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## Electronic structure of the valence shell of $SPF_3$

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# SEZIONE II

**(Fisica, chimica, geologia, paleontologia e mineralogia)**

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**Chimica.** — *Electronic structure of the valence shell of* $SPF_3$ (*). Nota di MARCO V. ANDREOCCI e CLAUDIO FURLANI, presentata (**) dal Socio G. SARTORI.

RIASSUNTO — Lo spettro fotoelettronico del composto in esame consente l'assegnazione dei livelli energetici per tutti gli orbitali di valenza della molecola (ad eccezione di quelli basati principalmente su orbitali atomici di tipo *s*) e la correlazione con i livelli energetici di altri alogenuri di fosforile e tiofosforile.

## 1. INTRODUCTION

Photoelectron spectroscopy with ultraviolet excitation (UPS) has been widely employed in the investigation of the electronic structure of several tetrahedral phosphorus compounds, including phosphoryl and thiophosphoryl halides $OPX_3$ and $SPX_3$ [1, 2, 3, 4]. A fairly detailed picture of the relevant part of the valence orbital shell of the latter compounds has thus been obtained, except for the iodides, which are unstable, and for $SPF_3$ whose spectrum was not reported in the literature until very recently. We therefore undertook the He(I) photoelectron spectral study of gaseous $SPF_3$, and report here its results, which enable us to present a full interpretation of the electronic structure of this molecule, together with a comparison with other phosphoryl and thiophosphoryl halides already investigated in UPS. While the present work was being completed, Elbel and Tom-Dieck published the p.e. spectrum of $SPF_3$ [5] and its assignment in substantial agreement with the results of our work; some experimental details do however differ, and our analysis of the electronic structure of $SPF_3$ is presented here in more detail than in the papers by Elbel and Tom-Dieck [5].

## 2. EXPERIMENTAL

$SPF_3$ was prepared by exhaustive fluorination of $SPCl_3$ with an anhydrous $SbF_3$ and $SbCl_5$ catalyst according to the method of Roesky [6]. The gas, stored in monel cylinders, was admitted into the p.e. spectrometer via a glass reservoir. P.e. spectra were taken with a PS–18 Perkin Elmer instrument calibrated by argon and xenon as the reference gases. Considerable experimental difficulties were encountered in handling the highly reactive

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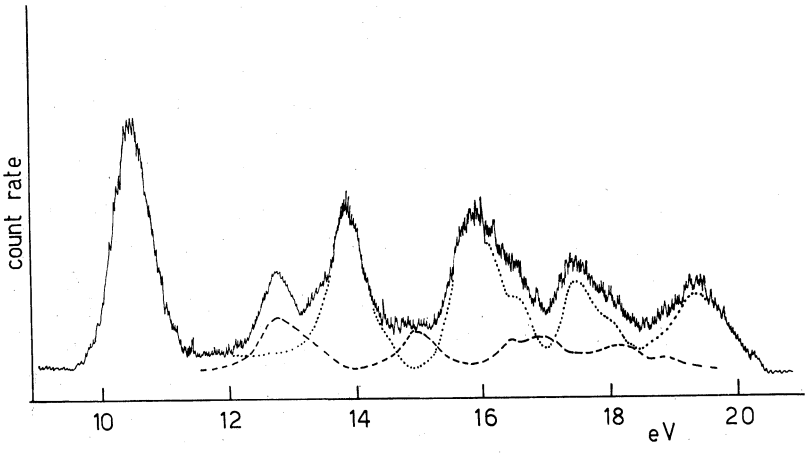
(**) Nella seduta dell'8 gennaio 1977.

$SPF_3$ gas within the spectrometer inlets and chamber. Although the gas was pure by physical standards, its p.e. spectrum became easily contaminated by small amounts of $OPF_3$, yielding spurious bands at 13.41 and 15.50 eV [1, 3], so we had to correct the experimental p.e. spectrum by subtracting the spectrum due to $OPF_3$ (almost the sole absorber at 13.4 eV), as given in previous works [1, 3].

## 3. Results

The He(I) p.e. spectrum is reported in the figure, and the measured vertical I.E.s are listed in the Table, together with the predicted energy values and orbital eigenvector data obtained from a CNDO/2 calculation [7]. The 32 valence electrons of $SPF_3$ occupy 16 m.o. levels (not all necessarily distinct, since the $C_{3v}$ point group allows degenerate representations) of which 5, mainly composed of atomic *s*-type valence orbitals, are expected to lie deep




He(I) p.e. spectrum of $SPF_3$, experimental and after correction for $OPF_3$ impurity (the dotted line is the extrapolated p.e. spectrum of $OPF_3$).

in energy, hence lower than the spectral range of He(I) radiation. All the remaining 11 orbitals can be identified in the experimental He(I) p.e. spectrum. A preliminary assignment can be reached on the grounds of the consideration that only three orbitals (the two $\pi$ lone pairs of S, and the P—S $\sigma$ bond) should fall at lower I.E. than the fluorine–based orbitals, which are expected in the region 16-20 eV by comparison with the known p.e. spectra e.g. of $PF_3$ and $OPF_3$ [1, 3, 8]. This immediately leads us to identifying the $\pi$ levels of S ($5\,e$) as the broad peak at 11.10, and the $\sigma$(P—S) ($5\,a_1$) bonding orbital at 14.47 eV, while the fluorine $\pi$ orbitals correspond to the sequence of peaks at 16.51 ($4e$), 16.95 ($1\,a_2$), 18.06 ($3\,e$) and 18.65 eV ($4\,a_1$). The last, intense band in the p.e. spectrum appears to be degenerate on the grounds of its relatively high intensity and should be the $2\,e$ level, mainly $\sigma$ (P—F), at 20.05 eV.

