

BIBLIOGRAPHIE

- [1] *M. Wieber & M. Schmidt*, *Z. Naturforschg.* **18b**, 847 (1963).
 [2] *S. Mathur, G. Chandra, A. K. Rai & R. C. Mehrotra*, *J. Organometal. Chem.*, **4**, 371 (1965).
 [3] *R. C. Mehrotra & S. Mathur*, *J. Organometal. Chem.* **6**, 425 (1966).
 [4] *E. Korb, G. Levy, M. Brini & A. Deluzarche*, *J. Organometal. Chem.* **23**, 437 et 445 (1970).
 [5] *M. Lesbre & J. Satgé*, *C.R. Acad. Sci.* **254**, 4051 (1962).
 [6] *R. C. Mehrotra & S. Mathur*, *J. Organometal. Chem.* **6**, 11 (1966).
 [7] *J. Satgé, M. Lesbre & M. Baudet*, *C.R. Acad. Sci.* **259**, 4733 (1964).
 [8] *F. Rijkens, M. J. Janssen & J. G. M. Van der Kerck*, *Rec. Trav. chim. Pays-Bas* **84**, 1597 (1965).
 [9] *J. C. Pommier, R. Calas & J. Valade*, *Bull. Soc. chim. France* **1968**, 1475.
 [10] *J. C. Pommier & J. Valade*, *J. Organometal. Chem.* **12**, 433 (1968).
 [11] *H. Buc*, *Ann. Chim.* **8**, 409 (1963).
 [12] *R. C. Mehrotra & V. D. Gupta*, *J. Organometal. Chem.* **4**, 145 (1965).
 [13] *A. K. Sawyer*, *Organotin. Compounds*, Vol. I, Ed. M. Dekker, New York 1971.
 [14] *J. Mendelsohn, J. C. Pommier & J. Valade*, *C.R. Acad. Sci. (C)* **263**, 921 (1966).
 [15] *G. Dousse*, Thèse de spécialité, Toulouse 1969.
 [16] *S. Mathur, R. Ouaki, V. K. Mathur, R. C. Mehrotra & J. C. Maire*, *Indian. J. Chem.* **7**, 284 (1969).
 [17] *A. Marchand, M. T. Forel, M. Lebedeff & J. Valade*, *J. Organometal. Chem.* **26**, 69 (1971).
 [18] *R. J. Cross & F. Glockling*, *J. Organometal. Chem.* **3**, 146 (1965).
 [19] *K. M. Mackay & R. Watt*, *J. Organometal. Chem.* **6**, 336 (1966).
 [20] *C. C. Hinckley*, *J. Amer. chem. Soc.* **91**, 5160 (1969).
 [21] *J. K. M. Sanders & D. H. Williams*, *Chem. Commun.* **1970**, 422.
 [22] *G. H. Wahl Jr. & M. R. Peterson Jr.*, *Chem. Commun.* **1970**, 1167.
 [23] *H. A. Bendt*, *Chem. Rev.* **1961**, 275.
 [24] *M. Gielen, M. Gofin & J. Topart*, *J. Organometal. Chem.* **32**, C38 (1971).
 [25] *A. F. Cockeril & M. D. Rackman*, *Tetrahedron Letters* **59**, 5149 et 5153 (1970).
 [26] *C. C. Hinckley*, *J. Org. Chemistry* **35**, 2834 (1970).
 [27] *M. Gielen*, *Red. Vl. Chem. Veren.* **31**, 203 (1969).
 [28] *R. B. King*, *J. Amer. chem. Soc.* **91**, 7211 (1969).
 [29] *G. Dousse, J. Satgé & M. Rivière-Baudet*, *Synth. Inorg. Metalorg. Chem.* (sous presse).
 [30] *M. Rivière-Baudet*, Thèse, Toulouse (France) 1972.
 [31] *M. Lesbre, P. Mazerolles & J. Satgé*, *The organic compounds of germanium*, Wiley-Interscience, New-York, N.Y. 1971.

239. The Photoelectron Spectra of NSCl, NSF and NSF₃¹⁾

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(30. VI. 72)

Summary. The photoelectron spectra of NSCl and NSF₃ have been recorded. By comparison with the PE.-bands of NSF and semiempirical calculations the first bands of NSCl and NSF₃ are assigned.

Recently the photoelectron spectrum of thiazyl fluoride (NSF) has been reported [2] [3]. The assignment of the bands was proposed on the basis of semiempirical

¹⁾ Part 39 of 'Applications of Photoelectron Spectroscopy'. Part 38: see [1].

