Photoelectron Spectra of Halides. Part III.[1] Trifluorides and Oxide Trifluorides of Nitrogen and Phosphorus, and Phosphorus Oxide Trichloride

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High-resolution photoelectron spectra, obtained with He^{I} (584 Å) and He^{II} (304 Å) resonance radiation, are reported for NF_3, PF_3, NOF_3, and POF_3. A low-resolution He^{I} spectrum of $POCl_3$ is also reported; vertical ionisation potentials (i.p.) and in many cases estimates of adiabatic i.p. also, are tabulated for all the compounds. The agreement of the experimental orbital assignments with *ab initio* calculations is excellent for PF_3, POF_3, PCl_3, $POCl_3$, good for NF_3, but less good for NOF_3. The correlations of the energy levels of PF_3 with those of POF_3, and of PCl_3 with $POCl_3$, follow a simple pattern of strong stabilisation of the lone pair of the donor molecule upon bonding to the O atom, with smaller stabilisations of the remaining orbitals. Correlations of the levels of $POCl_3$ with those of $SiCl_4$, and of POF_3 with SiF_4 are similarly satisfactory, but no simple pattern appears in the correlation of NOF_3 with CF_4 or with NF_3.

EARLIER papers in this series have examined the He^{I} photoelectron spectra of the boron trihalides,[1] and of the tetrachlorides and tetrafluorides of elements in Group IVB.[2] The occupied orbitals of Group V trihalides may be derived from those of the planar monomeric Group III trihalides by moving the central atom out of the X_3 plane and adding a pair of electrons.[3] The additional electron pair is usually associated with Lewis base or donor properties, but while phosphorus trifluoride forms a wide range of donor–acceptor complexes,[4] the only stable compounds so far prepared which may be regarded as donor complexes of nitrogen trifluoride are nitrogen oxide trifluoride [5] NOF_3 and some compounds containing the NF_4^+ unit,[6] though protonation of NF_3 has been observed in the gas phase.[7] It seemed possible that the photoelectron spectra of the compounds NF_3, PF_3, NOF_3, and POF_3 would provide some information about this difference in donor properties. For these compounds we have been able to extend the studies to ionisation potentials (i.p.) beyond 21 eV [†] by the use of the 304 Å ionised helium resonance line, in addition to the conventional 584 Å He^{I} line. The oxide trifluorides are isoelectronic with the Group IV tetrafluorides, so these compounds form an interesting link between the two previous papers in this series. Phosphorus oxide trichloride $POCl_3$ has been studied mainly because of its relationship with silicon tetrachloride. While this work was in progress we became aware that others were also studying the trihalides,[8,9] so we have not studied phosphorus trichloride except for some early low-resolution work which has been described.[10] Preliminary reports on some of the present work have been made.[11,12]

EXPERIMENTAL

He^{I} Studies were begun using a retarding grid analyser instrument,[2] but most of the work reported here has been carried out using a cylindrical deflection analyser instrument (Perkin-Elmer PS 15) which has much higher resolution. The first band in NOF_3 was also examined with a PS 16 spectrometer. The techniques of sample handling and spectrum calibration have been described.[1,2,13] $POCl_3$ was only studied with the grid analyser; POF_3 has been studied with both instruments, and the other compounds have only been studied with the deflection analyser. Since the latter instrument operates by scanning the analyser potentials, which produces an effective decrease in slit width through the spectrum, the apparent intensities of bands decrease approximately linearly with electron energy (21·22 − i.p.), but intensities from the grid instrument are constant throughout the range.[14]

He^{II} Spectra were obtained by Mr. H. J. Lempka with a Perkin-Elmer PS 16 instrument. Only a small number of runs could be carried out for each compound, and calibration relied upon the i.p. of helium (24·58 eV) and the bands in the spectrum whose i.p. had already been established by the He^{I} work. Consequently the precision of these measurements is considerably lower than those measured in the He^{I} spectra. The resolution used was not sufficiently high to detect the presence of vibrational fine structure.

$POCl_3$ was taken from laboratory stock, NF_3 was an Air Products sample supplied by Professor H. J. Emeléus, and PF_3 was a Matheson sample provided by Dr. M. J. Ware. NOF_3 was prepared by the pulsed discharge method described elsewhere,[15] and purified *via* the boron trifluoride complex.[5] POF_3 was prepared by heating a mixture of calcium fluoride and phosphorus(v) oxide to *ca.* 600 °C, and then purified by storage over sodium fluoride for several days.[16] Final purification of all compounds was carried

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[†] 1 eV = 1·6021 × 10^{-19} J, 1 Å = 100 pm.

[1] Part II, P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), **1971**, 1551.

