The Electronic Structure of Trifluorophosphine Studied by Photoelectron Spectroscopy with Variable Photon Energy†

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The photoelectron spectrum of PF_3 has been measured using synchrotron radiation. Relative partial photoionization cross-section and branching ratio data are reported for the valence bands (8–24 eV) over the photon-energy range 30–95 eV. Molecular orbitals regarded previously as purely fluorine lone pair in composition are shown to have significant phosphorus 3p character. Comparison of the results obtained on PF_3 with those obtained previously on $[Ni(PF_3)_4]$ shows that the complex molecular orbitals of the latter derived from the 5e orbitals of PF_3 have some nickel 3d character. Metal-to-phosphorus back donation, proposed to occur through the 7e PF_3 molecular orbitals, is thus shown also to involve the 5e.

The extent to which trifluorophosphine can act as a π acceptor in its complexes with transition metals has been the subject of widespread debate.[1–13] Empty, low-lying, PF_3 orbitals, of π character with respect to the metal–ligand bond, are cited as participating in metal-to-ligand back bonding, in a manner analogous to the π* orbitals in the carbon monoxide ligand. These orbitals could be of phosphorus 3d character, or P 3p/F 2p antibonding orbitals. Evidence for the role of PF_3 as a π acid comes from the similarities in occurrence and stoichiometry of M–PF_3 and M–CO complexes,[14,15] In a recent publication concerning our photoelectron (PE) spectroscopic study of the complex $Ni(PF_3)_4$[16] we presented evidence to support the existence of Ni→P back donation.

The valence electronic structure of PF_3, which has C_{3v} symmetry, is $(5a_1)^2(3e)^4(6a_1)^2(4e)^4(7a_1)^2(5e)^4(1a_2)^2(6e)^4(8a_1)^2$ using the numbering scheme of Xiao *et al.*[11] The $5a_1$ and 3e orbitals are predominantly F 2s in character and lie very low in energy in valence-orbital terms. The $6a_1$ and 4e orbitals are traditionally regarded as P–F σ-bonding orbitals and the $7a_1$, 5e, $1a_2$ and 6e orbitals as F $2p_\pi$ orbitals. The $8a_1$ orbital is viewed as primarily a phosphorus lone-pair orbital. The $6a_1$ orbital lies too low in energy to be ionized by He I radiation, although previous workers have identified the band at 22.55 eV in the He II PE spectrum of PF_3 as being due to ionization from this orbital.[17] The earlier photoelectron spectroscopic studies are in agreement as to the assignment of the spectrum, which is given in Table 1. Both self-consistent field-molecular orbital (SCF-MO)[9,10] and -discrete variational SCF-Xα-DV[11] calculations have been performed on PF_3 to give an MO ordering differing from that inferred (on the basis of Koopmans' approximation) from the experimentally determined ion-state ordering only in reversing the $1a_2$ and 6e orbitals.

Measurement of PE cross-sections over a range of photon energies can give information on the atomic orbital (AO) constituents of the molecular orbital (MO) from which ionization arises.[18–20] In the study of trifluorophosphine presented here we sought not only to shed further light on the MO structure of PF_3 itself, but also to confirm the Ni→P back donation observed previously.

Table 1 Assignment of the PE spectrum of PF_3[17]

Band	1	2	3	4	5	6
i.e. (eV)	12.3	15.9	17.4	18.5	19.4	22.6
Ion state	$^2A_1$	$^2E + {}^2A_2$	^2E	$^2A_1$	^2E	$^2A_1$
Related MO	$8a_1$	$6e + 1a_2$	5e	$7a_1$	4e	$6a_1$

Experimental

A sample of PF_3 was obtained commercially from Fluorochem. Its He I PE spectrum was compared with that obtained previously[17] and the sample was judged to be sufficiently pure to use without further purification.

The PE spectra of PF_3 were obtained using beam line 3.3 at the synchrotron source at the SERC Daresbury Laboratory. A full account of the angle-resolved photoelectron spectrometer employed and our experimental method has been given previously.[18,21] Spectral aquisition times varied from approximately 10 min at low photon energies (30–40 eV) to over 1 h at high photon energies (80–95 eV). Details of the output flux from the beam line and the spectral purity from the toroidal grating monochromator can be found in ref. 22. The experimental arrangement differed from that normally used in that the gaseous sample was held outside the spectrometer, and admitted to the ionization region through a needle valve.