TABLE

*Calculated and experimental ionization energies* (eV) *of phosphoryl and thiophosphoryl fluoride*

| Phosphoryl fluoride | | | Thiosphosphoryl fluoride | | |
|---|---|---|---|---|---|
| Symmetry [a] | CNDO/2 [d] | Expt. [b] | Symmetry [a] | CNDO/2 [d] | Expt. [c] |
| $5e$ | 16.67 | 13.52 | $5e$ | 14.73 | 11.10 |
| $5a_1$ | 17.74 | 15.68 | $5a_1$ | 16.52 | 14.57 |
| $1a_2$ | 21.10 | 17.09 | $1a_2$ | 20.43 | 16.51 |
| $4e$ | 22.10 | 17.68 | $4e$ | 21.43 | 16.95 |
| $3e$ | 24.00 | 18.83 | $4a_1$ | 23.30 | 18.06 |
| $4a_1$ | 24.51 | 19.61 | $3e$ | 23.38 | 18.65 |
| $2e$ | 24.87 | 20.84 | $2e$ | 24.24 | 20.05 |

(*a*) The numeration refers to the valence orbitals only.
(*b*) From Ref. [3].
(*c*) This work.
(*d*) This work, with *d* orbitals included for all second row elements.

## 4. DISCUSSION

The $\pi$ (S) ionization at 11.10 eV appears to have a particularly low I.P. value, if one compares the shift of 2.42 eV from $OPF_3$ (13.52 eV) to $SPF_3$, with the corresponding shift of 1.78 eV on replacing O through S in the couple $OPCl_3$ (11.89)–$SPCl_3$ (10.11). Also, the replacement of Cl through F causes a blue shift of 1.63 eV between $OPCl_3$ and $OPF_3$, but of only 0.99 eV between $SPCl_3$ and $SPF_3$. The easy ionization of the $\pi$ pairs of S in $SPF_3$ is in agreement with the particularly high reactivity and oxidability of the compound, which is the only one of the thiophosphoryl halides unstable and spontaneously inflamed in air.

The $\sigma$ (P—S) ionization at 14.47 eV shows a more normal I.E. shift with respect to $OPF_3$ (—1.21 eV), or to $SPCl_3$ (+ 2.07 eV); this results in a particularly large difference between the first and the second ionization energy of $SPF_3$ (3.37 eV), which is not common in complex molecules, and can be related to the high reactivity $SPF_3$, in a molecule-in-molecule model of reaction mechanism intermediates.

Fluorine $\pi$ ionizations are comprised between 16.51 and 18.65 eV in $SPF_3$ (16.1–18.0 in $PF_3$ [8], and 17.09–19.61 in $OPF_3$ [1]). The effect of replacing O through S on the energy of fluorine $\pi$ orbitals is small (< 1 eV on the average) and this confirms the typical occurrence of $\pi$ ionizations in the range between approximately 16 and 19 eV for phosphorus-fluorine compounds. The experimental sequence of i.p.s. is $4e \lesssim 1a_2 < 3e < 4a_1$ in $SPF_3$, as in $PF_3$ [8], whereas it is $1a_2 < 4e < 3e < 4a_1$ in $OPF_3$ [1, 3]. Our CNDO/2 calculations, which are in general in good agreement with experimental I.E.s. for both $OPF_3$ and $SPE_3$, except for a nearly constant linear regression of about 4 eV, support the latter ordering in $OPF_3$ but predict a slightly different sequence of i.p.s in $SPF_3$ (see Table), namely $1a_2 < 4e < 4a_1 \lesssim 3e$. The $e$ level ionized at 20.05 eV is too low in energy to be a fluorine $\pi$ ionization; we assign it as the $e$ component of the $\sigma$(P—F) bonding orbitals, and its energy value compares favorably with 20.84 eV in $OPF_3$ [1, 3].

No vibrational structure was evident in our p.e. spectrum of $SPF_3$, although the instrumental resolution was largely sufficient. The $(5e)$ peak is fairly broad and symmetric (much like $SPCl_3$ and $OPF_3$), despite the practically nonbonding character of the orbital, which is more strongly localised on S and less intermixed with the $e$ components of $\pi$(X) and $\sigma$(P—X) than in other $OPX_3$ and $SPX_3$ molecules (apart from a possible weak double bond character involving $d$-orbitals of P). Thus, Jahn-Teller distortion of the $(5e)^{-1}$ molecular ion state remains the most likely cause of the observed broad band shape.

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