[2] Part I, P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), **1971**, 641.

[3] A. D. Walsh, *J. Chem. Soc.*, 1953, 2031.

[4] R. Schmutzler, *Adv. Fluorine Chem.*, 1965, **5**.

[5] W. B. Fox, J. S. MacKenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. Juurik, *Inorg. Chem.*, 1968, **7**, 2064 and references cited therein.

[6] W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Chem.*, 1967, **6**, 1156.

[7] D. Holtz, J. L. Beauchamp, W. G. Henderson, and R. W. Taft, *Inorg. Chem.*, 1971, **10**, 201.

[8] A. W. Potts, Ph.D. Thesis, University of London, 1969.

[9] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans. A*, 1970, **268**, 59.

[10] D. R. Lloyd, *Internat. J. Mass Spectrometry Ion Phys.*, 1970, **4**, 500.

[11] P. J. Bassett and D. R. Lloyd, *Chem. Phys. Letters*, 1970, **6**, 166.

[12] P. J. Bassett, D. R. Lloyd, I. H. Hillier, and V. R. Saunders, *Chem. Phys. Letters*, 1970, **6**, 253.

[13] D. R. Lloyd, *J. Phys.* (*E.*), 1970, **3**, 629.

[14] O. K. Klemperer, 'Electron Optics,' 2nd edn., Cambridge University Press, Cambridge, 1963, p. 414.

[15] P. J. Bassett and D. R. Lloyd, *J. Chem. Soc.* (*A*), **1971**, **3377**.

[16] G. Montel, *Bull. Soc. chim. France*, 1952, 379.

out by fractional distillation *in vacuo*. The gas-phase i.r. spectra were checked for the presence of impurities, and none were found. However, in the i.r. spectrum of POF_3 a weak band was observed at 1980 ± 5 cm^{-1} which is not reported in the literature,[17] though this reference reports the presence of several impurity bands at unspecified wave numbers. No change in the relative intensity of this band could be detected after several fractional distillations, nor could any impurity be detected in the mass spectrum, so we consider that this band is a real feature of the i.r. spectrum, and may be assigned to $2\nu_4$ ($\nu_4 = 990$ cm^{-1}).

Attempts have been made to separate the components of the composite bands in the PF_3 and POF_3 photoelectron spectra, using a DuPont Curve Resolver. The results of these attempts are shown as dotted curves on Figure 1, and the modified i.p. values for the components are in the footnotes to the Table. The results of separate attempts at curve fitting were fully consistent in the relative intensities of the components, and it was certainly not possible to fit the curves with a high intensity component at the low i.p. side for either compound.

RESULTS AND DISCUSSION

The spectra of PF_3, NF_3, POF_3, and NOF_3, obtained with the deflection analyser instruments, are shown in Figure 1, and the measured vertical i.p., and where appropriate adiabatic i.p. also,* are given in the Table.

Adiabatic and vertical ionisation potentials, with vibrational intervals, in eV [a]

	NF_3	PF_3	NOF_3	POF_3	$POCl_3$ [b]
a	12·97(4)	11·66(1)	13·36(1)	12·77(4)	11·58(5)
v	13·73(3)	12·29(1)	14·11(5)	13·52(2)	12·13(4)
p		0·059(3)	0·127(3)		
a	15·49(4)	15·31(5)	14·83(6)	15·16(4)	
v	16·15(5)	15·89(2) [c]	15·54(5)	15·68(2)	12·52(4)
p					
a			16·34(3)	16·69(5)	
v	16·55(5)	16·31(7) [d]	16·88(8)	17·09(2) [g]	13·18(5)
p					
a	17·16(3)	17·08(1)	19·90(2)		
v	17·52(3)	17·45(1)	20·17(1)	17·68 [g]	13·63(4)
p					
a	19·24(3)	18·26(1)		18·45(2)	
v	19·71(3)	18·57(1)	21·1(1)	18·83(2)	13·99(5)
p		0·086(1) [e]		0·089(3)	
a		19·06(1)			15·35(6)
v	21·14(7)	19·36(1)		19·61	15·54(6)
p		0·082(1) [f]		0·089(6)	
a				20·36(2) [b]	16·34(2)
v		22·6		20·82(2) [b]	16·63(2)
p				0·081(10)	
a					19·48(3)
v				23·4(1)	

[a] Standard deviations are shown in parentheses, in units of the immediately preceding digit; a = adiabatic i.p., v = vertical i.p., p = vibrational interval of a progression. [b] Determined using a retarding grid spectrometer. [c] Band maximum; using curve resolver, maximum is 15·83(2). [d] Band shoulder; using curve resolver, maximum is 16·34(6). [e] Progression interval; the band shows a doublet spacing of 0·049(3). [f] Progression interval; doublet spacing 0·044(3). [g] Curve resolver value.

