Photoelectron Spectra and Molecular Properties, XLVIII [1]
Carbonates and Thiocarbonates

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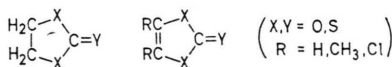G. Graeffe and H. Juslén

Tampere Institute of Technology, Tampere/Finland

Photoelectron (PE) spectra of ethylene and vinylene carbonates and thiocarbonates as well as of methylene trithiocarbonate and some open-chain derivatives are reported.

The low energy bands, well separated in the unsaturated compounds, are assigned to lone pair and π type ionizations. The assignment is based on comparison of PE spectra, modified CNDO calculations, and sulfur K_β emission spectra. The pronounced substituent effects due to which the first ionization potential varies from 8.4 eV to 11.1 eV are discussed.

Compounds of general type $A_2B=C$ have repeatedly stimulated photoelectron spectroscopic investigations [2-6] for several reasons:

i) MO models for simpler derivatives of C_{2v} molecular symmetry, e.g. 1,1-disubstituted ethylenes [2-4] or thiocarbonyl halides [5a], do contain only one occupied π orbital of a_2 character. The shift of this π ($1 a_2$) orbital as deduced from comparison of pe spectra can be correlated with inductive substituent effects [3]. The corresponding π ($1 a_2$) ionization energy may be taken as an internal standard [2], relative to which π MO models are easily parametrized using the PE data.

ii) The rather complex interdependence between π and σ subsystems in MO models can be ela-

borated advantageously for $A_2B=C$ type molecules, in which the atom C is incorporated both into the π conjugation and – additionally via an in-plane lone pair – into the σ skeleton. According to semiempirical calculations [5], substituent dependent variations of π and σ charges can exceed changes in the total charges, e.g. for $Cl_2C=S$ and $F_2C=S$.

iii) Most of the compounds are small and relatively rigid, easy to evaporate and very often their PE spectra display vibrational fine structures, helpful in the assignment. Furthermore, due to their molecular properties [7] and their reactivity $A_2B=C$ type compounds are of general chemical interest.

In the following, PE spectra as well as some X-ray emission spectra of mainly cyclic (vinylene and vinylidene) carbonates and thiocarbonates are reported. Some recently published data [6] are included into the discussion for completeness.

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Requests for reprints should be sent to Prof. Dr. H. Bock, Chemische Institute der Universität, *D–6000 Frankfurt a. M.*, 70, Sandhofstr., FRG.
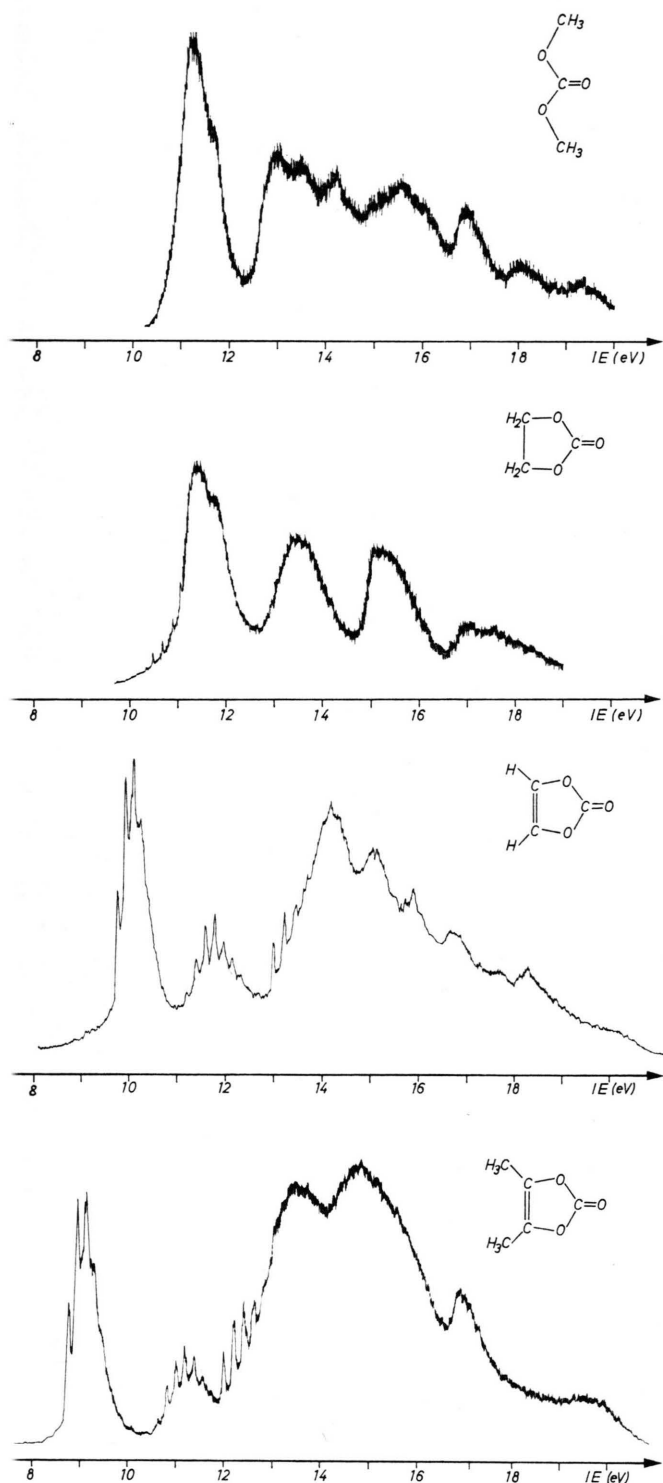
Fig. 1. PE spectra of dimethylcarbonate, 1,3-dioxolan-2-one, 1,3-dioxol-2-one, and 4,5-dimethyl-1,3-dioxol-2-one.

A. Carbonates

The PE spectra of the carbonates investigated are shown in Fig. 1, the vertical ionization energies, together with observed cation vibrational frequencies, are collected in Table I.

The discussion starts best with ethylene carbonate, the PE spectrum[8] of which displays many near-degeneracies. The structure of this compound has been repeatedly discussed because a dihedral angle ⊀ OCCO ~ 40°[9] was determined by X-ray diffraction, whereas IR spectroscopic investigations in the liquid and in the gaseous phase indicate planarity[10]. The results of a later microwave spectroscopic study[11] could only be interpreted by assuming a slightly nonplanar skeleton with the dihedral angle significantly reduced relative to that found in the solid. The dependence of the eight lowest ionization potentials on the dihedral angle was simulated by CNDO calculations (Fig. 2).

