H_4\rangle = 95.821$ $\langle H_5\rangle = 2.047$ $\langle H_r\rangle = 27.42$	$\Delta E(K_\alpha) = 5.24$ $\Delta E(K_\beta) = 4.90$
-2	$[1s^{-1},3s^23p_0^23p_+^23p_-^2]$	$K_K = 15.520$ $K_L = 6.182$ $K_M = 2.013$	$\langle H_1\rangle = -79.490$ $\langle H_4\rangle = 56.659$ $\langle H_5'\rangle = 0.430$ $\langle H_r\rangle = -22.40$	$[2p_0^{-1},3s^23p_0^23p_+^23p_-^2]$	$K_K = 15.445$ $K_L = 5.914$ $K_M = 1.978$	$\langle H_1\rangle = -125.754$ $\langle H_4\rangle = 96.247$ $\langle H_5'\rangle = 1.828$ $\langle H_r\rangle = 27.65$	$\Delta E(K_\alpha) = 5.25$

[a] Only valence shell electrons are explicitly indicated: the exponent -1 signifies a vacancy [1, 2].

divergence of the nuclear field on $2s$ electrons is too high and $\langle H_4 \rangle$ is overestimated*. However, in K_α and K_β emissions the occupational number of the $2s$ orbitals does not change. Thus even if the absolute value of $\langle H_r \rangle$ may not be very accurate, relativistic corrections to transition energies are expected to be sufficiently reliable. The results in Tab. 1 show that relativistic corrections to K_α transition energies are practically independent from q so that their influence on the correlating function (1) must be considered negligible. For elemental sulphur, the computed energy for the baricenter of K_α-doublet, is raised now to 2314.84 eV.
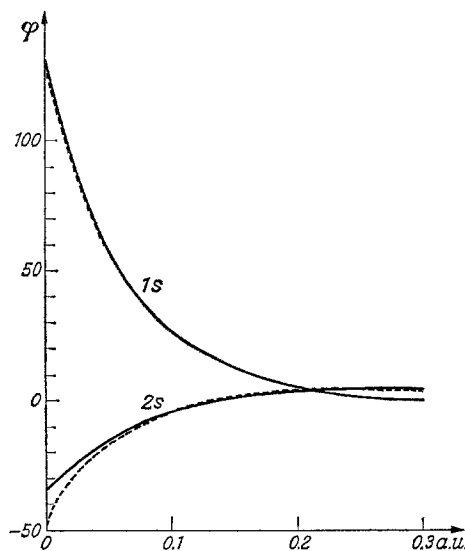

Fig. 1. Comparison between $1s$, $2s$ analytical S.C.F. orbitals [10] (full lines) and orthonormal Slater orbitals employed in the present calculations (dashed lines)

K_β- and L-transitions

In the monocentric approximation, here expected to be rather crude since valence electrons are involved, K_β-transitions can be computed through Eq. (6):

$$\Delta E_\beta = E[1s^{-1}, q] - E[q + 1] \tag{6}$$

where $E[q + 1]$ refers to an atom with complete inner shells minus one valence electron. Because of the selection rules, in the monocentric approximation the latter ought to be a p electron. The ligand field (and crystal field) is likely to cause perturbations on the valence orbitals and thus the forbidden transition $3s \rightarrow 1s$ may also occur. At the same time, the possibility of exchange of excitation among neighbouring atoms cannot be ignored in principle. Another feature which must be mentioned is that electrons in the valence shell of sulphur participating to bonding with ligands are expected to be energetically more stable that the non-bonding p^2-pair: this will result in a splitting of the $3p \rightarrow 1s$ transition with the component involving non-bonded $3p$-electrons lying at higher frequencies (see

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* Nonetheless the relativistic energy (-27.76 eV) for the valence state $S[2p^{-1}]$ computed with the functions here employed compares favourably with the value (-28.65 eV) obtained by E. CLEMENTI [7] for S^0 $[3_P]$.
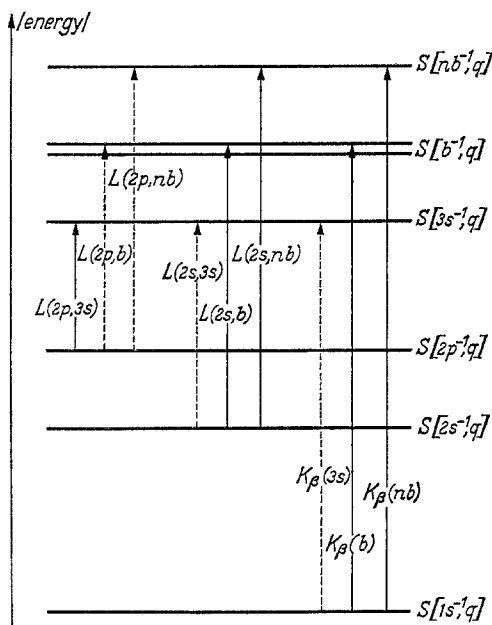
Fig. 2. $K\beta$ and L transitions: nb and b stand for $3p$-nonbonding and $3p$-bonding electrons respectively. Dotted lines indicate forbidden lines in the free atom

Fig. 2). The energy of upper states of K_β-transitions is the same as that of K_α-transitions which have already been computed [2]: thus only the term $E[q + 1]$ of lower states need to be evaluated.

