The Ultraviolet Photoelectron Spectra † and Electronic Structure of Gas-phase and Condensed SnF_2 and PbF_2

Igor Novak and Anthony W. Potts *
Department of Physics, Kings College, Strand, London WC2R 2LS

He(Iα) and He(IIα) photoelectron spectra of SnF_2 and PbF_2 in the gas phase and as condensed solids have been recorded and analysed. The assignments of the molecular spectra were based upon correlation with established assignments for the lighter Group 4 difluorides which are normally considered to be metastable species. A close similarity was noted between the gas-phase and solid-state spectra. In the spectra of gas-phase SnF_2 features were identified corresponding to the presence of Sn_2F_4. No polymeric species were identified in the spectrum of PbF_2. Valence *d* shell ionization was observed for all systems.

Group 4B elements are normally either tetravalent or divalent. The elements carbon and silicon are primarily tetravalent, divalent species being metastable while germanium, tin, and lead exist in both valence states with increasing stability of the divalent species for the heavier elements. Perhaps because of their metastable nature the difluorides of carbon[1] and silicon[2,3] have attracted attention previously and their electronic structure has been essentially established from photoelectron study and molecular orbital calculation. Recently an ultraviolet photoelectron spectrum of GeF_2 has been reported[4] and assignments made on the basis of *ab initio* molecular orbital calculations shown to be consistent with those made for the lighter fluorides.[1,3] It would therefore seem of value to extend this work on the Group 4B difluorides to the less volatile but stable species SnF_2 and PbF_2.

In the solid state only SnF_2[5] and PbF_2[6] have been studied because of the instability of the lighter fluorides. Assignments of the observed features have been made in terms of orbitals for MF_3 molecular units.

Experimental

He(Iα) and He(IIα) photoelectron spectra of gas-phase SnF_2 and PbF_2 were recorded with a molecular beam photoelectron spectrometer. Samples in alumina furnace tubes were heated with a resistive furnace and the vapour beam crossed with an He(I)–He(II) photon beam. Spectra of the condensed solids were recorded with the same spectrometer using the continuous deposition technique to produce clean surfaces.[7] High purity commercial samples were used (Alfa Ventron GmbH and Hopkin and Williams Ltd) and purified by vacuum sublimation before use. Spectra were calibrated using internal gas calibrants such as He $1s^{-1}$ or Ar $3p^{-1}$ lines.

Results and Discussion

The He(Iα) and He(IIα) photoelectron spectra of SnF_2 and PbF_2 in the gas phase together with the He(IIα) spectra of the condensed solids are shown in Figures 1 and 2 and observed ionization energies are given in Table 1.

The geometries of molecular SnF_2 and PbF_2 have not so far been determined although since the molecules CF_2, SiF_2, and GeF_2 are known to be increasingly bent with F–M–F bond angles of 105, 101, and 97° respectively[8] it is reasonable to assume non-linear C_{2v} geometries for tin and lead difluorides with bond angles of around 90°. We have assumed a *y–z* molecular plane ($C_2 = z$ axis) for orbital assignments.

On the basis of similarities between features in the ultraviolet photoelectron spectra of the Group 4B difluorides it is possible to draw a correlation diagram for ionization energies and on the basis of existing assignments for the lighter fluorides to make assignments for the heavier fluorides (Figure 3). The regular trends shown in this correlation and the close similarity between the spectra observed here and those reported for GeF_2 make the suggested assignments virtually certain although detailed ordering of ionized states in the overlapped fluorine lone-pair region must remain uncertain.