For a planar or nearly planar arrangement, the grouping into three ionization regions *i.e.* around 11 eV to 12 eV, 13 eV to 14 eV and 15 eV to 16 eV is well reproduced by the calculations. However, if the dihedral angle is greater than 20° the pattern changes significantly. In accordance with the infrared and microwave investigations[10, 11], a nearly planar structure is suggested by the PE spectrum.
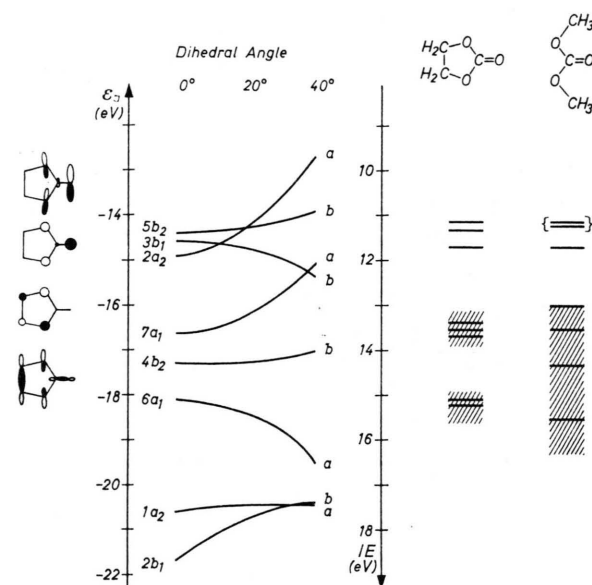

Fig. 2. Orbital energies, orbital diagrams, and experimental ionization potentials of ethylene carbonate.

Table I. Vertical ionization energies IE_n (eV) and cation vibrational frequencies $\nu^{\oplus}$ (cm^{-1}) of some carbonates.

	$\begin{smallmatrix}H_3CO\\H_3CO\end{smallmatrix}$ C=O	$\begin{smallmatrix}H_2C-O\\H_2C-O\end{smallmatrix}$ C=O	$\begin{smallmatrix}H-C-O\\H-C-O\end{smallmatrix}$ C=O	$\begin{smallmatrix}H_3C-C-O\\H_3C-C-O\end{smallmatrix}$ C=O	$\begin{smallmatrix}Cl-C-O\\Cl-C-O\end{smallmatrix}$ C=O [a]
IE_1 ($\nu^{\oplus}$)	11.2	11.1[b] (1570)	10.08 (1350; 700)	9.10 (1370)	9.68 (1300)
IE_2 ($\nu^{\oplus}$)	11.2	11.3	11.76 (1550; 1050)	11.21 (1450)	12.1 (1370)
IE_3 ($\nu^{\oplus}$)	11.7	11.7	13.4 (1950; 1550; 1110; 700)	12.4 (1700)	13.0
IE_4	13.0	13.5	14.2	13.6	13.3
IE_5	13.0	15.2	15.1	14.8	13.5
IE_6	14.3	17.0	15.9	16.9	13.6
IE_7	15.5		16.7		14.5
IE_8					15.3
IE_q					18.0

[a] Unpublished results H.-D. SCHARF, Technical High School Aachen.
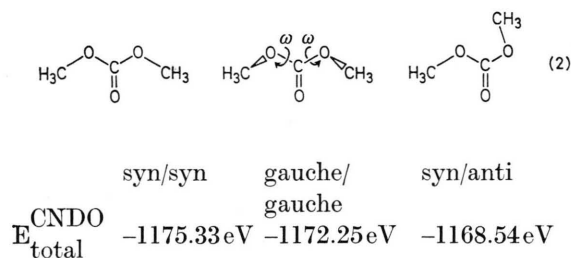[b] Adiabatic ionization energy.

Therefore the assignment for ethylene carbonate as well as for related compounds will be based – whenever applicable – on the assumption of a C_{2v} molecular skeleton.

YOKOYAMA, JINNO, WATANABE, and IKEDA[8] assigned the progression observed on the low energy flank of the first peak ($\nu^{\oplus} = 1570$ cm^{-1}) to the oxygen lone pair orbital $5b_2$, although the vibration most likely is a reduced carbonyl stretching frequency $\nu_{C=O} = 1820$ cm^{-1} [10,12]. It should however be kept in mind, that normal modes in ring compounds often are highly coupled and that CNDO calculations (Fig. 2) suggest a strong admixture of σ-bonding orbitals to the "oxygen lone pair". This assignment is further supported by the band shape of the corresponding ionization in vinylene carbonate.

The orbitals $3b_1$ and $2a_2$ (Fig. 2) are assigned to the ionizations at 11.3 eV and 11.7 eV respectively; $3b_1$ being destabilized relative to $2a_2$ by conjugative interaction with the carbonyl group π-orbital. The next bands around 13 eV to 14 eV and 15 eV to 16 eV most probably contain three and two ionizations respectively, which according to the CNDO calculations would have to be assigned to CH bonding orbitals $2b_1$, $4b_2$, $7a_1$, $1a_2$ and to the σ orbital $6a_1$ (Fig. 2). Nevertheless, considering all uncertainties involved, no detailed assignment will be proposed.

Ring-opening to dimethylcarbonate yields a completely different pattern, although the first ionization energies do not change much (Fig. 1, Table I). CNDO calculations favour a planar syn/syn-conformation (2) as has been recently deter-

mined by electron diffraction for the corresponding trithiocarbonate[13]

$$E_{total}^{CNDO} \quad \begin{array}{ccc} \text{syn/syn} & \text{gauche/gauche} & \text{syn/anti} \\ -1175.33\,\text{eV} & -1172.25\,\text{eV} & -1168.54\,\text{eV} \end{array}$$

The first peak again is assigned to comprise three ionizations, $3b_1$ at about 11.2 eV, $2a_2$ at 11.7 eV, and $5b_2$ somewhere in between.

On the contrary, a replacement of the $-H_2C-CH_2-$ linkage by a vinylene unit $-HC=CH-$ strongly shifts the ionization potentials (Fig. 1, Table I). Major differences concern not only the additional π interactions, but also that there remains only one orbital of a_2 symmetry which is almost completely localized on the two oxygen atoms. Consequently its ionization energy increases considerably (Fig. 3 A). Alternatively, the π system of the planar[14] vinylene carbonate can be derived from that of the isoconjugated fulvene[15] by first order perturbation with standard parameters as displayed in Figure 3 (B).

