164. The Photoelectron Spectrum of Thiazyl Fluoride (NSF)[1]

by **D. O. Cowan**[2], **R. Gleiter**[2], **O. Glemser**[3], **E. Heilbronner**[2] and **J. Schäublin**[2]

Physikalisch-Chemisches Institut der Universität Basel and
Anorganisch-Chemisches Institut der Universität Göttingen

(24. V. 71)

Summary. The photoelectron spectrum of thiazyl fluoride has been recorded. An assignment of the first five bands has been attempted, using semi-empirical calculations.

Within the last few years there have been exciting developments in the field of sulfur-nitrogen compounds [2]. One of the key compounds is thiazyl fluoride, NSF, which can be conveniently prepared by thermal decomposition of $Hg(NSF_2)_2$ [3]. Microwave [4] and infrared [5] spectral analyses lead to the following structural data [4] [6]:

$$\begin{array}{llll} R(\mathrm{NS}) & = 1.446\,\text{Å}; & k(\mathrm{NS}) & = 10.72\cdot 10^5\,\mathrm{dyn\,cm^{-1}} \\ R(\mathrm{SF}) & = 1.646\,\text{Å}; & k(\mathrm{SF}) & = 2.88\cdot 10^5\,\mathrm{dyn\,cm^{-1}} \\ \alpha(\mathrm{NSF}) & = 116°52'; & k(\alpha) & = 0.98\cdot 10^{-11}\,\mathrm{dyn\,cm\,rad^{-2}} \end{array}$$

In order to learn more about the electronic structure of NSF we have investigated its photoelectron (PE.) spectrum and performed Extended *Hückel* (EHT) [7] and CNDO/2 [8] calculations on this molecule.

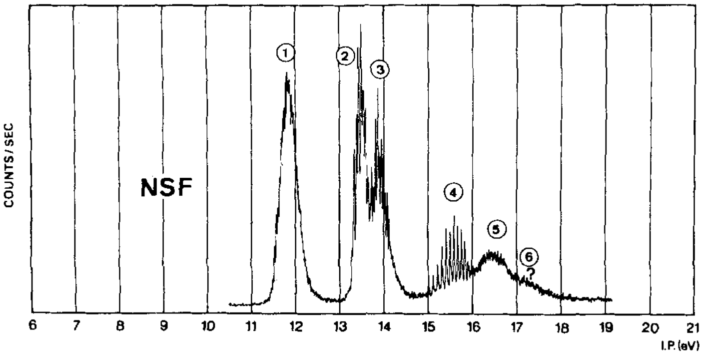

Figure 1. *Photoelectron spectrum of thiazyl fluoride (NSF)*

Fig. 1 shows the PE.-spectrum of NSF, as recorded on a *Turner*-type instrument [9] (PE.-spectrometer PS-16 of *Perkin-Elmer Ltd.*, Beaconsfield); the relevant data are collected in Table 1.

In the range 10 to 19 eV the PE.-spectrum of NSF consists of five clearly recognizable bands labelled ① to ⑤ in Fig. 1, and of a shoulder ⑥. The assignment of the first

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[1] Part 26 of 'Applications of Photoelectron-Spectroscopy'. Part 25: [1].

[2] Universität Basel.

[3] Universität Göttingen.

Table 1. *Vertical Ionization Potentials for NSF and Orbital Energies*

EHT: Extended *Hückel* Theory [7]; CNDO/2 [8]. All values in eV. The assignment of orbitals follows from the EHT results

			Orbital energies [c]		
Band J	$I_{v,J}$	Orbital	EHT [d]	[e]	CNDO/2 [d]
①	11.82	13**a**′ (σ)	–12.58	–12.80	–13.69
②	13.50	12**a**′ (σ)	–14.32	–14.39	–16.22
③	13.87	3**a**″ (π)	–14.99	–14.99	–15.36
④	15.61 [a]	11**a**′ (σ)	–16.85	–16.92	–19.53
⑤	16.47 [b]	10**a**′ (σ)	–18.20	–18.21	–20.15

[a] Vibrational maximum at 15.69 eV of same intensity.
[b] Shoulder ⑥ at 17.2 eV.
[c] Calculations assuming the experimentally determined geometry of the molecule.
[d] With neglect of *d*-orbitals on S.
[e] Including *d*-orbitals on S.

four bands follows from the *Walsh*-diagram of Fig. 2, which shows the dependence of the corresponding orbital energies on the bond angle α. This diagram, which is based on the numerical results of EHT calculations, is essentially the one given many years ago by *Walsh* for the general case of a triatomic molecule ABC [10].