Early attempts to understand orbital ordering for lead and tin dihalides assumed a largely ionic model.[9,10] The orbital ordering was deduced on the basis of simple overlap considerations between the two valence p^6 halogen shells. *Ab initio* calculations carried out for the lighter fluorides[1,4] show that for the Group 4B elements there can be appreciable mixing between F $2p$ a_1 orbital combinations and central atom valence p_z and *s* orbitals. Thus the highest $4a_1$ orbital has not only halogen lone-pair character but also appreciable Sn or Pb valence p_z and *s* orbital character and the $2a_1$ orbital which on energy grounds might be considered as a simple metal valence *s* orbital is predicted also to have considerable fluorine $2p$ character. Between these two orbitals lie five orbitals which for SnF_2 and PbF_2 are expected to have predominantly fluorine lone-pair character.

Although of less value than the *ab initio* calculations carried out for the lighter fluorides[4] extended Hückel calculations carried out by us for SnF_2 and PbF_2 reveal similar orbital character to that deduced for corresponding orbitals of GeF_2.

Experimental support for the heavy-atom orbital character of the $4a_1$ orbitals comes from He(I)–He(II) relative intensity changes. For both SnF_2 and PbF_2 the $4a_1^{-1}$ (minus superscript indicates electron ionization) band loses intensity relative to the adjacent fluorine lone-pair bands in the He(II) spectra. Assuming that molecular-orbital photoionization cross-section changes can be linked with atomic orbital characters[11] this loss in intensity is consistent with a substantial metal *p* character for the $4a_1$ orbital. This follows from calculations on the photoionization cross-sections of Pb[12] and F[13] which show that while the F $2p$ and Pb $6s$ shell cross-sections change little between the He(I) and He(II) photon energies the Pb $6p$ photoionization cross-section shows a substantial decrease. The apparently irregular trend in the ionization energies of the $4a_1$ orbitals of the Group 4B difluorides (Figure 3) can also be used to comment on orbital character. This trend is similar to that observed for the $2a_1$ orbitals of the Group 4B tetramethyls[14] and tetrachlorides[15]

---

* Jointly at S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD.

† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

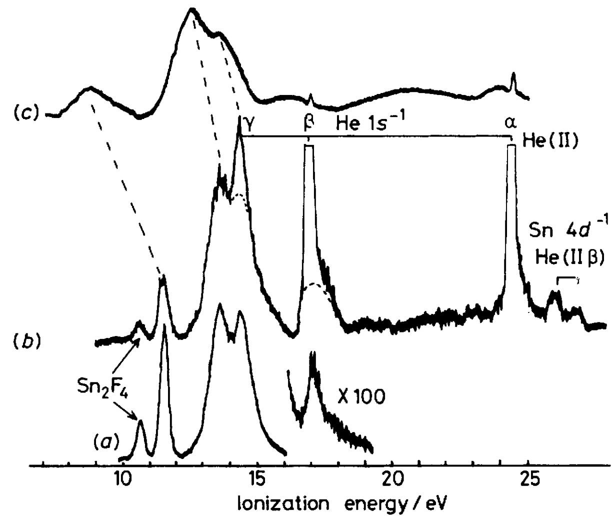

Figure 1. (*a*) He(Iα) and (*b*) He(IIα) photoelectron spectra of molecular SnF_2 and the (*c*) He(IIα) photoelectron spectrum of condensed SnF_2

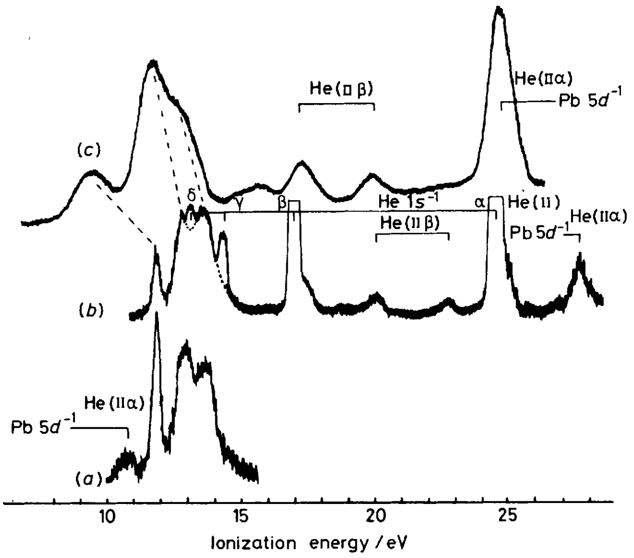

Figure 2. (*a*) He(Iα) and (*b*) He(IIα) photoelectron spectra of molecular PbF_2 and the (*c*) He(IIα) photoelectron spectrum of condensed PbF_2