The fulvene perturbation clearly evidences that the order of occupied π orbitals for vinylene carbonate must be $3b_1$, $2b_1$, $1a_2$, $1b_1$ with the oxygen lone pair $5b_2$ inserted in between $3b_1$ and $2b_1$ (Fig. 3). The extensive vibrational fine structures of the $5b_2$ PE band (Fig. 4: 11.1 eV to 12.2 eV) indicates strong mixing of symmetry coordinates[16]

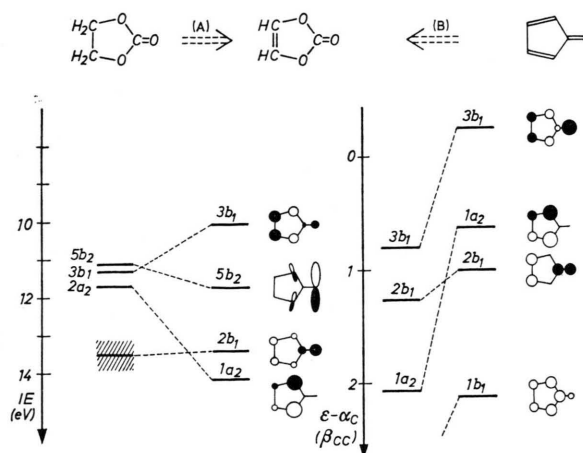and/or considerable delocalization of the lone pair (Fig. 3).

Fig. 3. Sequence of highest occupied orbitals for vinylene carbonate as deduced by perturbation arguments from those of ethylene carbonate (A) and of the iso-conjugated π system of fulvene (B).

Inspite of the long and pronounced progressions observed, the cation frequencies can not be related unequivocally to those of the neutral molecule[17].

Substitution of the vinylene hydrogens by methyl groups produces the expected changes in the PE spectrum (Fig. 1, Table I): Both π-orbitals $3b_1$ and $2b_1$ are destabilized by about 1 eV, whereas the lone pair $5b_2$ is only shifted by 0.5 eV. This observation corresponds to large contributions of the vinylene π group orbital to the molecular orbitals $3b_1$ and

$2b_1$, and only small delocalization of the oxygen lone pair into C–C- or C–H-bonds (Fig. 3).

Analogous arguments apply to dichloro vinylene carbonate (Table I), the lone pair now being stabilized by the electron accepting chlorine substituents. The ionizations in the 13 to 14 eV region are due to electron removal from the chlorine lone pair orbitals, which are found *e.g.* in *cis*-dichloro ethylene[2] between 11.6 eV and 12.5 eV. This shift clearly demonstrates the electron-attracting power of both the ring oxygens and the carbonyl group when not bonded to alkyl groups.

The assignments derived above for the carbonates will subsequently be used in the discussion of the thio-derivatives.

B. Vinylene Thiono-carbonate and Vinylene Trithio-carbonate

The PE spectra of vinylene thiono-carbonate, its dimethyl derivative, and of vinylene trithiocarbonate are shown in Fig. 5. The vertical ionization energies together with observed cation vibrational frequencies are collected in Table II.

The assignment for vinylene thiono-carbonate is less straightforward than that for vinylene carbonate: Although qualitative reasoning as well as CNDO calculations predict a considerable destabilization of the lone pair orbital $5b_2$ and a smaller one for the π orbital $3b_1$, no indication for near degeneracy in the 9 to 10 eV region can be obtained from its PE spectrum (Fig. 9 A). However, assuming only one ionization in the first PE band
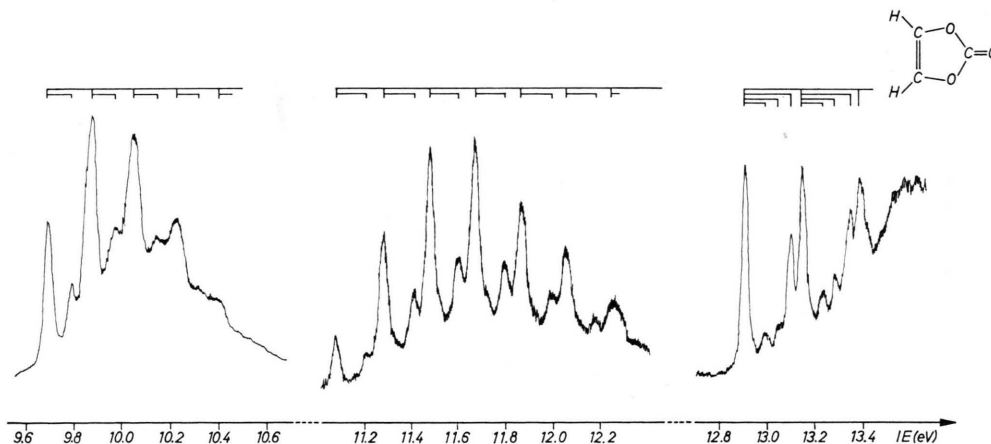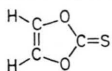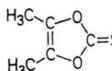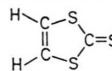

Fig. 4. Details of the first three PE bands of vinylene carbonate.

Table II. Vertical ionization energies (eV) and vibrational frequencies $\nu^{\oplus}$ (cm^{-1}) of 1,3-dioxol-2-thione, 4,5-dimethyl-1,3-dioxol-2-thione, and of 1,3-dithiol-2-thione.

IE$_1$ ($\nu^{\oplus}$)	9.05 } (1300)	8.4 } (1500)	8.3 } (900)[a]
IE$_2$ ($\nu^{\oplus}$)	9.3	8.6	8.5
IE$_3$ ($\nu^{\oplus}$)	11.4 (~500)	10.3	10.5
IE$_4$ ($\nu^{\oplus}$)	13.7 (1200)	13.1	10.8
IE$_5$	14.8	13.7	11.9
IE$_6$	16.6	14.8	12.3
IE$_7$	17.4		12.6
IE$_8$			12.9
IE$_9$			13.0