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calculations [2] and of an analysis of the vibrational band finestructure [3]. Both assignments agree as far as the first four bands are concerned (see Fig. 1 and Table 1).

In order to provide additional information and as a check of the assignment derived for NSF, we have measured the PE.-spectra of thiazyl chloride (NSCl) and of thiazyl trifluoride (NSF₃).

Analysis of the infrared spectrum of NSCl suggests [4] that this molecule has a structure very similar to that of NSF: $R(NS) = 1.45 \text{ \AA}$, $R(SCl) = 2.00 \text{ \AA}$ and $\angle(NSCl) = 116^\circ$. To a first approximation the structure of NSF₃ can be thought of as being derived from SF₆ by substituting a nitrogen atom for the three fluorines: $R(NS) = 1.416 \text{ \AA}$, $R(SF) = 1.552 \text{ \AA}$; $\angle(FSF) = 94.2^\circ$; Symmetry C_{3v} [5]. Because of the short

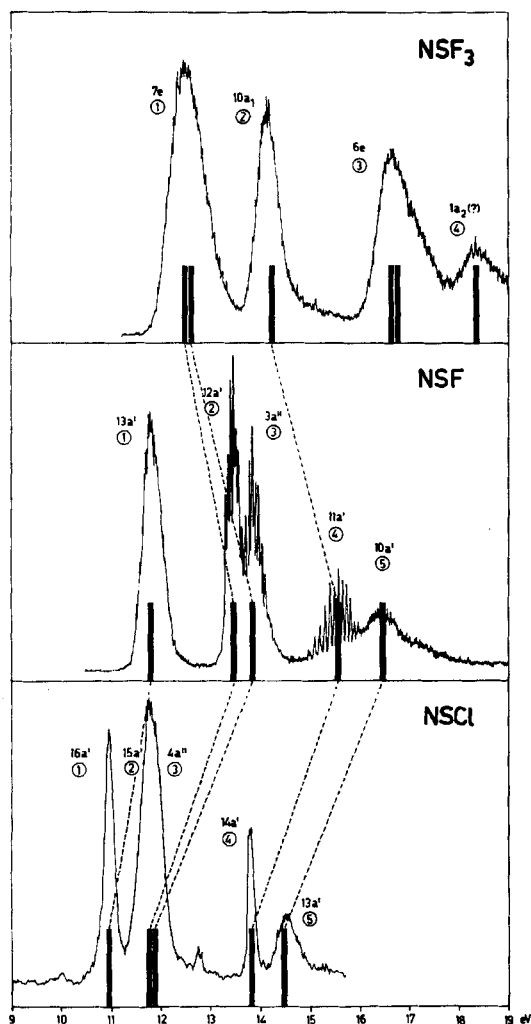


Fig. 1. Correlation of the PE-bands of NSF₃, NSF and NSCl

SN-bond lengths and of the large bending and stretching force constants, these molecules are often assumed to possess a SN-triple-bond [6].

Fig. 1 shows the PE.-spectra of NSCl, NSF and NSF₃ as recorded on a modified PS-16 photoelectron *Turner*-type spectrometer [7] (*Perkin-Elmer Ltd.*, Beaconsfield, England). The vertical ionization potentials I_{v, J}, i. e. the positions of the band maxima are collected in Table 1.

The electronic structure of NSCl should be closely related to that of NSF. Qualitative considerations lead one to expect that those bands in the spectrum of NSCl, which are associated with ejection of an electron from valence-shell orbitals should be shifted to lower ionization potentials relative to the corresponding bands in the spectrum of NSF. This seems to be the case (see Fig. 1) if one assumes that the second band in the spectrum of NSCl is due to the superposition of the bands correlated with the orbitals 15a' (σ) and 4a'' (π) as indicated by the integrated intensity. The larger shift of the π-band relative to that of the σ-band is in agreement with the results of semi-empirical calculations (see Table 1). We believe that the correlation given in Fig. 1 confirms the previous assignments for NSF [2] [3].

Formally one can derive NSF₃(C_{3v}) from NSF by letting the sulfur lone pair interact with two fluorine atoms. Thus we are left with two degenerate SN π-orbitals and a lone pair orbital on the nitrogen atom. The PE.-spectra of NSF and NSF₃ are consistent with this interpretation. The band at 12.5 eV in the spectrum of NSF₃ has twice the intensity of the band at 14.15 eV. Consequently we assign the first band to an ionization process involving the SN π-orbitals 7e (π) and the second to the lone pair orbital 10a₁ (σ) on the nitrogen atom.