The spectra at the right hand side of Figure 1 are obtained with He^{II} radiation; the voltage scale for these spectra is half that for the He^{I} spectra. PF_3, POF_3, and NOF_3 show fine structure on some of the bands, which are shown in detail in Figure 2; no closing up from anharmonicity could be detected on these bands, so averaged values of the intervals are reported, also in the Table. Grid analyser spectra of POF_3 and $POCl_3$ are shown in Figure 3; i.p. for $POCl_3$ in the Table are all measured from such spectra, and the values recorded

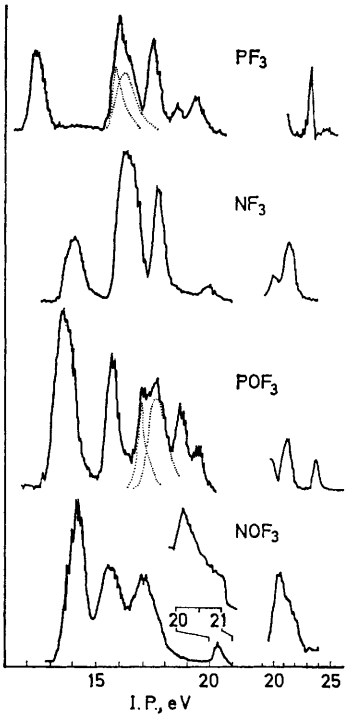

FIGURE 1 Photoelectron spectra, obtained with a deflection analyser instrument, for PF_3, NF_3, POF_3, and NOF_3. The left-hand spectra are obtained with He^{I} radiation, the right-hand spectra with He^{II} radiation. The energy scale for the He^{II} spectra is compressed by a factor of 2. The inset shows an expansion of the last band of NOF_3 in the He^{I} spectrum

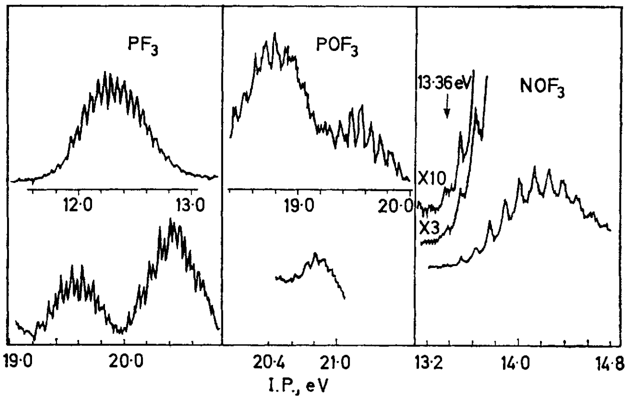

FIGURE 2 The fine structure in the photoelectron spectra of PF_3, POF_3, and NOF_3

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* Reservations concerning the adiabatic i.p. have been discussed in Part II.

[17] H. S. Gutowski and A. D. Liehr, *J. Chem. Phys.*, 1952, **20**, 1652.

for the last band in the He^I spectrum of POF_3 are also taken from the grid spectra, since the band is so weak on the analyser instrument (it is not visible at the scale expansion used for Figure 1). However, to detect the poorly resolved fine structure on this last band, the analyser instrument was necessary (Figure 2). The first band in the He^I spectrum of POF_3 is very intense, but in the He^{II} spectrum the intensity of this first band is intermediate between the intensities of the third and fourth bands.

NF_3 shows five bands, one of which is only detectable with He^{II} radiation. The second band has a distinct shoulder. PF_3 shows six bands, of which the first five have a very similar pattern of intensities and band widths to the first five in NF_3. The second and third bands of PF_3 and NF_3 have very similar i.p., which suggests that the corresponding orbitals are mainly localised on F atoms. All the other PF_3 bands are at lower i.p. than the corresponding NF_3 bands, which indicates some central-atom character for the orbitals which give rise to these bands. Some recently published He^I spectra of these two compounds [9] are in good agreement with our results, except that the PF_3 fine structure was not observed. Some minor i.p. discrepancies occur on the incompletely resolved bands.