Results and Discussion

The PE spectrum of PF_3, obtained at photon energies of 45 and 60 eV, is shown in Fig. 1. Asymmetric Gaussian functions were used to fit the peaks and thus obtain the band-area data used in the relative partial photoionization cross-section (r.p.p.i.c.s.) calculations.

The photoionization cross-section behaviour of MOs is to a large extent controlled by the cross-section behaviour of their constituent AOs[23,24] though molecular features such as shape resonances[25] and autoionization[26] also play their part. Over a wide photon-energy range such as the 30–95 eV used here we expect the overall trend in relative cross-section to be dominated by atomic effects. For PF_3 the principal AOs involved are the P 3p and 3s orbitals and the F 2p orbitals, the F 2s orbitals lying too deep to be part of the valence shell. Fig. 2 shows calculated cross-section data for these three AOs,[27] the most striking feature of which is that the cross-section of the fluorine 2p orbital is much greater than that of the phosphorus 3s and 3p orbitals over the photon-energy range employed in

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† *Non-SI units employed:* eV ≈ 1.60×10^{-19} J; b = 10^{-28} m^2.

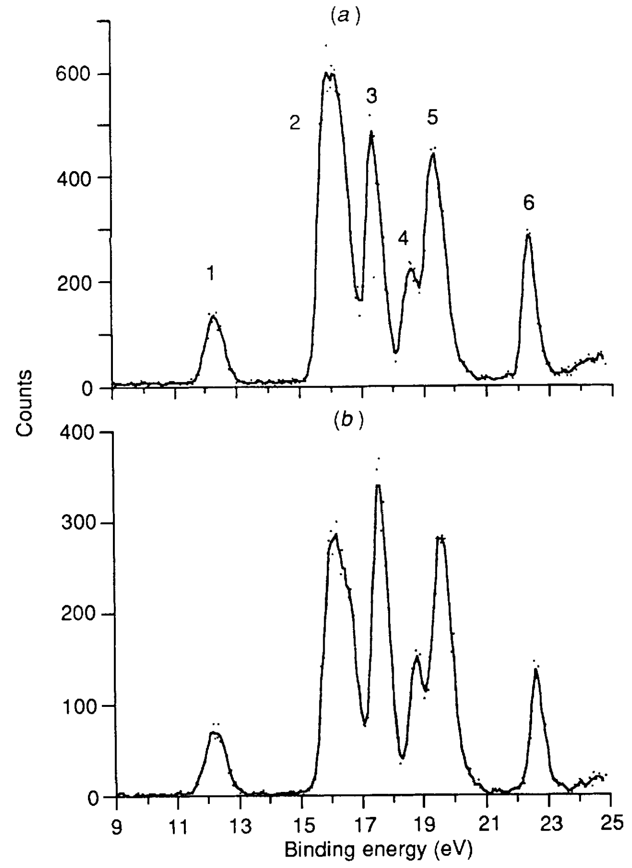

Fig. 1 The photoelectron spectrum of PF_3, obtained at photon energies of (*a*) 45 and (*b*) 60 eV

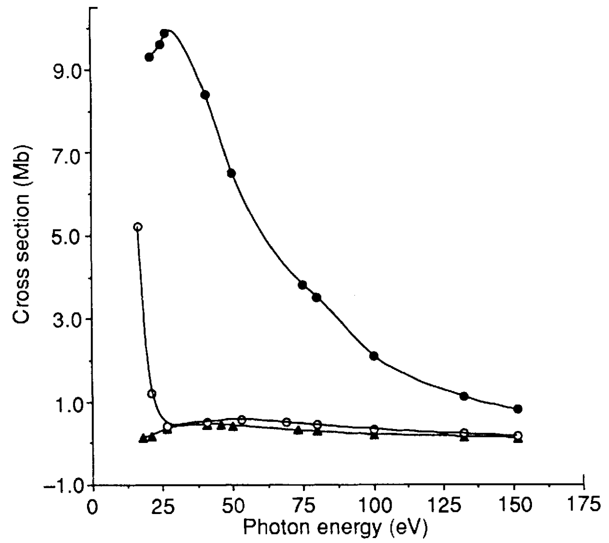

Fig. 2 Calculated cross-section data for the 3s (▲) and 3p (○) atomic orbitals of phosphorus and the 2p (●) atomic orbital of fluorine