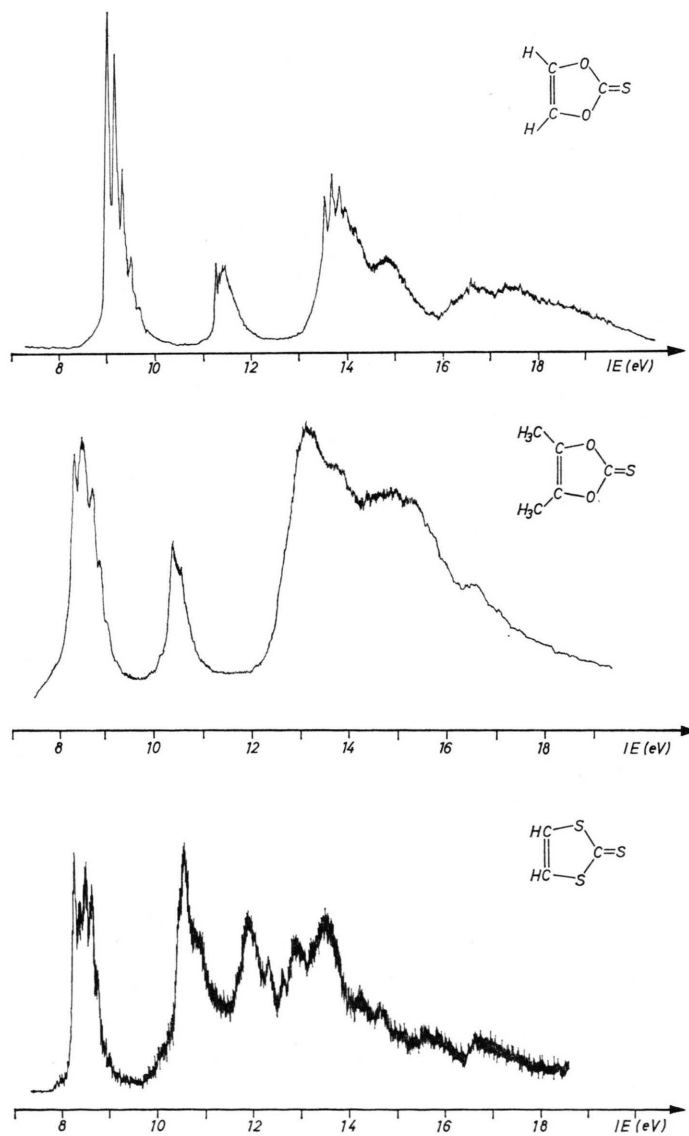[a] Difference between successive peaks, progressions not separated.

Fig. 5. PE spectra of 1,3-dioxol-2-thione, 4,5-dimethyl-1,3-dioxol-2-thione and 1,3-dithiol-2-thione.

would involve either i) the assignment $5b_2$ at 9.05 eV and $3b_1$ at 11.4 eV with the π orbital stabilized by about 1.3 eV; or ii) the assignment $3b_1$ at 9.05 eV and $5b_2$ at 11.4 eV with the π orbital destabilized and the lone pair orbital slightly stabilized. Both choices i) and ii) would comprise absurd substituent effects and, therefore, an assignment with ionizations $5b_2$ and $3b_1$ between 9–10 eV is proposed. Consequently the ionization $2b_1$ is attributed to the 11.4 eV band, and $7a_1$ as well as $1a_2$ are placed below 13 eV. CNDO calculations support the qualitative arguments (Fig. 6).
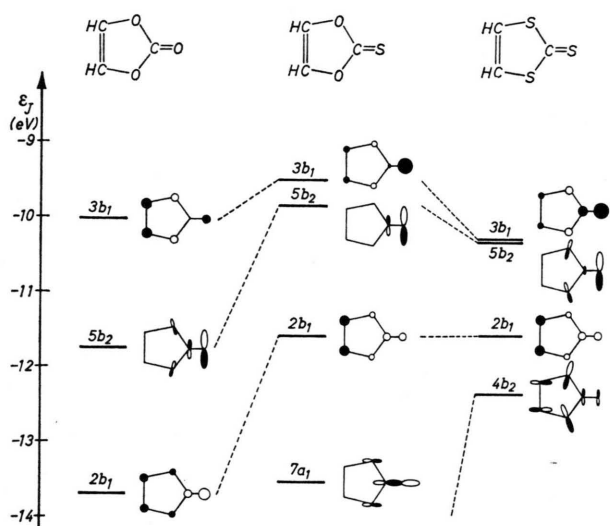

Fig. 6. CNDO eigenvalues and orbital diagrams for vinylene carbonate, its thiono- and trithio-derivatives (neglecting differing methyl substitution).

Obviously, both the orbitals $3b_1$ and $5b_2$ contain high sulfur 3p contributions and therefore should be rather similar in ionization energy.

The assignment of the vinylene trithio-carbonate proceeds along the same lines (*cf.* Figs. 5 and 6, Table II). Again, the fine-structure in the first PE band prevents to read off definite energies for the ionizations $3b_1$ and $5b_2$. The third and fourth ionization potentials correspond to the π orbital $2b_1$ and the largely CS bonding orbital $4b_2$ in yet undecided ordering.

Dimethyl substitution of the thiono-carbonate yields the expected shifts. There is some faint indication that the second peak of the first band, which is broadened, also contains the second ionization. As a consequence of the above assignment, the a_2 orbital of trithiocarbonate is placed below 11 eV. Comparison with the corresponding values for ethylene trithio-carbonate[6] and *trans*-dimethylthio-ethylene[3], 9.42 eV and 9.20 eV, respectively, demonstrates the extent of hyperconjugation in the a_2 lone pair standard in RO- and RS-substituted systems (*cf. e.g.* Fig. 3).
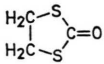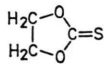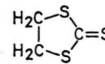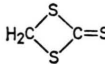
C. Saturated Thiocarbonates

The PE spectra of some saturated thiocarbonates are presented in Fig. 7; their vertical ionization energies are collected in Table III.

The discussion of the PE spectra follows best a CNDO correlation diagram (Fig. 8).

Although the agreement with experimental ionization energies is far from being perfect, it should be noted that the thiocarbonyl lone pair (5b) and the two π orbitals b_1 and a_2 are found among the three highest occupied ones. Furthermore, for the dithiolo-carbonate, a large sulfur contribution results for the b_2 lone pair corresponding to a low ionization potential. The calculated inversion a_2/b_1 for this compound is presumably due to a twist angle of about 20° (*cf.* Fig. 2). For both thiono-carbonate

Table III. Vertical ionization potentials IE_n (eV) and vibrational fine structures $\nu^{\oplus}$ (cm^{-1}) of 1,3-dithiolane-2-one, 1,3-dioxolane-2-thione, 1,3-dithiolane-2-thione[6], and 1,3-dithietane-2-thione.