Table 1. Ionization energies (eV) for molecular SnF_2 and PbF_2 [a]

SnF_2 [b]	PbF_2	Assignment
11.48	11.84	$4a_1$
13.61	12.89	$3b_2 + 1a_2$
14.37	13.59	$1b_1 + 2b_2 + 3a_1$
17.04	[c]	$2a_1$
33.7	27.63	$^2D_{\frac{5}{2}}$
34.5	30.34	$^2D_{\frac{3}{2}}$

[a] Orbital numbering is for valence-shell orbitals only. [b] Feature at 10.63 eV assigned to Sn_2F_4. [c] Not observed.

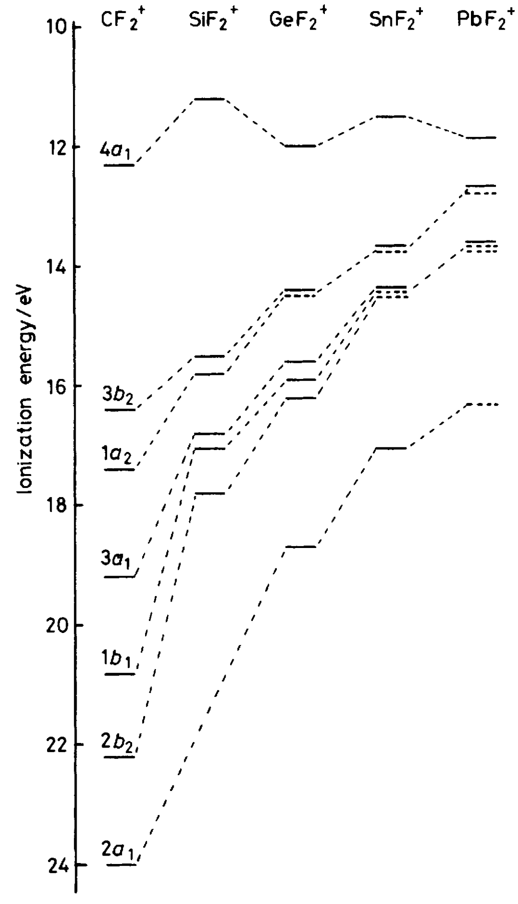

Figure 3. A correlation diagram for valence-shell ionization energies of Group 4B dihalides

and of the $1a_1$ orbitals of the Group 4B hydrides.[16] In all cases these orbitals are known to have substantial Group 4B valence *s* orbital character supporting the assignment of similar character to the $4a_1$ orbitals of the Group 4B difluorides.

Just as photoionization cross-section can suggest the atomic orbital composition of the $4a_1$ molecular orbital it also enables a comment to be made on the atomic character of the $2a_1$ orbital. The photoelectron feature associated with ionization from this orbital in the He(I) photoelectron spectrum of SnF_2 has very low intensity while that for PbF_2 has not been identified at all. This suggests that the $2a_1$ orbital has predominantly metal valence *s* character with a substantially smaller contribution from the high cross-section fluorine 2*p* orbital than is suggested by calculation. It might be expected therefore that the $2a_1$ ionization energies of the Group 4B difluorides would show a similar trend to that observed for the related $4a_1$ orbitals (Figure 3). However, there are at present insufficient data available to establish such a trend and interaction with the F 2*p* $3a_1$ orbital may confuse the issue.