our investigation. If this were the case in reality we would expect the cross-section behaviour of the bands in the PE spectrum of PF_3 to be totally dominated by the F 2p contribution to the ionizing MOs. That this is not found to be so leads us to regard the absolute numerical values for the calculated AO cross-sections with some suspicion, although the general trends should be more reliable. The F 2p cross-section falls steeply over the photon-energy range 30–95 eV whereas the P 3s and 3p cross-sections are less variable over this range. We can use these features to get a qualitative estimate of F 2p character in the various MOs.

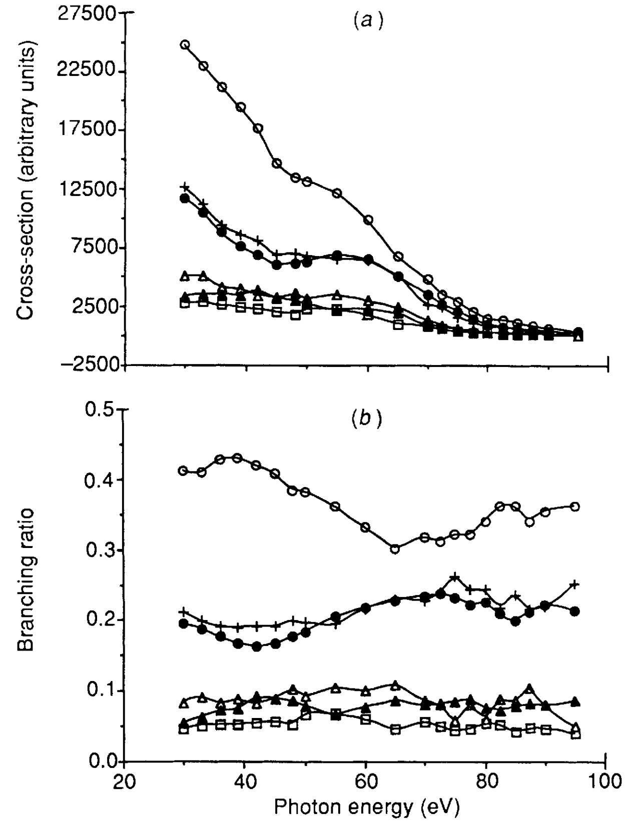

Fig. 3 Plots of (*a*) r.p.p.i.c.s. and (*b*) b.r.s of bands 1–6 in the photoelectron spectrum of PF_3, as a function of incident photon energy. Bands: 1 (□), 2 (○), 3 (●), 4 (△), 5 (+) and 6 (▲)

Fig. 3(*a*) gives the r.p.p.i.c.s. for the first six PE bands of PF_3 and Fig. 3(*b*) presents their branching ratios (b.r.s). The r.p.p.i.c.s. plot reveals band 2 to have the steepest fall off in cross-section, followed by bands 3 and 5 and finally 1, 4 and 6. In relating cross-section behaviour to the amount of F 2p character in the MOs giving rise to a PE band we must take account of the number of orbitals ionizing under that band. The gradient of the r.p.p.i.c.s. plot of a band due to ionization from three MOs will be three times as great as that from a band arising from only one MO if all of the MOs have similar AO constituents. Band 2 arises from ionization of three orbitals (6e + $1a_2$), 3 and 5 from ionization of degenerate orbitals (5e and 4e respectively) and 1, 4 and 6 from singly degenerate ($8a_1$, $7a_1$ and $6a_1$). At 30 eV, for example, the b.r. per orbital is *ca.* 0.14 for band 2, 0.1 for bands 3 and 5, 0.08 for band 4 and 0.05 for bands 1 and 6. As the photon energy is increased the b.r. ordering remains largely unaltered, although the differentiation between them becomes smaller. This results from the differing rates of fall off in cross-section of the six bands and we therefore estimate the F 2p contribution to decrease in the series $1a_2 \approx 6e > 4e \approx 5e > 7a_1 > 6a_1 > 8a_1$. The percentage atomic characters of the various MOs calculated by Xiao *et al.*[11] are given in Table 2. From these it can be seen that our experimental results differ from the calculation with regard to the F 2p content of the 5e MO. Xiao suggests that the $1a_2$, 6e and 5e MOs are almost pure F 2p, whereas the behaviour of band 3 in both the r.p.p.i.c.s. and b.r. plots indicates a F 2p content more in line with that of the 4e MO. The fluorine contribution to the 5e MO is therefore found to be smaller than that predicted by the calculation.