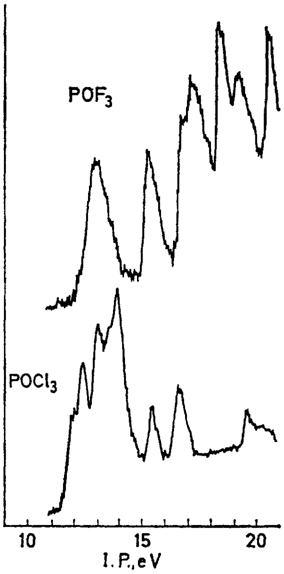

FIGURE 3 Photoelectron spectra, obtained with a retarding grid instrument, for POF_3 and $POCl_3$

POF_3 shows seven bands, and again one of these is clearly composite, but NOF_3 shows only four bands, and the He^{II} spectrum shows no additional bands between 21 and 24 eV. A shoulder on the last band is just detectable before the ionisation limit of He^I (see the inset on Figure 1) and the He^{II} spectrum confirms the presence of this shoulder; the different appearance of the band in the two spectra is due to the very different electron energies being analysed.

NOF_3 and NF_3 have also been examined by photoionisation mass spectrometry.[18] The threshold of ionisation reported for NF_3, 13·00 ± 0·02 eV, is in excellent agreement with our value of 12·97 ± 0·04 eV, but that reported for NOF_3, 13·26 ± 0·01 eV, is appreciably less than our value, though subtracting one quantum of the vibrational progression from our value gives 13·23 ± 0·02 eV. It seems therefore that our value probably corresponds to the first vibrationally excited state of the ion and that the Franck–Condon factor for ionisation to the ground state must be very low. Inspection of the photoionisation yield curves [18] shows that the total ion yield at the first vibrationally excited state is only about 1% of that at 14·1 eV, so it is not surprising that our ionisation threshold is too high. No correlation can be made between the various fragmentation onsets and our band onsets. The NOF_3 fine structure which we observe continues through the energy region where the probability of ONF_2^+ production is increasing rapidly, so the fragmentation processes are clearly complex, and in this first fragmentation the time scale is at least several N–O vibrations.

The orbitals expected for pyramidal trihalides may readily be developed from group theory, and using qualitative arguments such as those of Walsh [3] an approximate orbital energy sequence may be deduced. Throughout this discussion, only those molecular orbitals derived from the atomic valence orbitals are included in the numbering scheme, so that similar orbitals in nitrogen and phosphorus compounds have the same numbering. The z axis for the central atom is the C_3 axis, negative at the halogen end; halogen p orbitals are aligned along the bond direction (p_σ) or perpendicular to it (p_π).

Orbitals $1a_1$ and $1e$, derived from combination of the halogen s orbitals with smaller amounts of the central atom s or p_x, p_y orbitals, will have i.p. beyond 21 eV, and, in the case of fluorides, beyond 41 eV, so these will not be detected by the present experiments. The $2a_1$ orbital is derived mainly from combination of halogen p_σ orbitals with the central atom s (or $s - p_z$) orbital, to give a strongly bonding molecular orbital. This orbital is also expected to be beyond 21 eV for the trifluorides, but not for the trichlorides, since the corresponding $2a_1'$ orbitals of BF_3 and BCl_3 appear at 21·4 and 17·7 eV.[9] All the remaining orbitals may possibly have i.p. less than 21 eV, though from correlation with BF_3 the two lowest-lying ones in fluorides will be quite close to this limit. These two are $2e$ (bonding between p_x, p_y, and halogen p_σ) and $3a_1$ (bonding between p_z and halogen p_σ,p_π) which correlates with the strongly π-bonding $1a_2''$ orbital of the planar trihalides. Orbitals $3e$, $4e$, and $1a_2$ are mainly halogen p_π, essentially non-bonding, correlating with $3e'$, $1e''$, and $1a_2'$ of BX_3. The highest-lying orbital is expected to be the 'lone pair' orbital $4a_1$, mainly central atom ($s + p_z$). Since occupation of this orbital is intimately connected with the pyramidal nature of the molecules,[3] removal of an electron will

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[18] V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, 1969, **8**, 1728.

probably excite the ν_2 vibration (A_1 species, M–X bending) as in ammonia and phosphine.[19]

The orbitals of oxide trihalides may to a first approximation be derived from the above by using the lone-pair orbital $4a_1$ to form a σ donor bonding orbital $5a_1$ with the vacant p_σ orbital of the O atom (the presence of the O 2*s* orbital changes the numbering of the a_1 orbitals by one). The O p_π orbitals become the 5*e* orbitals of the molecule and may be stabilised by π bonding to the central atom. In the oxide trifluorides this description will probably be a reasonable approximation to the form of the highest *e* set, but in the oxide trichlorides there may be considerable mixing with Cl orbitals, because of the closeness in energy of Cl 3*p* and O 2*p*. Alternatively these orbitals may be derived from those of the Group IV tetrahalides by consideration of the lowering of orbital degeneracies on changing from T_d symmetry, to C_{3v}, and this correlation will be considered below.