This was done by deriving the energies of the appropriate valence states through a variational procedure. The results are collected in Tab. 3, where are given the energies of the lower states configurations $3s^2 3p^{4-q}$ and $3s 3p^{5-q}$ for q ranging between -2 and $+3$.

From these data K_β-transition energies for sulphur derivatives can be obtained, once charges q on sulphur are known. By adopting q-values derived from the experimental shift of K_α-transitions through Eq. (1), K_β-transition energies were computed for elemental sulphur, inorganic sulphides and sulphates. The results are given in Tab. 4 and compared with experimental data. For elemental

Table 3. *Lower state energies $E(q + 1)$ (eV) for $K\beta$ transitions in sulphur*

q	Configuration	Energy
-2	$[3s^2 3p^5]$	-10781.53
-1	$[3s^2 3p^4]$	-10782.29
0	$[3s^2 3p^3]$	-10773.82
	$[3s 3p^4]$	-10760.71
$+1$	$[3s^2 3p^2]$	-10752.35
	$[3s 3p^3]$	-10741.36
$+2$	$[3s 3p^2]$	-10707.93
$+3$	$[3s 3p]$	-10661.70

Table 4. *Computed and experimental K_β transition energies (eV) in sulphur derivatives*

Compound	Experimental	Tentative attribution	Computed value
MnS	2464.92		
SrS	2465.45	[$1s \leftarrow 3p$ (non bonding)]	$\rightarrow$ 2465.80 ($q = -0.55$)
	2465.00		
CaS	2465.30	[$1s \leftarrow 3p$ (bonding)]?	—
	2463.93		
$S_{rhombic}$	2467.69	[$1s \leftarrow 3p$ (non bonding)]	$\rightarrow$ 2467.64 ($q = 0$)
	2465.03	[$1s \leftarrow 3p$ (bonding)]?	—
	2463.56	—	—
K_2SO_4	2465.70		
	2452.88	[$1s \leftarrow 3p$]	$\rightarrow$ 2474.65 ($q = +2$)
$CaSO_4$	2466.60		
	2453.47	[$1s \leftarrow 3s$]	$\rightarrow$ 2461.99

sulphur, three transitions are observed: the first at higher frequency which appears as a relatively sharp line, probably involves non-bonding $3p$-electrons. The exceptional agreement between experimental and computed energy is to be considered partly fortuitous. By adding the relativistic correction estimated in the preceeding section (see Tab. 1), the deviation rises in fact to about 4.9 eV. The transition observed 2465.03 eV may be tentatively attributed to bonding electrons: the energy stabilization involved seems to be of the right order of magnitude for a sulphur-sulphur bond energy. As far as the third transition is concerned, at present no interpretation is offered: it must be remembered however that in elemental sulphur exchange of excitation cannot be ruled out, while the attribution $3s \rightarrow 1s$ can be excluded since this transition ought to occur at much lower frequencies (about 10 eV lower). For SrS, CaS, MnS, the K_β-transition energy was computed at $q = -0.55$ (value derived from the shift of K_α-transitions). The agreement is again very good. For sulphates, the computed transition energies are a little higher than those observed: here however all the electrons involved are bonding electrons and the valence orbitals of sulphur are likely to be strongly perturbed by the field of the oxygen atoms. The difference in energy between the levels $3s^{-1}$, $3p^{-1}$ is well reproduced.

L-transitions can be defined in the monocentric approximation as in Eq. (8):

$$\Delta E_L = E[\varphi^{-1}, q] - E[q + 1] \qquad (8)$$

where φ is either a $2s$ or a $2p$ electron (see Fig. 2). For the previously mentioned reasons concerning ligand perturbation, besides the allowed $3s \rightarrow 2p$ and $3p \rightarrow 2s$ transitions, also $3s \rightarrow 2s$, $3p \rightarrow 2p$ may be expected to occur as well as a splitting

Table 5. *Computed and experimental L transition energies (eV) in elemental sulphur*

	experimental [12, 13]	computed
$S[2p^{-1}] \rightarrow S[3s^{-1}]$	149.2	144.9
$S[2p^{-1}] \rightarrow S[3p^{-1}]$	158	158.1
$S[2s^{-1}] \rightarrow S[3p^{-1}]$	203	—

Table 6. *Computed and experimental X-ray terms in rhombic sulphur*

	experimental [14]	computed
S[1s^{-1}]	2474.2	2476.1
S[2s^{-1}]	224.4	—
S[2p^{-1}]	164.1	166.5
S[3s^{-1}]	16.7	21.6
S[3p^{-1}]	~ 5.4	8.5
S	0	0

of the latter. Experimental data are available only for elemental sulphur and these are shown together with the computed values in Tab. 5. Again a good agreement is obtained.

At this point, a comparison can be made between experimental and computed X-ray terms for rhombic sulphur, which gives a clear picture of the accuracy that can be attained with a monocentric model (see Tab. 6). The energy of S[2p^{-1}], S[3p^{-1}] is predicted with reasonable accuracy so that the discrepancy between experimental and calculated shifts of K_β-transitions in sulphates must be due to changes in shape and energy of 3s and 3p functions from the atomic case.

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