Fig. 4 presents the r.p.p.i.c.s. of each of the six valence bands, plotted against the kinetic energy (k.e.) of the photoelectron rather than against the incident photon energy [as in Fig. 3(*a*)]. This method is useful for directly comparing MO cross-section features with those of AOs, in that it eliminates difficulties that may arise from the shift in ionization energy (i.e.) between atom and molecule. Molecular orbital cross-sections may also be more effectively compared with each other in this manner. Several of the bands show a feature in their r.p.p.i.c.s. between k.e.s of 30 and 50 eV, which in some cases corresponds to a distinct maximum (bands 1, 3 and 6) and in others to a change in gradient or 'shoulder' (bands 4, 5 and, to a lesser extent, 2). As the strength of the feature seems to correlate inversely with fluorine content, it may well be associated with the phosphorus content of the related MO. The Cooper minimum of the P 3p AO is calculated to occur at a photoelectron k.e. of 18 ± 5 eV. The AO cross-section then passes through a maximum at a k.e. of 45 ± 5 eV, and it is this feature that may be giving rise to the MO cross-section maxima in the k.e. range 30–50 eV. The possibility that these maxima may be due to a shape resonance should also be considered, but the fact that the feature occurs at the same k.e. for all of the bands strongly suggests that it is related to the P 3p content of the MOs.

Bands 1 and 6 (the $8a_1$ and $6a_1$ MOs respectively) have similar cross-section behaviour. Both have the distinct maximum at k.e. of *ca.* 40 eV, which is stronger in band 1, and there is another maximum in both cross-sections at low photoelectron k.e.s (20.70 and 13.40 eV), which is more pronounced in band 6. This can be attributed to the maximum in the P 3s AO cross-section which occurs at a k.e. of 24 ± 5 eV. The magnitude of the maxima suggests that the $8a_1$ MO has a larger P 3p contribution than 3s, and that the $6a_1$ MO has more 3s than 3p. The sharp feature in the cross-section of band 6 at a k.e. of 19.40 eV cannot be readily explained on AO grounds, and is attributed to a molecular shape resonance. The cross-section data support the calculation in revealing a P 3s contribution to the $8a_1$ and $6a_1$ MOs, and in suggesting that this is greater in the

Table 2 Ground-state valence orbitals of PF_3 calculated by the SCM-Xα-DV method[11]

	Atomic composition						
	P			F			
Orbital	3s	3p	3d	2s	3s	2p	3p
$6a_1$	0.35			0.23	0.01	0.40	0.01
4e		0.16	0.01	0.06	0.01	0.76	
$7a_1$	0.06	0.14	0.02	0.01		0.77	
5e			0.02			0.97	
6e			0.01			0.99	
$1a_2$						0.99	
$8a_1$	0.29	0.32	0.01		0.01	0.36	