In the photoelectron spectrum of PF_3, the vibrational interval of the progression on the first band is indistinguishable from ν_2 (487 cm^{-1}), the M–X bending mode in the molecule.[20] We assign this band to ionisation from the lone-pair $4a_1$ orbital. The second band of PF_3 has been resolved into a weak component at low i.p. and a component of about double the intensity at higher i.p. The third band has an intensity comparable with this more intense component, and so we assign these bands as corresponding to orbitals $1a_2$, 4*e*, and 3*e*. The fourth and fifth bands have well resolved doublet progressions, in which the doublet interval is 79 and 71% of ν_2 in the molecule. The progression intervals on these two bands can only be reasonably related to ν_1, the P–F stretching frequency; they are respectively 77 and 73% of ν_1 in the molecule. This reduction in frequency and the length of the progressions indicate that the corresponding orbitals must be strongly P–F bonding. The excitation of one quantum of ν_2 is not surprising since all these orbitals have some F–F interaction, and changing this will probably change the pyramid angle. The intensity of the fourth band is half that of the fifth, so these are assigned to ionisation from orbitals $3a_1$ and 2*e*, both strongly P–F bonding. The final band at 22·6 eV is then assigned to $2a_1$, which is expected to be strongly bonding, though the resolution under He$^{\text{II}}$ conditions was insufficient to resolve any fine structure.

NF_3 may be assigned in a similar manner. The first band is broad as in PF_3, and the breadth is expected from excitation of ν_2 if the corresponding orbital is $4a_1$. No fine structure can be detected, and such lack of structure is often ascribed to a short lifetime for the ion.[21] However, the photoionisation mass spectrum of NF_3 shows a fragmentation threshold well above (1·14 eV) the ionisation threshold,[18] so the ground electronic state of NF_3^+ is stable. The second and third bands probably correspond respectively to $1a_2 + 4e$ and to 3*e*; the second band is insufficiently well resolved to allow a certain decision as to whether $1a_2$ or 4*e* is the higher lying, though if the components are of similar width 4*e* must be above $1a_2$. In our earlier report [11] we suggested that the fourth band could contain both $3a_1$ and 2*e* since calculations indicated that these orbitals have very similar eigenvalues,[22] but from the He$^{\text{II}}$ spectrum it is evident that the 19·7 eV band must be $3a_1$ and that 2*e* appears at 21·1 eV. We have not detected a band corresponding to the $2a_1$ orbital; this is expected [22] to lie at *ca.* 30 eV.

The assignment of POF_3 follows simply from the PF_3 assignments, and the arguments given earlier. The first band corresponds to the 5*e* orbital pair, probably mainly O p_π. The intensity of this band in the He$^{\text{II}}$ spectrum is consistent with this, though the intensity seems to be abnormally high in the He$^{\text{I}}$ spectrum. The second band is expected to correlate with the lone-pair orbital of PF_3, and the low intensity supports this. The i.p. is 3·2 eV greater than that of $4a_1$ in PF_3; considerable stabilisation is expected from the formation of the σ bond. The third band, like the second in PF_3, is composite, and the same assignment of $1a_2 > 4e$ is indicated, where the separation of the two orbitals has increased slightly from PF_3. The intensities of these and the later bands are better represented by the grid spectrum in Figure 3 than by Figure 1, and on the basis of intensity the fourth, fifth, and sixth bands are assigned as 3*e*, $4a_1$, and 2*e*. The vibrational progressions upon these bands all correspond to ν_1, the P–F stretching frequency, reduced to respectively 82, 82, and 75% of its value in the molecule. We conclude that $4a_1$ and 2*e* are strongly P–F bonding, as are the corresponding orbitals $3a_1$ and 2*e* in PF_3. However, 3*e* is apparently also strongly bonding in POF_3 though no fine structure could be detected on this band in PF_3. The differences may be due to changing bonding characters from mixing with the $e(\pi)$ orbitals of O, though since the 3*e* band in PF_3 is broad, the difference may be only one of lifetime for the corresponding ionic states. Except for this detail, the spectrum of POF_3 correlates very closely with that of PF_3, with a large stabilisation of the lone-pair orbital, and smaller ($\frac{3}{4}$—$1\frac{1}{2}$ eV) stabilisations of all the other orbitals.

Since the $1a_2$ orbital in both molecules can have neither P nor O character, it is reasonable that this orbital should be less affected by the P–O bond formation than the *e* orbitals, resulting in the increased separation of $1a_2$ and 4*e*. However, since there is only a small difference in the effects, it is probable that most of this stabilisation of the *e* and a_2 orbitals in POF_3 is a charge effect rather than a bonding effect. From these experiments it is not possible to say whether the stabilisation is due to withdrawal of charge from the F atoms or to the changing positive charge on the P atom. Whereas the *e* orbitals are uniformly stabilised by 1·3—1·4 eV, the

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[19] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley, London, 1970, p. 360.