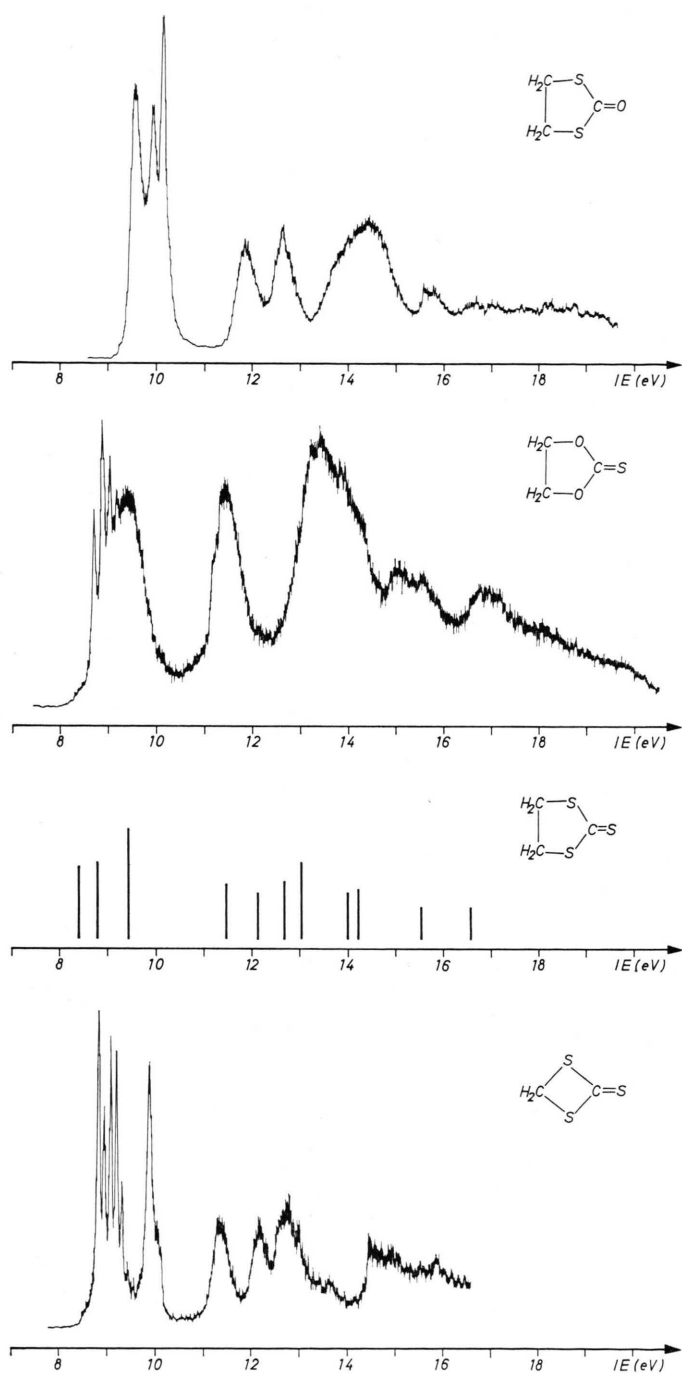|	$\begin{matrix} H_2C-S \\ | \quad\;\; C=O \\ H_2C-S \end{matrix}$	$\begin{matrix} H_2C-O \\ | \quad\;\; C=S \\ H_2C-O \end{matrix}$	$\begin{matrix} H_2C-S \\ | \quad\;\; C=S \\ H_2C-S \end{matrix}$	$\begin{matrix} S \\ H_2C \quad C=S \\ S \end{matrix}$	
IE_1 ($\nu^{\oplus}$)	9.58	8.88 (1350)	8.40	8.83	$\Big\}$ (900)
IE_2 ($\nu^{\oplus}$)	9.93	9.4	8.87	9.09	
IE_3	10.14	11.4	9.42	9.89	
IE_4	11.9	13.4	11.42	11.3	
IE_5	12.7	15.0		12.2	
IE_6	14.4	16.9		12.8	

Fig. 7. PE spectra of 1,3-dithiolane-2-one, 1,3-dioxolane-2-thione, 1,3-dithiolane-2-thione[6], and 1,3-dithiethane-2-thione.
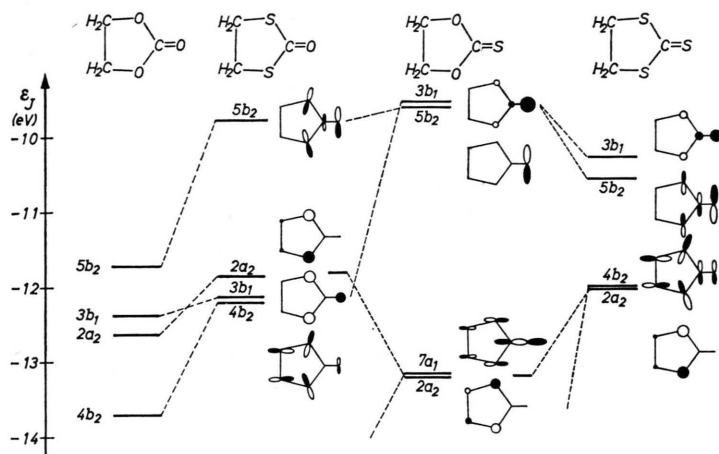
Fig. 8. CNDO correlation diagram for etylene carbonate and several cyclic thiocarbonates.

and methylene trithio-carbonate two ionization potentials have to be assigned to the 9–10 eV and 8–9.5 eV regions, respectively. The FRANCK CONDON envelope clearly indicates two bands for the latter compound (Fig. 9 B).

Due to the relative closeness of the first bands no definite assignment can be given. We choose, however, to assign the 11.4 eV peak in ethylene thiono-carbonate and the one at 9.89 eV in methylene trithio-carbonate to an A_2 state.