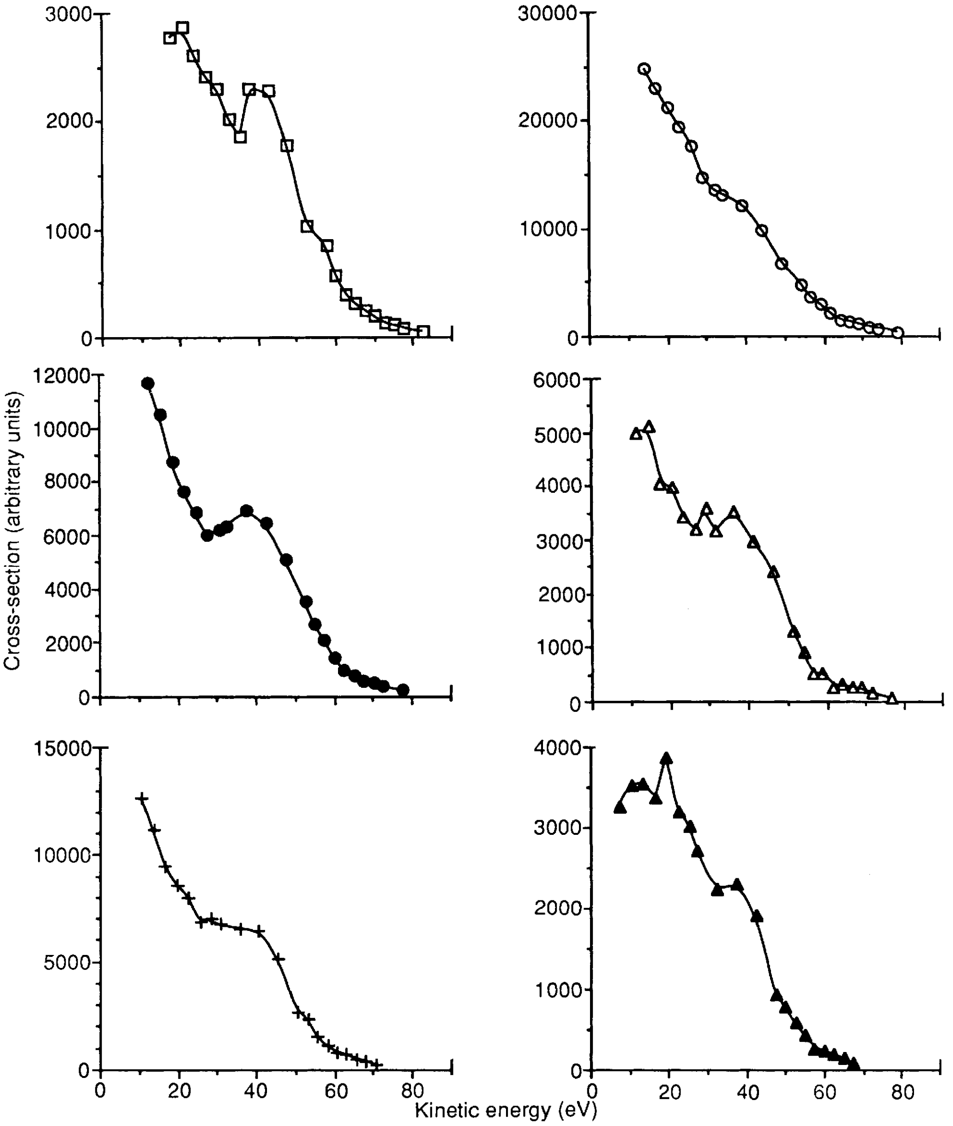

Fig. 4 Plots of r.p.p.i.c.s. of the six valence bands (symbols as in Fig. 3) in the photoelectron spectum of PF_3, as a function of photoelectron kinetic energy

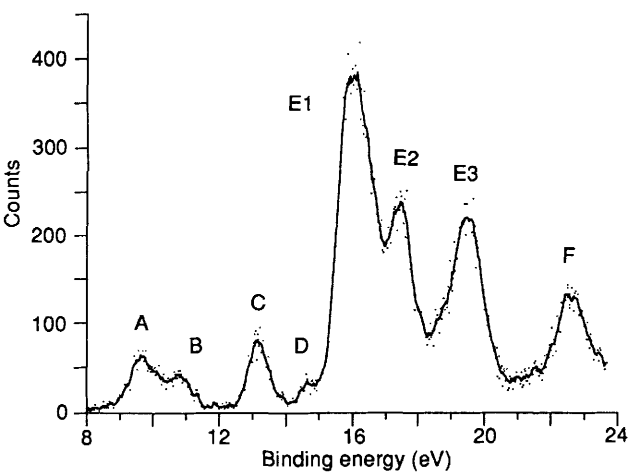

Fig. 5 The photoelectron spectrum of [Ni(PF$_3$)$_4$], obtained at a photon energy of 45 eV

Table 3 Assignment of the PE spectrum of [Ni(PF$_3$)$_4$][16,28]

Band	i.e. (eV)	Assignment	PF$_3$ parent orbital
A	9.69	2t$_2$ (Ni 3d)	
B	10.74	1e (Ni 3d)	
C	13.17	1t$_2$ (M–P)	8a$_1$
D	14.65	a$_1$ (M–P)	8a$_1$
E1	15.97	F lone pair	6e, 1a$_2$
E2	17.48	M–P–F bonding*	5e
E3	19.42	P–F bonding	4e, 7a$_1$
F	22.40	P–F bonding	6a$_1$

* Original assignment (to fluorine lone pair) in ref. 28 altered following the work reported in ref. 16.