[20] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 1st edn., Wiley, New York, 1963, p. 86.

[21] Ref. 19, p. 69.

[22] M. L. Unland, J. H. Letcher, and J. R. Van Wazer, *J. Chem. Phys.*, 1969, **50**, 3214.

a_1 orbitals are stabilised by only 0·9 or 0·8 eV. This is most probably to be ascribed to mixing of these orbitals with the 2*s* orbital of the O atom.

These interpretations of the PF_3 and POF_3 spectra are strongly supported by *ab initio* SCFMO calculations,[12] which predict orbital sequences identical with those deduced above, and quantitatively predict the orbital stabilisations, referred to above. The absolute i.p. are not very well predicted by the calculations, but this has been observed previously with *ab initio* calculations.[23] It has been found [23] that multiplication of the eigenvalues from such calculations by an arbitrary factor of 0·92 gives considerable improvement in the agreement with experiment. This is also true of the calculations upon PF_3 and POF_3; introducing this factor decreases the mean deviation between eigenvalue and i.p. from *ca.* 1·8 to 0·5 eV for both compounds. A correlation of these corrected values is shown in Figure 4. A point of difference with our deductions is that the $3a_1$ orbital in PF_3 and orbitals $4a_1$ and $3e$ in POF_3 are predicted to be essentially non-bonding, while Figure 2 shows that all these orbitals are strongly P–F bonding. Since the general agreement of calculations and experiment is so good, we have considerable confidence in our assignments for these two compounds. A correlation of these experimental i.p. with those [2,8] of SiF_4 is shown in Figure 5, and is discussed below.

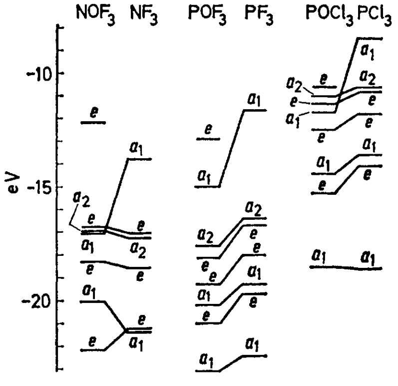

FIGURE 4 A correlation of the higher-lying eigenvalues of *ab initio* calculations upon the compounds studied here. All the eigenvalues have been multiplied by 0·92 (*cf.* ref. 23). Values for PF_3 and POF_3 are from ref. 12, for NF_3 and NOF_3 from ref. 25, for PCl_3 and $POCl_3$ from ref. 27

Interpretation of the NOF_3 spectrum is less clear, but evidently our preliminary assignment [11] is incorrect since it required some of the bands to be in the 21—25 eV region, where we find none. The i.p. of the first band is comparable with that of the first band in POF_3, too low for a mainly F-type orbital, so we consider the first band of NOF_3 to correspond to 5*e*. The intensity of this band in the He^{I} spectrum is high, but this is also true of 5*e* in POF_3. Because of the small amount of NOF_3 available, only rapid scans were made in this region in the He^{II} spectrum, but it seemed probable that, as with POF_3, this band has a similar intensity to those of the second and third bands under these conditions. Thus we do not consider that the first band corresponds to more than one orbital. From comparison with POF_3 and NF_3, another six orbital sets are expected before 25 eV, but there are only three bands. The final band at 20·2 eV has a shoulder at about 21 eV; from the form of this band it is probable that it consists of an *e* component at 20·2 eV and an *a* component causing the shoulder at 21 eV. Since there are no detectable bands at higher i.p. these orbitals must be 2*e* and $3a_1$. We therefore have to assign the orbitals 3*e*, 4*e*, $4a_1$, and $1a_2$ to the two bands at 15·5 and 16·9 eV. It is most unlikely that 3*e* and 4*e* would approach each other closely enough for them to appear as one band, so we assign 3*e* to the 16·9 eV band and 4*e* to the other. Since these two bands have similar intensities, each probably also contains an *a* component. The energy sequence of $4a_1$ and $1a_2$ cannot be definitely ascertained, but if $1a_2$ lies above $4a_1$ the correlation of the NOF_3 orbitals with those of CF_4 (see Figure 5) is rather better than if the reverse is assumed. In particular, $4a_1$ and 4*e* correlate with $3t_2$ of CF_4, and it would be unlikely that there should be no separation in energy of these orbitals in NOF_3, as is required if $4a_1$ is a component of the second band. We therefore consider that the observed bands may most probably be assigned in order of increasing i.p. as 5*e*, 4*e* + $1a_2$, 3*e* + $4a_1$, 2*e*, $3a_1$.