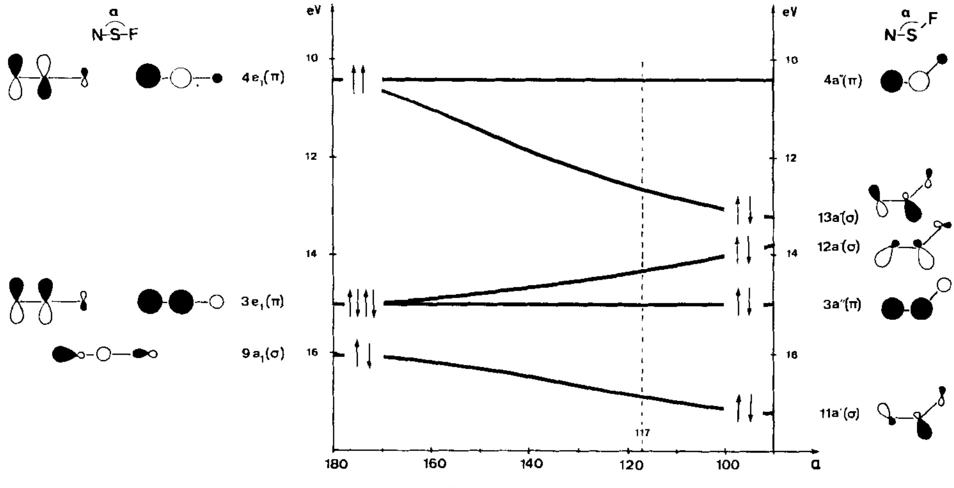

Figure 2. Walsh-*diagram for NSF*

The orbitals shown on the left are for $\alpha = 180°$ and those on the right for $\alpha = 117°$

For $\alpha < 180°$, the 32 electrons of the molecule occupy 16 orbitals, of which 1**a**″(π) to 3**a**″(π) belong to the irreducible representation A'' of C_s, and 1**a**′(σ) to 13**a**′(σ) to A'. In the limiting case of a linear molecule ($\alpha = 180°$) each of the two pairs of highest occupied orbitals, 4$\mathbf{e}_1$(π) and 3$\mathbf{e}_1$(π), is degenerate (belonging to E_1 of $C_{\infty v}$), but 4$\mathbf{e}_1$(π) contains only two electrons with parallel spin, so that a linear NSF molecule would be in a triplet ground state.

Neglecting the 14 inner-shell electrons, we are left with 18 valence electrons. For this number *Walsh* predicts [10] a mean bond angle of $\alpha \sim 120°$ (*e.g.* NOCl: $\alpha = 116°$; NOBr: $\alpha = 117°$; SO_2: $\alpha = 119°$; O_3: $\alpha = 130°$ [11]), in agreement with the experimental value of $\alpha = 117°$ found for NSF.

As can be seen from the orbital diagram of Fig. 2, the numbers and positions of the nodes in the upper occupied orbitals of NSF are also those expected on the basis of qualitative arguments.

Removal of an electron from $13\mathbf{a}'(\sigma)$, which yields the radical cation NSF^+ in its $^2\mathbf{A}'$ ground state, should lead, according to *Walsh,* to an increase in α (*e.g.* NO_2, 17 valence electrons, $\alpha = 154°$). On the other hand the first electronically excited state of the same symmetry ($^2\mathbf{A}'$), obtained by vacating $12\mathbf{a}'(\sigma)$, should be associated with an equilibrium geometry of NSF^+ with $\alpha < 117°$. Finally the first electronically excited $^2\mathbf{A}''$ state (ejection from $3\mathbf{a}''(\pi)$) should leave α essentially unaltered. For ionization processes in which electrons are removed from even lower lying orbitals, the predictions concerning changes in equilibrium geometry become increasingly doubtful.

The correlation between observed band positions and calculated orbital characteristics (symmetry and energy), such as shown in Table 1, is based on the validity of *Koopmans'* theorem, *i.e.* $\varepsilon_J = -I_{v,J}$. For experimental reasons the vertical ionization potentials $I_{v,J}$ are identified with the positions of the band maxima, *i.e.* with the positions of the respective fine-structure maxima with highest *Franck-Condon* factor.

EHT [7] and CNDO/2 [8] type calculations give similar level orderings, except for the $12\mathbf{a}'(\sigma)$ and $3\mathbf{a}''(\pi)$ orbitals. The bands ② and ③, which correspond to the ejection of an electron from one or the other of these orbitals, are separated by only 0.37 eV. As can be seen from Table 1, the EHT model places $12\mathbf{a}'(\sigma)$ above $3\mathbf{a}''(\pi)$ while CNDO/2 predicts the inverse order. In our experience EHT is often a better guide than CNDO/2 for the interpretation of photoelectron spectra (*e.g.* [12]), so that we propose tentatively the assignment given in Table 1.