In addition to valence-shell ionization it is known that Sn $4d^{-1}$ and Pb $5d^{-1}$ ionization energies should lie within the He(IIα) region.[17] Features associated with *d* shell ionization have been identified in our spectra (Figures 1 and 2) and show characteristic $^2D_{\frac{5}{2}}/^2D_{\frac{3}{2}}$ splittings. Ionization energies are consistent with measurements for the dichlorides, dibromides, and di-iodides showing the expected shift to higher ionization energies with increasing halogen electronegativity.[17]

In addition to the features discussed so far a feature was observed in the low ionization energy region of the SnF_2 spectrum. This feature at 10.63 eV showed a variable intensity

Table 2. Ionization enegies (eV) for condensed SnF_2 and PbF_2

SnF_2	PbF_2	Assignment
8.7	9.5	$4a_1$ (see molecular assignment)
12.4	11.8	F lone pairs
13.5	13.3	
15.7	15.5	Pb 6*s*
20.6	—	?
31.1 *	25.0, 27.7	^2D

* Unresolved doublet.

with furnace temperature when compared with other features in the SnF_2 spectra and could not therefore be associated with SnF_2. At ' best ' the intensity of this feature was of the order of 25% of the SnF_2 $4a^{-1}$ band which suggests strongly that it corresponds to the Sn_2F_4 species reported in a mass spectrometric study of SnF_2 vapour by Zmbov *et al.*[18] These workers report that while SnF_2 is the main component of ' SnF_2 ' vapour (79.5%) the dimer Sn_2F_4 forms a considerable contribution (20.5%). It would therefore appear that our feature corresponds to ionization from the outermost orbital of the Sn_2F_4 dimer. Since no higher energy Sn_2F_4 features are observed in the spectrum it seems reasonable to suppose that other orbitals are essentially fluorine lone-pair combinations and that as for the C_2F_4–CF_2 mixtures [1] the fluorine lone-pair ionizations of the dimer and monomer are overlapped. It is generally assumed that the Sn_2F_4 dimer is a fluorine bridged structure consisting of a four-membered $(SnF)_2$ ring with additional fluorine atoms attached to each tin atom [18,19] rather than the π-bonded structure applying for C_2F_4. The feature at 10.63 eV is then to be associated with an antibonding combination of the SnF_2 $4a_1$ orbitals. No similar feature has been observed in the spectrum of PbF_2 vapour which is consistent with the failure to detect Pb_2F_4 in the mass spectrometric study.

Condensed Solids.—The He(IIα) photoelectron spectra of condensed PbF_2 and SnF_2 are presented in Figures 1 and 2. Apart from minor intensity discrepancies they are essentially similar to spectra already reported for these solids.[5,6] Spectra were calibrated with respect to He $1s^{-1}$ features and the positions of the band maxima are given in Table 2. Stability of the surface spectrum with respect to the gas-phase calibration was taken to indicate absence of charging. Ionization energies however appear to show a shift of around 0.6 eV to higher ionization energies compared with results published by Poole *et al.*[5,6] This effect could be due to surface charging, however, as mentioned we find no evidence for this in our spectra.

Figures 1 and 2 show the close correlation between spectra of the gas and condensed phases. There is a one to one correspondence between the principal features in both spectra although of course the spectrum of the solid is shifted to lower ionization energies because of the change in relaxation energies between the solid and molecular fluoride. The main apparent change is the relatively large destabilization of the ' $4a_1$ ' band in the solid spectrum. This destabilization is similar to that observed for the outermost orbital of the Sn_2F_4 dimer and is consistent with the interpretation of the solid SnF_2 structure in terms of irregular cyclic tetramers.[20] The He(IIα) photoelectron spectra of condensed SbF_3 and BiF_3 [6] have been discussed in terms of a molecular solid and it has been shown that there is a close correspondence between the solid and molecular spectra of all bismuth trihalides [21] supporting the view of a molecular solid. PbF_2 and SnF_2 cannot be regarded as molecular solids as no MF_2 units are identifiable.[20] Spectra of condensed SnF_2 [5] and PbF_2 [6] have however been discussed in terms of a solid composed of MF_3 trigonal pyramidal units. The close correspondence between the spectra of molecular and condensed SnF_2 and PbF_2 (Figures 1 and 2) would seem to suggest that much of the MF_2 molecular orbital character is carried over to the extended orbital structure of the solid as suggested in Table 2. This interpretation is not inconsistent with that reached in terms of MF_3 units.