6a$_1$ MO. Calculation and experiment differ, however, in that the 6a$_1$ MO is predicted to have no P 3p character whatsoever; we find this to be inconsistent with the experimental evidence. The fluorine contribution to the 8a$_1$ MO is predicted to be smaller than that of phosphorus. Experiment suggests that this is indeed the case, and that it is also true for the 6a$_1$ MO, contrary to the results of the calculation.

As stated above, the 6e and 1a$_2$ (band 2) and the 5e MOs (band 3) are calculated to be pure F 2p. However, the r.p.p.i.c.s. results for band 3 indicate significant P 3p AO character to the MO in that its cross-section profile is reminiscent of that of an AO passing through its Cooper minimum, which the F 2p cannot have as it does not possess a radial node. The behaviour of band 2 suggests that the 6e and 1a$_2$ MOs are in closer agreement with the results of the calculation. The cross-section data for the three bands arising from ionization of e-type MOs indicate that the 5e have the greatest P 3p AO contribution. Very little phosphorus character is found for the 6e MO, with the 4e intermediate between the two.

The 7a$_1$ (band 4) and 4e (band 5) MOs are calculated by Xiao *et al* to be predominantly F 2p ($\approx 75\%$), although a P 3p contribution ($\approx 15\%$) is predicted. The cross-section profiles of bands 4 and 5 are very similar, although the data for band 4 are somewhat erratic between k.e.s of 26 and 41 eV. Both have an initial fall (≈ 11 to ≈ 26 eV), a region in which the cross-section decrease is halted (≈ 26 to ≈ 41 eV) and another subsequent fall. This suggests that these two MOs have very similar AO constituents, in proportions consistent with the Xα calculation.

It is therefore possible to explain the experimentally determined MO cross-sections adequately in terms of AO cross-section behaviour. The results indicate that the degree of P 3p–F 2p AO mixing in the valence orbitals of PF$_3$, notably the 5e orbital, is greater than that predicted by calculation.

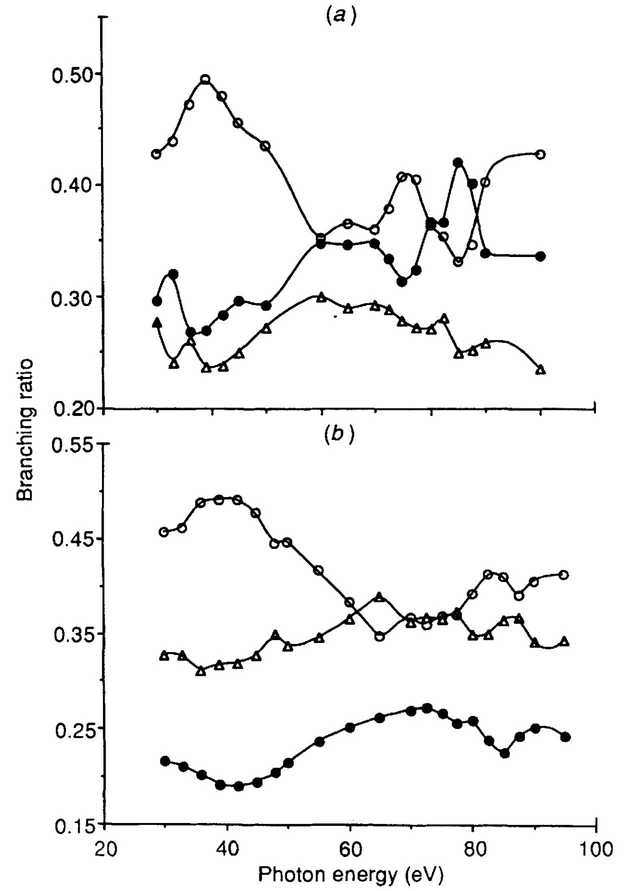

Fig. 6 Renormalized b.r.s of (*a*) bands E$_1$ (○), E$_2$ (●) and E$_3$ (△) in the photoelectron spectrum of [Ni(PF$_3$)$_4$] and (*b*) bands 2 (○), 3 (●) and (4 + 5) (△) in the photoelectron spectrum of PF$_3$