The bands ②, ③ and ④ of the PE.-spectrum of NSF exhibit well resolved vibrational fine structure, as shown in Fig. 3.

A normal coordinate analysis for the neutral NSF molecule has been carried out by *Sawodny, Fadini & Ballein* [6]. We have repeated the vibrational analysis with the help of a recently described computer-program [13], using the force constants given by these authors [6]. The amplitude vectors and frequencies of the three normal modes are given in Table 2.

From our normal coordinate analysis the highest and lowest frequencies, $1372\ \mathrm{cm}^{-1}$ and $366\ \mathrm{cm}^{-1}$, correspond to an almost pure N–S stretching mode and to the N–S–F bending mode, respectively. The vibration with frequency $640\ \mathrm{cm}^{-1}$ is more mixed, but dominated by the stretching of the S–F bond.

In decomposing the vibrational pattern of the bands ② and ③ we have assumed that the almost complete separation of the normal modes relative to the three internal coordinates, observed for the neutral molecule NSF, is conserved in the radical cation NSF^+ in its respective electronically excited states. The relatively small changes in frequency of these normal modes on ionization can then be determined from an analysis of the vibrational fine structure of the appropriate PE.-band (see Fig. 3a and 3b, and Table 3).

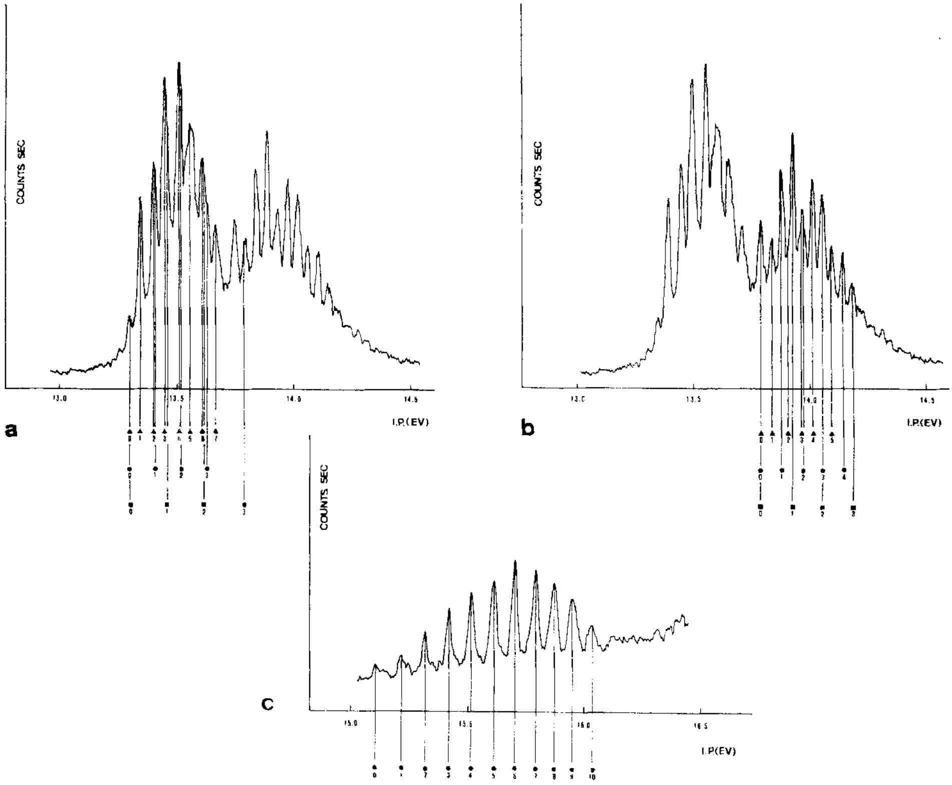

Figure 3. *Vibrational fine structure of the bands* ② (a), ③ (b) *and* ④ (c)
The vibrational progressions are characterized by the symbols ▲, ■, ●

Table 2. *Amplitude Vectors and Frequencies for the Three Normal Modes of the Neutral NSF Molecule*
The table lists the matrix elements of the **L**-matrix for the transformation **S** = **LQ**. The units of the elements in the columns r_{N-S} and r_{S-F} are 10^{20} Å $g^{-1/2}$ cm^{-1}, and in column α_{N-S-F} 10^{20} rad $g^{-1/2}$ cm^{-1}. The Q_i are in $g^{1/2}$ cm, interatomic distances in Å, and α_{N-S-F} in radian.