For the series of trithio-carbonates a tentative assignment is given in Fig. 10. Three of the PE spectra have been assigned already in the literature *i.e.* ethylene trithio-carbonate[6, 18], dimethyl trithio-carbonate[6], and bis(trifluormethylmercapto)thio-carbonyl[5b].
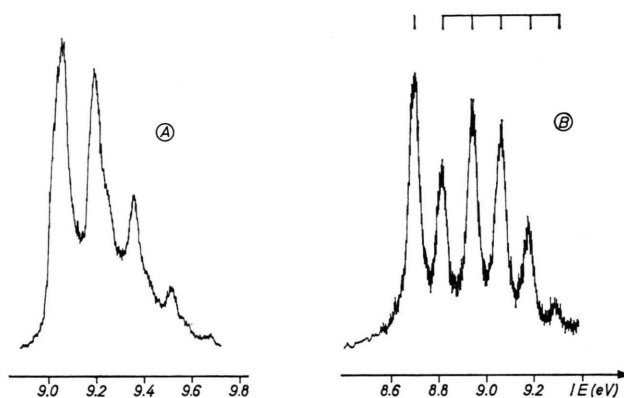

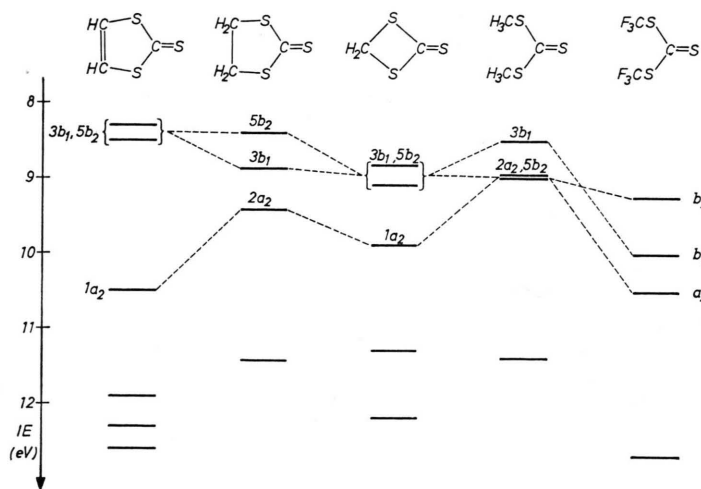Fig. 9. Expanded records of the first bands of vinylene thionocarbonate (A) and methylene trithio-carbonate (B).

Fig. 10. Correlation diagram for several trithio-carbonates.

Both IR[19] and X-ray[20] investigations prove a non-planar skeleton for ethylene trithio-carbonate in the liquid and solid phase ($\star$ SCCS $\sim 40°$ [20]) whereas electron diffraction[13] and IR studies[21] indicate a planar syn/syn-structure for the open-chain di-methyltrithiocarbonate. Therefore for both compounds the $3 b_1/a_2$ splitting should be about the same or possibly a little larger in the open-chain derivative. This assumption leads to the PE spectroscopic assignment for dimethyl trithiocarbonate as given in Fig. 10 and in contrast to the previous one[6]. The other assignments are based on the assumption that the b_2 orbital changes can be neglected and that the $2 a_2$ orbital should be somewhat sensitive to hyperconjugation.

Summarizing, a more detailed discussion of thiocarbonate PE spectra based on semiempirical SCF calculations hardly seems possible, because the latter generally are not reliable enough to predict the ordering of bands closer to each other. Even *ab initio* SCF calculations invoking KOOPMANS theorem[22] would be of doubtful help if individual radical cation states are separated by only small energy differences as often found for these compounds.

D. Sulfur Kβ Emission Spectra

In order to support the assignments and the interpretation of the PE spectra (chapters B and C) by additional experimental evidence, X-ray emission spectra of some thiocarbonates have been investigated.

A molecular cation, produced by ionization of an inner-shell electron (core ionization), relaxes either by emission of one further electron (AUGER effect)

or by an optical transition with a valence electron filling the core vacancy. For these dipole-allowed transitions the intensity is given by

$$I \sim E^3 \cdot |< \Psi_i | \vec{er} | \Psi_t >|^2 \tag{3}$$

Following MANNE[23-26], one can use the LCAO MO approximation for the initial and final states and neglect two-center terms as well as the variation of the X-ray energy. The intensity of the Kβ emission ($1 s^{-1} \rightarrow 3 p^{-1}$) should correlate with the sum of the squared sulfur 3p-coefficients of the finally vacated valence molecular orbital

$$I \sim \sum_{j \varepsilon p_S} c_j^2 k \tag{4}$$

The experimental X-ray emission spectrum may therefore be simulated by using the experimental valence ionization energies as furnished by PE spectroscopy and the calculated intensities derived from some crude MO approach like Extended HÜCKEL (EHMO) calculations. An immediate check between experimental and calculated intensities becomes possible if the latter are convoluted by a Lorenzian line shape with full width at half maximum of 2 eV[23-26] (*cf.* Fig. 11). For a testing of different assignments the X-ray emission spectra thus supply a probe into the shape of molecular orbitals.

Fig. 11 displays the sulfur Kβ emission spectra of some thiocarbonates. The EHMO calculated relative intensities – together with experimental ionization energies and their assignment to molecular orbitals assuming C_{2v} symmetry – are collected in Table IV.

Table IV. Calculated X-ray emission intensities $\sum_{j \varepsilon p_S} c_j^2 k$ (ionization energies (ev) and their assignment assuming C_{2v} symmetry are given in brackets).