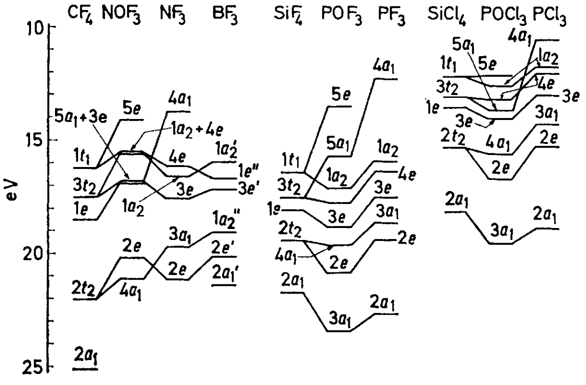

FIGURE 5 A correlation of experimentally measured vertical i.p. Values for PCl_3, BF_3, and CF_4 are from ref. 9, for SiF_4 and $SiCl_4$ from refs. 2 and 8.

This assignment leads to the rather unexpected correlation diagram shown in Figure 5. As in the PF_3–POF_3 correlation, $4a_1$ of NF_3 is stabilised by more than 3 eV on formation of NOF_3, but there are no further resemblances. It follows directly from the absence of bands beyond 21 eV in the NOF_3 spectrum that the correlation cannot follow the simple pattern of orbital stabilisations found with PF_3 and POF_3. If the above assignment is accepted then the pattern is that on formation of NOF_3 from NF_3 the a_1 orbitals are stabilised, but the *e* and a_2 orbitals are destabilised. There is no obvious rationalisation of this observation, but it suggests that the bonding in NOF_3 is rather different from that in POF_3. The availability of *d* orbitals in the latter molecule will probable lead to greater charge

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[23] C. R. Brundle, M. B. Robin, and G. R. Jones, *J. Chem. Phys.*, 1970, **52**, 3383.

equalisation through π back-donation. If the N–O bond were essentially of the single Lewis donor–acceptor type, this would give considerable negative charge on the O atom, and it has been suggested that the high N–O force constant is due to a strong polar character in this bond.[24]

The fine structure on the first band of the photoelectron spectrum of NOF_3 can only reasonably be assigned to ν_1 (1689 cm^{-1}, N–O stretch [24]) or ν_2 (740 cm^{-1}, N–F stretch [24]). There is no evident reason for excitation of ν_2 nor for the increase in frequency upon ionisation which assignment of this fine structure to ν_2 would require. However, the interval of this progression is only 58% of ν_1 in the molecule, while the $5e$ orbital is not expected to be strongly bonding. Since $5e$ is probably mainly localised on the O atom, removal of an electron from this orbital will remove much of the polar character of the N–O bond, and this could account for the reduction in frequency.

Molecular orbital calculations have been carried out by Breeze [25] for NOF_3 and NF_3, using the same method as was employed for the POF_3 and PF_3 calculations. The eigenvalues for NF_3 are similar to those reported from calculations using a larger Gaussian basis set.[22] The correlation diagram for these calculations is shown in Figure 4, and agreement with experiment is clearly much poorer than for the PF_3–OPF_3 results.[12] This situation is an interesting contrast with that found in comparisons of calculation and experiment [26] for complexes of BH_3, which is isoelectronic with the O atom. Here the single donor–acceptor system of NH_3,BH_3 shows good agreement between theory and experiment, while the BH_3,CO system, with the possibility of back-donation, shows considerable discrepancies. The orbital sequence calculated [25] for NOF_3 differs slightly from that deduced above from experiment, but any changes in assignment to bring the i.p. into better agreement with the calculations demand considerable deviations from proportionality of orbital degeneracies with photoelectron band intensities. The calculations also show very little polar character in the N–O band, but if this is so, we have no ready explanation for the vibrational progression on the first band. The nature of the bonding in NOF_3 is still not fully explained.