Q \ **S**	r_{N-S}	r_{S-F}	α_{N-S-F}	$\tilde{\nu}$ (cm^{-1})
Q_1	0.248	−0.042	−0.042	1372
Q_2	0.009	0.219	−0.087	640
Q_3	0.004	0.026	0.214	366

From Table 3 it is evident that it is rather difficult to draw definite conclusions from this analysis concerning the state of the radical cation NSF^+ to be associated with a given band in the PE.-spectrum. The only significant result is the reduction in the frequency of mode ν_1 in the progression of band ③. This is in agreement with what one might deduce from the orbital assignment given in Table 1 and Fig. 2. However, this 'confirmation' should be taken *cum grano salis*.

Table 3. *Frequencies (in Wavenumbers) of the Normal Modes of* NSF^+ *and NSF*

All values in cm^{-1}. The values in brackets are the 90 percent confidence limits, the values in italics the central values (see appendix)

	NSF^+			NSF
	$^2A'$	$^2A''$	$^2A'$	$^1A'$
	band ②[a]	band ③[a]	band ④[a]	[b]
$\tilde{\nu}_1$ (N–S)	(1227) *1334* (1441)	(977) *1058* (1139)		*1372*
$\tilde{\nu}_2$ (S–F)	*889*	(642) *707* (770)	(693) *746* (799)	*640*
$\tilde{\nu}_3$ (N–S–F)	(385) *422* (459)	(371) *476* (581)		*366*

[a] Frequencies deduced from an analysis of the vibrational fine structure of the corresponding PE.-band (see fig. 3b and 3c).

[b] Frequencies for the neutral molecule deduced from its infrared spectral analysis [6].

Table 4. *Analysis of the Vibrational Progressions in the Bands ②, ③ and ④ of the PE.-Spectrum of NSF*

The spacings are in eV, the results of the analysis in cm^{-1} (see text)

Band	②			③			④
Mode	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3	ν_2
Spacing 1–0	0.15_7	0.11_0	0.04_3	0.13_8	0.08_7	0.04_7	0.11_0
2–1	0.16_5	0.11_0	0.05_9	0.12_6	0.09_4	0.06_7	0.10_2
3–2	0.17_3	0.11_0	0.04_7	0.13_0	0.07_9	0.05_5	0.10_2
4–3			0.05_9		0.09_1	0.07_9	0.09_4
5–4			0.04_7			0.04_7	0.09_8
6–5			0.05_5				0.08_7
7–6			0.05_5				0.08_7
8–7							0.07_9
9–8							0.07_9
10–9							0.08_7
Results of the least squares analysis:							
Mean value	1334	889	422	1058	707	476	746
Standard error	64	–	51	48	54	110	86
Student's t (P = 0.1)	2.92	–	1.94	2.92	2.35	2.13	1.83
90% Confidence limit							
upper	1441	–	459	1139	770	581	799
lower	1227	–	385	977	642	371	693

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Appendix. Table 4 lists the analysis of the vibrational fine structure of bands ②, ③ and ④. The numbering of the spacings refers to Fig. 3. The spacings have been measured in arbitrary, units, which have been converted into the values in eV of Table 4 by multiplication with a scale factor.

The results of the least-squares analysis are given, for convenience, in cm^{-1}. The *Student-t*-values are those for P = 0.1 *i.e.* for 90 percent confidence limit.

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165. Synthesis and Absolute Configuration of Cryptostylines I, II, and III

by **A. Brossi** and **S. Teitel**

Chemical Research Department, *Hoffmann-La Roche Inc.*, Nutley, New Jersey 07110

Dedicated to Professor Dr. *H. H. Inhoffen* on the occasion of his 65th birthday

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Zusammenfassung. Die Darstellung der drei optisch aktiven natürlichen Alkaloide Cryptostyline I, II und III aus *Cryptostylis fulva Schltr.* und ihrer drei unnatürlichen Antipoden wird beschrieben. Es wird gezeigt, dass die drei natürlichen Cryptostyline *S*-Konfiguration besitzen. Die berichtete leichte Racemisierbarkeit der natürlichen Cryptostyline wird auf optische Unreinheit der ursprünglichen Präparate zurückgeführt.

The optically active alkaloids cryptostyline I, II, and III isolated by *Leander et al.* from *Cryptostylis fulva Schltr.* (*Orchidaceae*) are substituted 1-phenyl-tetrahydroisoquinolines whose basic chemical structures (shown below) have been elucidated by physical methods and verified by a straightforward synthesis of their (±)-isomers [1].