| H2C—O, C=S	H3C—O, C=S	H2C—O, C=S	H2C—S, C=S	H2C—S, C=O
.960 ($5 b_2$ 9.05 eV)	.960 (b_2 8.37 eV)	.962 ($5 b_2$ 8.88 eV)	.712 ($3 b_1$ 9.58 eV)	1.017 ($5 b_2$ 8.47 eV)
.490 ($3 b_1$ 9.30 eV)	.230 ($3 b_1$ 8.60 eV)	.554 ($3 b_1$ 9.40 eV)	.846 ($2 a_2$ 9.93 eV)	.842 ($3 b_1$ 8.92 eV)
.123 ($2 b_1$ 11.40 eV)	.372 ($2 b_1$ 10.30 eV)	.032 ($2 a_2$ 11.4 eV)	.466 ($5 b_2$ 10.14 eV)	.976 ($5 a_2$ 9.46 eV)
.449 ($7 a_1$ 13.7 eV)	.281 (a_1 13.1 eV)	.176 ($7 a_1$ 13.4 eV)	.370 (a 11.9 eV)	.726 (b 11.0 eV)
	.123 (a_1 13.7 eV)	.250 ($6 a_1$ 13.4 eV)	.364 (b 12.7 eV)	.460 (a 11.5 eV)
			.284 (a 14.4 eV)	.330 (b 12.0 eV)
			.202 (a 14.4 eV)	.704 ($a+a$ 13.0 eV)
				.418 ($b+a$ 14.0 eV)
				.275 ($b+a$ 16.0 eV)
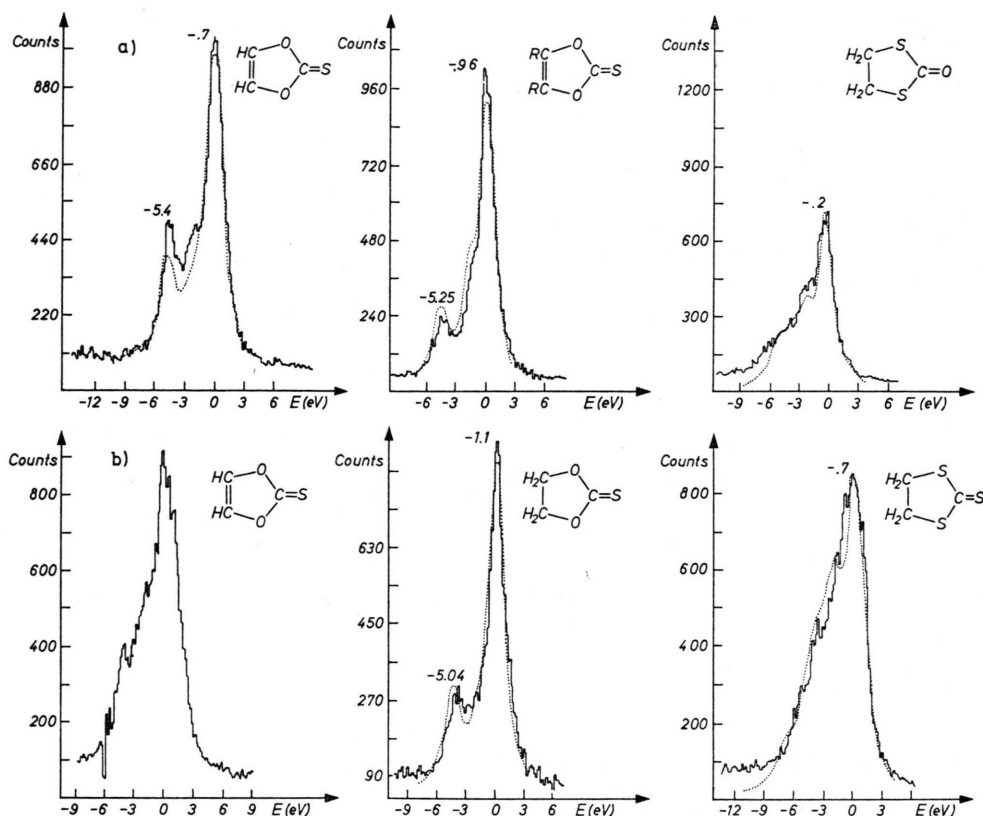
Fig. 11. Experimental (———) and calculated (....) sulfur Kβ spectra of some thiocarbonates. a) first spectrum; b) last spectrum of a series.

In the sulfur Kβ emission spectrum of vinylene thiono-carbonate, some intensity is built up between the first and the third peak during the measurement (Fig. 11: (a) and (b)), which we attribute to decomposition of the sample induced by the bombardment with X-rays. Similar changes are observed for all other compounds investigated. Nevertheless, the X-ray emission spectra clearly lend support to some of the assignments discussed. Thus for vinylene thiono-carbonate (*cf.* Figs 5 and 6) the ionizations $3b_1/5b_2$ in the 9.3 eV band as well as $2b_1$ at 11.4 eV and $7a_1$ at about 13.7 eV are confirmed by the satisfactory agreement of experimental and calculated X-ray emission spectra (Figure 11: (a)). Any other assignments, in particular those attributing only one ($3b_1$ or $5b_2$) ionization in the 9–10 eV region or 2 bands in the 11–12 eV region convincingly are ruled out judging from the sulfur Kβ intensities. However, the sequence $3b_1/5b_2$ cannot be established and the position of the $7a_1$ orbital energy remains

uncertain within 1 eV to 2 eV. Analogous remarks apply to the dimethyl vinylene thiono-carbonate emission spectrum which shows as somewhat better overall agreement between calculated and experimental intensities. The orbital sequence of ethylene thiono-carbonate (*cf.* Figs 7 and 8) partly resembles that of unsaturated vinylene thiono-carbonate (Fig. 6) with the ionizations $5b_2$ and $3b_1$ close to each other and generating highest intensity (Fig. 11), while the $7a_1$ and $6a_1$ orbitals account for the second maximum.

The dithiolo- and trithio-carbonates display rather unstructured spectra (Fig. 11). Permutations among the first three ionization energies do not change the calculated intensity curves; thus no decision can be made concerning the symmetry assignment of the first three ionization processes. The ethylene dithiolo-carbonate shows a strong sulfur contribution in the "oxygen lone pair $5b_2$" (*cf.* Fig. 8).

Further information from the X-ray emission data (Table IV and Fig. 11) concerning σ ionizations *i.e.* the shapes and energies of σ-bonding orbitals will not be explicitly discussed in this context.

E. Concluding Remarks

Even today – after several years of world-wide research – a detailed PE spectroscopic assignment is a difficult task and beyond the power of semi-empirical calculations. Also *ab initio* SCF-calculations may be undecisive if the ionic states under consideration are not farther apart than about 1 eV [27], since the reliability of KOOPMANS' theorem values has to be questioned. Of some help – especially for larger molecules – are correlations among chemically related compounds[28]. X-ray emission spectra can well supplement PE spectroscopy: X-ray intensities allow quite unambigously to extract the number of ionizations hidden under some PE bands.

All in all, in the PE spectroscopic discussion of carbonates and their thio-derivatives doubtful assignments *i.e.* those only based on the CNDO orbital sequence have largely been omitted. However, for most compounds investigated, number and origin of PE bands in the low energy region is quite understandable on the basis of CNDO calculations and/or chemical reasoning. Although based on incompletely assigned spectra, the comparison with methoxy- and methylthio-substituted ethylenes[3] demonstrates a striking difference concerning the ionizations assigned to electron removal from a_2 orbitals:

IE(a_2)	$\begin{array}{c} H_3CX \quad H \\ \diagdown C{=}C \diagup \\ H_3CX \quad H \end{array}$	$\begin{array}{c} H_2C{-}X \\ \diagup \qquad \diagdown C{=}X \\ H_2C{-}X \end{array}$	$\begin{array}{c} H{-}C{-}X \\ \diagup \ \| \ \diagdown C{=}X \\ H{-}C{-}X \end{array}$	
X = O	10.6 eV	11.7 eV	>14.2 eV	(5)
X = S	8.8 eV	9.42 eV	>11.0 eV	

As stated in the introduction in disubstituted ethylenes or in vinylene carbonates the a_2 orbitals are the only ones occupied of this irreproducible representation and therefore might be defined as internal standards for the lone pair energy a_x. The values collected in (5), however, suggest considerable and different hyperconjugative destabilization by methyl groups and methylene linkages. Therefore, the applicability of parameters a_x is limited,

and the term "lone pair" should only be used with restrictions.