If this interpretation is correct, then the correlation shown in Fig. 1 indicates that the orbitals 7e (π) and 10a₁ (σ) of NSF₃ lie above the corresponding 'parent' orbitals

Table 1. *Vertical Ionization Potentials and Orbital Energies for NSF, NSCl and NSF₃*
All values in eV

	Band	①	②	③	④
NSF	I _{v, J}	11.82	13.50	13.87	15.61
	ε _J (EH) ^{a)}	-12.58	-14.32	-14.99	-16.85
	Orbital	13a'(σ)	12a'(σ)	3a''(π)	11a'(σ)
NSCl	I _{v, J}	10.96	11.80 ^{b)}	13.77	14.46
	ε _J (EH) ^{a)}	-11.69	-12.89-13.04	-14.33	-15.25
	Orbital	16a'(σ)	15a'(σ) 4a''(π)	14a'(σ)	13a'(σ)
NSF ₃	I _{v, J}	12.50	14.15	16.65	18.35
	ε _J (EH) ^{a)}	-13.78	-15.14	-17.88	-17.94
	Orbital	7e(π)	10a ₁ (σ)	6e(π)	1a ₂ (?)

^{a)} Extended *Hückel* (EH) model [8] without 3d orbitals on sulfur.

^{b)} Double band.

12a' (σ), 3a'' (π) and 11a' (σ) of NSF. It may seem surprising that the formal addition of two fluorine atoms to the sulfur lone pair of NSF has the effect of shifting those orbitals to higher energy. However, this effect can be rationalized as follows on the basis of semiempirical calculations: In NSF and NSCl the orbitals that contribute to

the formal triple bond are centered on both the N and S atoms. In contrast in NSF_3 these orbitals are localized on the nitrogen atom. In addition the nitrogen lone pair in NSF_3 is more strongly localized on the nitrogen atom than in NSF.

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BIBLIOGRAPHY

- [1] *G. Bieri, F. Brogli, E. Heilbronner & Else Kloster-Jensen*, *J. El. Spec. 1*, (1972), in print.
- [2] *D. O. Cowan, R. Gleiter, O. Glemser, E. Heilbronner & J. Schäublin*, *Helv. 54*, 1559 (1971).
- [3] *R. N. Dixon, G. Duxbury, G. R. Fleming & J. M. V. Hugo*, private communication.
- [4] *O. Glemser & H. Richert*, *Z. anorg. allg. Chem. 307*, 313 (1961).
- [5] *O. Glemser*, *Endeavour*, Vol. XXVIII, 86 (1969).
- [6] *O. Glemser*, *Angew. Chem. 75*, 676 (1963).
- [7] *D. W. Turner*, *Proc. Roy. Soc. A307*, 15 (1968).
- [8] *R. Hoffmann*, *J. chem. Physics 39*, 1397 (1963); *R. Hoffmann & W. N. Lipscomb*, *ibid. 36*, 2179, 3489 (1962); *37*, 3872 (1962) and subsequent papers.

240. The Loss of CH_3COCH_2 Moieties from Methylketo Esters upon Electron Impact: A Discussion of Possible Long-Range Functional Group Interaction

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(3. VII. 72)

Summary. *Methyl 10-oxoundecanoate* and related long-chain methylketo esters exhibit loss of the terminal CH_3COCH_2 moiety as one of the most prominent modes of fragmentation in analogy to comparable long-chain diketones. In view of its absence in simple monoketonic analogues this process is thought to be induced by the distant ester function, e.g. *via* hydrogen abstraction from a suitable site (C(7)) within the alkyl portion of the molecule to be retained in the fragment. Rearrangement indicative of functional group interaction is thus concealed, and the attempt is made to unravel its incidence and true course by analysis of the further decomposition of the ($M - \text{CH}_3\text{COCH}_2$) fragment *via* sequential losses of MeOH and CO, with the emphasis on establishing the origin of the —OH hydrogen of the former of these two particles. Extensive deuterium labelling of most of the positions of the central chain, as well as analysis of pertinent high-resolution data and metastable transitions, is employed in the pursuit of this objective.

Introduction. — *Long-range interaction* of two functional groups within linear organic molecules frequently represents one of the more latent facets of mass spectrometric fragmentation, more amenable to conjecture by extrapolation from monofunctional compound behaviour than to experimental proof and elucidation. The occurrence of this phenomenon appears, however, to be the rule rather than the exception¹). In few instances, interaction of remote functions was readily recognized and

¹) For leading references see *M. Sheehan, R. J. Spangler & C. Djerassi* [1].