Acknowledgements

I. Novak thanks the Institute ' R. Boskovic ', Zagreb, for leave of absence. We thank the S.E.R.C. for financial assistance and our referees for helpful comments.

References

1 J. M. Dyke, L. Golob, N. Jonathan, A. Morris, and M. Okuda, *J. Chem. Soc., Faraday Trans. 2*, 1974, 1828.

2 T. P. Fehlner and D. W. Turner, *Inorg. Chem.*, 1974, **13**, 754.

3 N. P. C. Westwood, *Chem. Phys. Lett.*, 1974, **25**, 558.

4 G. Jonkers, S. M. Van der Kerk, R. Mooyman, and C. A. de Lange, *Chem. Phys. Lett.*, 1982, **90**, 252.

5 R. T. Poole, P. J. Orders, J. G. Jenkin, R. C. G. Leckey, and J. Liesegang, *Chem. Phys. Lett.*, 1978, **54**, 220.

6 R. T. Poole, J. Liesegang, R. C. G. Leckey, J. G. Jenkin, and J. B. Peel, *Phys. Rev. B*, 1976, **13**, 896.

7 A. W. Potts, P. J. Brigden, D. S. Law, and E. P. F. Lee, *J. Electron Spectrosc. Relat. Phenom.*, 1981, **24**, 267.

8 E. Vajda, I. Hargittai, M. Kolonits, K. Ujszaszy, J. Tamas, A. K. Maltsev, R. G. Mikaelian, and O. M. Nefedov, *J. Organomet. Chem.*, 1976, **105**, 33.

9 S. Evans and A. F. Orchard, *J. Electron Spectrosc. Relat. Phenom.*, 1975, **6**, 207.

10 J. Berkowitz, in ' Electron Spectroscopy,' ed. D. A. Shirley, North-Holland, Amsterdam, 1972, p. 391.

11 R. G. Egdell, A. F. Orchard, D. R. Lloyd, and N. V. Richardson, *J. Electron Spectrosc. Relat. Phenom.*, 1977, **12**, 415.

12 S. M. Goldberg, C. S. Fadley, and S. Kono, *J. Electron Spectrosc. Relat. Phenom.*, 1981, **21**, 285.

13 S. T. Manson, A. Msezane, A. F. Starace, and S. Shahabi, *Phys. Rev. A*, 1979, **20**, 1005.

14 S. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner, and J. P. Maier, *J. Chem. Soc., Faraday Trans. 2*, 1972, 905.

15 J. C. Green, M. L. H. Green, P. J. Joachim, A. F. Orchard, and D. W. Turner, *Philos. Trans. R. Soc. London, Ser. A*, 1970, **268**, 111.

16 A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A*, 1972, **326**, 165.

17 A. W. Potts and M. L. Lyus, *J. Electron Spectrosc. Relat. Phenom.*, 1978, **13**, 327.

18 K. Zmbov, J. W. Hastie, and J. L. Margrave, *Trans. Faraday Soc.*, 1968, **64**, 861.

19 R. H. Hauge, J. W. Hastie, and J. L. Margrave, *J. Mol. Spectrosc.*, 1973, **45**, 420.

20 R. C. McDonald, H. Ho-Kuen Hau, and K. Eriks, *Inorg. Chem.*, 1976, **15**, 762.

21 I. Novak and A. W. Potts, *J. Chem. Soc., Dalton Trans.*, 1983, 635.

Received 17*th January* 1983; *Paper* 3/064