In addition to CNDO eigenvalues and orbital coefficients, which provide an useful framework for discussion of the number and type of ionizations observed, the analysis of calculated charge densities yields interesting information: It offers an explanation for the failure of simple perturbation arguments in PE spectroscopic correlations of carbonates and thiocarbonates. On partition into σ and π charges, for molecules $X_2C{=}Y$ satisfyingly linear correlations result between the σ charges ϱ_σ^X at centers X and the π charge ϱ_π^Y at the center Y (Fig. 12).
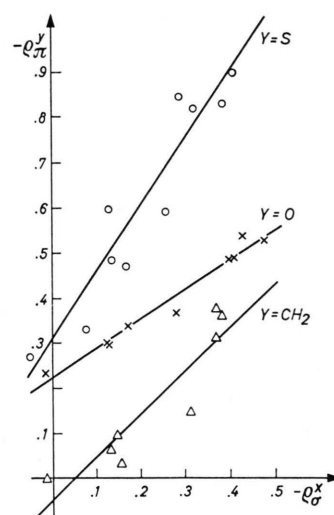
Fig. 12. Correlation between σ charges $\varrho_\sigma{}^X$ and π charge $\varrho_\pi{}^Y$ for molecules $X_2C = Y$ (ethylene derivatives: △, carbonyls: ×, and thiocarbonyls: ○).

The slopes of the individual regression lines *i.e.* 0.97 for ethylene derivatives (Fig. 12: △), 0.65 for carbonates (Fig. 12: ×) and 1.44 for thiocarbonates (Fig. 12: ○) differ markedly. Therefore a new measure of polarizability is proposed:

$$P = \frac{\partial \varrho_\pi^Y}{\partial \varrho_\sigma^X} \qquad (6)$$

is proposed. The increasing polarizabilities from carbonyl to thiocarbonyl are intimately related to the energies of the antibonding π*-orbital, because its admixture to the bonding π increases with decreasing orbital distance. Although the actual numerical values will depend on the choice of substituents X (X: –H, –F, –Cl, –OCH$_2$CH$_2$O–, –OCH=CHO–, –SCH$_2$CH$_2$S–, and –SCH=CHS–)

as well as on the method of calculation, such a definition is justified by *e.g.* the following observations:

i) Sulfur π charges ϱ_π^S calculated by an *ab initio* SCF-method[29] for $O=C=S$ and $S=C=S$ are significantly larger for the oxygen derivative.

ii) Dipole moments μ^π, calculated neglecting the σ framework by π MO methods, are usually too large, *e.g.*[30]

iii) The small dipole moment of $F_2C=S$, $\mu = 0.08$ D[31] can only be explained by counteracting F–C and C–S moments.

iv) The highest occupied π orbital $2b_1$ of $F_2C=S$ is essentially nonbonding

$$\qquad\qquad (7)$$

in agreement with an unreduced vibrational frequency of the corresponding cation state $(\nu_{C=S} = 1368\,\mathrm{cm}^{-1}; \nu^\oplus_{C=S}\,1370\,\mathrm{cm}^{-1})$[5a].

Thus "polarizability" finds its explanation in σ/π-interactions and can well be accounted for within the framework of KOOPMANS' theorem[22] and the MO approximation.

Experimental Part

All compounds, which are not commercially available, have been prepared by literature procedures, namely 1.3-dioxolane-2-one (MERCK), 1.3-dioxol-2-one (EGA-Chemie), dimethylcarbonate (SCHUCHARDT, 1.3-dioxolane-2-thione[32], 1.3-dithiolane-2-one[32], 1.3-dioxol-2-thione[33], 4.5-dimethyl-1.3-dioxol-2-one[33], 4.5-dimethyl-1.3-di-oxol-2-thione[33], 1.3-dithiol-2-thione[34], 1.3-dithietane-2-thione[35], and 4.5-dichlor-1.3-dioxol-2-one[36]. Due to poor yield, the 1.3-dithiol-2-thione could not be purified.

PE spectra were recorded using a PERKIN-ELMER PS 16 and calibrated partly with argon, partly with argon and xenon. A resolution of about 20 meV to 25 meV on the argon line was obtained.

The sulfur $K\beta$ emission spectra were taken on a double crystal spectrometer[37] with calcite (211) crystals, $2d = 6.06$ Å for 1st order reflection. The mechanical construction was the same as in the spectrometer published in ref.[38]. The rocking curve half width for sulfur in the $(1,-1)$-position was 0.50 eV. The excitation was accomplished by a SIEMENS KRISTALLOFLEX 4 Cr-tube (45 kV,

30 mA). The temperatures of the samples were below 30 °C. The samples were sealed and covered by a polypropelene film in order to avoid the vaporization of the samples. The spectra were calibrated using rhombic sulfur[39], the first maximum of which is used as zero in figure 11. The quality of the spectra can be judged from that of rhombic sulfur (Fig. 13) obtained under the same experimental conditions.
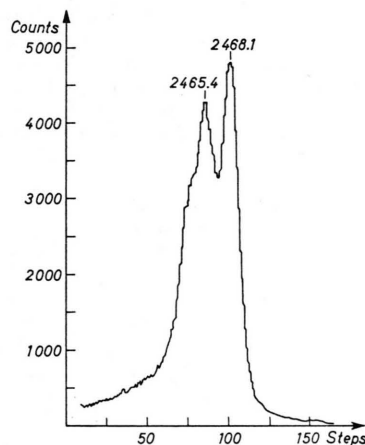

Fig. 13. X-ray emission spectrum of rhombic sulfur (1 step = o. 1727 eV).

For each sample, several successive spectra were taken; the appearance of them changed in a characteristic way (see chapter D). Therefore, only the first spectrum of each series has been used in the discussion.

The calculations have been performed on the UNIVAC 1108 at the Hochschul-Rechenzentrum of Frankfurt University. For CNDO-calculations a modified[40] QCPE program 141 was used, the version of the Extended Hückel program is also described elsewhere[41]. The geometrical parameters used in the calculations have, unless known, been deduced from structures of similar compounds[42, 43]. The geometry of the ethylene thiocarbonates was assumed to be nonplanar with a twist angle of 20°.

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