Finally, the orbitals of $POCl_3$ may be assigned on the basis of intensities, and comparison with POF_3. From Figure 3, though the bands are not fully resolved, the most probable sequence of orbital energies is e (12·1 eV) $>$ a (12·5 eV) $>$ e (13·2 eV) $>$ $(a + e)$ (13·6, 14·0 eV) $>$ $a >$ (15·5 eV) $>$ e (16·6 eV). From comparison with PCl_3 and with POF_3 it seems most probable that the 12·5 eV band corresponds to $1a_2$ and the 13·6 eV shoulder to $4a_1$, since if $4a$ is above $1a_2$, then $1a_2$ is stabilised much more than the e orbitals on formation of $POCl_3$ from PCl_3. The 15·5 eV band must then be $3a_1$, and the band at 19·5 eV can only be $2a_1$. The apparently high intensity of this last band is probably partly due to scattered electrons, since the base line is rising in this region of the spectrum. The correlation diagram for $SiCl_4$, $POCl_3$, and PCl_3 is shown in Figure 4, where data for PCl_3 are taken from ref. 9.* This assignment for $POCl_3$ is in very satisfactory agreement with the results of calculations by Hillier and Saunders,[27] which are shown † in Figure 4. As with PF_3 and POF_3, the pattern for PCl_3 and $POCl_3$ is one of strong stabilisation (3·1 eV) of the PCl_3 lone pair on bonding to O, with smaller stabilisation (0·5—1·4 eV) of the remaining orbitals. Again, the smallest stabilisation is of the lowest a_1 orbital (0·5 eV), probably because of interaction with the O $2s$ orbital.

The correlation of the experimental values of SiF_4 with those of POF_3 has been briefly discussed in Part I of this series,[2] but the i.p. beyond 21 eV were not then available. The $2a_1$ orbital of SiF_4 correlates with $3a_1$ of POF_3; the considerable stabilisation is indicative of the $3s$ character in these orbitals. Similarly the stabilisation of $4a_1$ and $2e$ of POF_3 referred to $2t_2$ of SiF_4 is probably due to $3p$ character from the central atom. The contrasting rise in energy of $5a_1$ from $3t_2$, and $5e$ from $1t_1$, is a result of the change from F $2p$ character to O $2p$ in POF_3. The correlation of $SiCl_4$ and $POCl_3$ shows a very similar pattern to that of SiF_4 and POF_3 in the orbitals $2a_1$, $2t_2$, and $1e$. The splitting pattern for the higher orbitals $1t_1$ and $3t_2$ of $SiCl_4$ is different from that of SiF_4, but this is not surprising since O $2p$ and Cl $3p$ orbitals have similar energies, and the calculations [27] indicate considerably more mixing of the O orbitals with the halogen orbitals in $POCl_3$ than in POF_3. The assignment of orbital energies for SiF_4 in Figure 5 is that of refs. 2 and 8, but recently it has been proposed that the orbital sequence is $1t_1 > 3t_2 > 2a_1 > 1e > 2t_2$ on the basis that fine structure is observed on the fourth band which is similar to that on the third ($1e$) band of CF_4.[28] Since the $2t_2$ band in the He^{II} spectrum of CF_4 also shows fine structure [29] this change in assignment, which requires that the Si s-type orbital be above the p-type by 4 eV, is not necessary.

Direct correlation between the higher-lying orbitals of the Group IV tetrahalides and the corresponding orbitals of Group V trihalides is not expected, but the lower orbitals $3a_1$ and $2e$ are bonding between central atom p orbitals and the halogen, as is $2t_2$, and similarly $2a_1$ in the tetrahalide may be correlated with $2a_1$ of the corresponding trihalide, from the central atom s character. The s-type orbital $2a_1$ of PF_3 is slightly more stable than

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* In ref. 9, two different assignments are given for PCl_3; we have taken the assignments given in the illustration of the spectrum as being more consistent with the observed band intensities.

† For consistency, the eigenvalues for the chlorides have been multiplied by 0·92, though this worsens the agreement with experiment.

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$2a_1$ of SiF_4, and the same is true for PCl_3 and $SiCl_4$, while the average *p*-type orbital energies in these trihalides are very similar to those in the corresponding tetrahalides. In NF_3 the *p*-type orbital energy has risen compared with that in CF_4, but otherwise the relation between NF_3 orbitals and CF_4 orbitals is very similar to the relationship of PF_3 with SiF_4 and of PCl_3 with $SiCl_4$. The correlation of NF_3 with BF_3 (assigned as in ref. 1) shows exactly the pattern expected, with a stabilisation of the *p*-type central atom orbital energies of NF_3 compared with BF_3, and probably very considerable stabilisation of the *s*-type orbital. The energy difference of $4e$ and $3e$ in NF_3 is considerably greater than that of $3e'$ and $1e''$ in BF_3, and this ' repulsion ' of the *e* orbitals on bending the planar molecule is fully consistent with that observed in trichlorides and tribromides.[9] We conclude that all the parallel correlations which may be made on Figure 5 are consistent, with the evident exception of those involving NOF_3.

Very recently, He^I spectra of NOF_3 and POF_3 have been reported by other workers.[30] The results are in moderate agreement with those reported here, though the first adiabatic i.p. given for NOF_3 is one vibrational quantum higher than that in the Table. Our value was obtained using a 10 cm radius analyser, but our earlier experiments, using the less sensitive 5 cm analyser, gave the same value as in ref. 30.

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