One of our aims in carrying out this study of PF$_3$ was to compare the results with those obtained on [Ni(PF$_3$)$_4$]. The spectrum of [Ni(PF$_3$)$_4$], obtained at a photon energy of 45 eV, is given for comparison in Fig. 5. Table 3 gives the assignment of the spectrum, the details of which have been discussed elsewhere.[16,28] Bands A and B are due to ionizations from the Ni 3d-based 2t$_2$ and 1e MOs, while bands C and D are assigned to the orbitals responsible for binding the PF$_3$ units to the metal (the 1t$_2$ and a$_1$ MOs). Above an i.e. of 15.5 eV, the PE spectra of [Ni(PF$_3$)$_4$] and PF$_3$ are very similar, and the three E bands correlate directly with features in the PE spectrum of PF$_3$. The E1 band arises from ionization of MOs derived from the PF$_3$ 6e and 1a$_2$ MOs (band 2), the E2 from the 5e (band 3) and the E3 band from the 7a$_1$ and the 4e PF$_3$ MOs (bands 4 + 5).

Fig. 6 shows the renormalized b.r.s of the E bands in [Ni(PF$_3$)$_4$], and those of the corresponding bands in PF$_3$. It is immediately clear that the PF$_3$ 5e band is of lower relative intensity than the E2 band in [Ni(PF$_3$)$_4$]. In addition, the marked b.r. behaviour of the E2 band in the photon-energy range 70–90 eV is not observed for band 3 in the PE spectrum of PF$_3$. The behaviour of the E2 band in this region may be explained by assuming some Ni 3d character to the MOs from which ionization is occurring. The cross-section of PE bands with Ni 3d character may be enhanced in the region of the Ni 3p subshell i.e.s (3p$_{3/2}$, 73; 3p$_{1/2}$, 75 eV) on account of the p $\longrightarrow$ d giant resonance effect.[29] This occurs when the photon energy causes excitation of an inner p electron, of the same primary quantum number as that of the valence d electron ionized, to an empty d level. A super Coster–Kronig transition may then occur, in which an electron falls back into the p hole and a valence electron is ionized. d Photoionization cross-sections at such photon energies can be substantially enhanced as another favourable channel for ionization becomes available. Increases in the r.p.p.i.c.s. of PE bands in the region of metal p subshell i.e.s are taken as evidence of metal d character to the ionizing MOs. That the E2 band's b.r. behaviour in the photon-energy region 70–90 eV is not mirrored by that of band 3 in PF_3, together with the fact that the E2 band has a higher relative intensity at all photon energies, is strong evidence to support a Ni 3d contribution to the MOs giving rising to the E2 band.

The 7e (unoccupied) MOs of PF_3 are believed to be the main ones involved in $M \rightarrow PF_3$ back donation, but our studies of $[Ni(PF_3)_4]$ and PF_3 suggest that the levels derived from the PF_3 5e MOs are also involved in the metal–ligand π-bonding process. The cross-section results on band 3, which indicate a significant P 3p contribution to the 5e MOs, tie in with the b.r. behaviour of the E2 band. Any largely ligand-based MO in $[Ni(PF_3)_4]$ that exhibits Ni 3d character must have some P 3p contribution as direct Ni–F overlap will be small, and our results strongly indicate that the 5e level is P–F π bonding.

Conclusion

The r.p.p.i.c.s. of the valence bands of PF_3 show contributions from P AOs, not only to the $8a_1$ (lone pair) orbital and the 4e and $6a_1$ σ-bonding orbitals, but also to the 5e and $7a_1$ orbitals which may be regarded as π bonding.

A comparison of branching ratios for ionizations from corresponding bands in the spectra of PF_3 and $[Ni(PF_3)_4]$ demonstrates a Ni 3d contribution to the orbitals in $[Ni(PF_3)_4]$ derived from the 5e orbital of PF_3. Thus the π-back donation which is proposed to occur between the Ni 3d orbitals and the 7e lowest unoccupied molecular orbital (LUMO) of PF_3 is also seen to affect the composition of the 5e-derived orbitals.

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