The Ultra-violet Photoelectron Spectra † of Gas-phase and Condensed Bismuth Halides and Antimony Trifluoride

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He(Iα) and He(IIα) photoelectron spectra of BiX_3 (X = F, Cl, Br, and I) and of SbF_3 molecules have been recorded and analysed on the basis of empirical considerations such as He(I)–He(II) intensity variations, the relative intensities of bands, and correlations with the spectra of related compounds for which assignments are established. Spin-orbit interaction was observed in systems corresponding to ionization from both halogen lone pair orbitals and BiX bonding orbitals. Photoelectron spectra of condensed BiX_3 solids are also reported and shown to correspond closely with the molecular spectra, indicating a close relationship between the solid state and molecular electronic structure.

The electronic structure of the Group 5B trihalides has been studied in considerable detail. Previous work has been concerned largely with the He(Iα) photoelectron spectra of these molecules in the gas phase.[1—6] Spectra were analysed either by correlation with the photoelectron spectra of similar molecules such as the boron halides, trihalogenomethanes, or other Group 5B trihalides [1,2,4] or by correlating spectra with ionization potentials deduced from various molecular orbital calculations with the inclusion of spin-orbit coupling effects to predict the detailed structure for the heavier halides.[3,5,6] However, to date no He(I)–He(II) studies of these molecules have been reported and no reports have been made on the gas-phase spectra of SbF_3, or of the bismuth trihalides. This report, therefore, fills in some of the remaining gaps in our knowledge of the electronic structure of the Group 5B trihalides. The bismuth halides also have added interest being the heaviest commonly occurring members of the group. Appreciable spin-orbit effects are thus possible for both halogen localized and bonding orbitals and interaction between different ionized states as a result of second-order spin-orbit effects can become important.

Experimental

He(Iα) and He(IIα) photoelectron spectra of gas-phase BiX_3 and SbF_3 were recorded with the molecular beam photoelectron spectrometer described previously.[7] Spectra of the condensed solids were recorded with the same spectrometer using the technique of continuous deposition to provide a clean surface.[8] The samples were of commercial origin (B.D.H., Hopkin and Williams Company, and Aldrich Chemical Co. Ltd.). All compounds were purified by vacuum sublimation before use.

Results and Discussion

The He(Iα) and He(IIα) photoelectron spectra of the molecules studied together with the He(IIα) spectra of their condensed solids are shown in Figures 1—3. Assignments of the gas-phase spectra are also given in these diagrams. Ionization potentials and assignments are given in Table 1.

Although the geometry of the gas-phase bismuth halides has been determined only for $BiCl_3$ and $BiBr_3$,[9] it is reasonable to assume that as for other Group 5B trihalides the C_{3v} geometry applies to all trihalides. On this basis the valence-shell electronic configuration of lighter Group 5B trihalides can be written as $1a_1^2$, $1e^4$, $2a_1^2$, $2e^4$, $3a_1^2$, $3e^4$, $4e^4$, $1a_2^2$, $4a_1^2$.[1,3]

For the bismuth trihalides the $1a_1$ and $1e$ orbitals are associated with combinations of halogen valence *s* orbitals, the $2a_1$ orbital with the Bi 6*s* shell, the $2e$ and $3a_1$ orbitals are bonding orbitals involving overlap between the halogen and bismuth valence *p* orbitals, while the remaining $3e$, $4e$, $1a_2$, and $4a_1$ orbitals can be considered essentially halogen lone pair orbitals, although there will be variable interaction between the $3a_1$ and $4a_1$ orbitals depending upon the halogen. The above assignment has been adopted for the analysis of all lighter Group 5B halides with the exception of $AsBr_3$ and AsI_3 where a reversal of the $4e$, $1a_2$ order was inferred.[5] The assignment of the first photoelectron band in the spectrum of PBr_3 to the $1a_2$ orbital by Potts *et al.*[1] has previously been commented upon.[5] This was clearly an error in the correlation of features in related spectra, the correct assignment of the first feature in the photoelectron spectrum being to the $4a_1$ orbital as indicated for PCl_3 and PF_3 correlations.[1] Accepting the given configuration, it is clear from a correlation of the features in the chloride spectra (Figure 4) that this electronic configuration is retained for $BiCl_3$ but that with the increased bond length for the heavier bismuth halides there is a contraction in the energy spread of the valence shell. The similarity in the relative He(I)–He(II) intensity change between features associated with the $3e$, $4e$, $1a_2$, and $4a_1$ orbitals suggests that the $4a_1$ orbital, which for the lighter 5B trihalides was assumed to have considerable 5B valence p_z character, is now essentially halogen lone pair with little interaction occurring between the $3a_1$ bismuth 'lone pair' orbital and the $4a_1$ orbital.

For lighter members of the Group 5B halides the $2e^{-1}$ feature (minus superscript indicates electron ionization) shows variable spin-orbit splitting. Thus, there is no observable splitting for $AsCl_3$ but a splitting of 0.25 eV for AsI_3, presumably resulting from the iodine character of this orbital and the associated large coupling constant.[5] A similar situation is observed for the antimony halides,[6] however for all the bismuth halides a marked splitting of the $2e^{-1}$ band is observed. This is presumably associated with the large bismuth coupling constant which from the photoelectron spectrum of Bi_2^+ is around 1.3 eV.[10] Assuming the assignment of the $3a_1^{-1}$ feature implied by our photoelectron correlation (Figure 4) suggests that the features at 13.19 and 13.79 eV in the spectrum of $BiCl_3$ should be associated with the $^2E_{\frac{3}{2}}$ and $^2E_{\frac{1}{2}}$ states respectively using the extended point group notation. This reduction in the $^2E_{\frac{3}{2}} - {}^2E_{\frac{1}{2}}$ separation from the value of 1.3 eV which would apply for ionization from a pure bismuth *e* orbital reflects the bonding character of this orbital. Calculations for AsX_3 and SbX_3 [5,6] have shown the $2e^{-1}$ ionized states to be inverted from the normally expected $^2E_{\frac{3}{2}} < {}^2E_{\frac{1}{2}}$ order. The inversion must arise from second-order spin-orbit

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

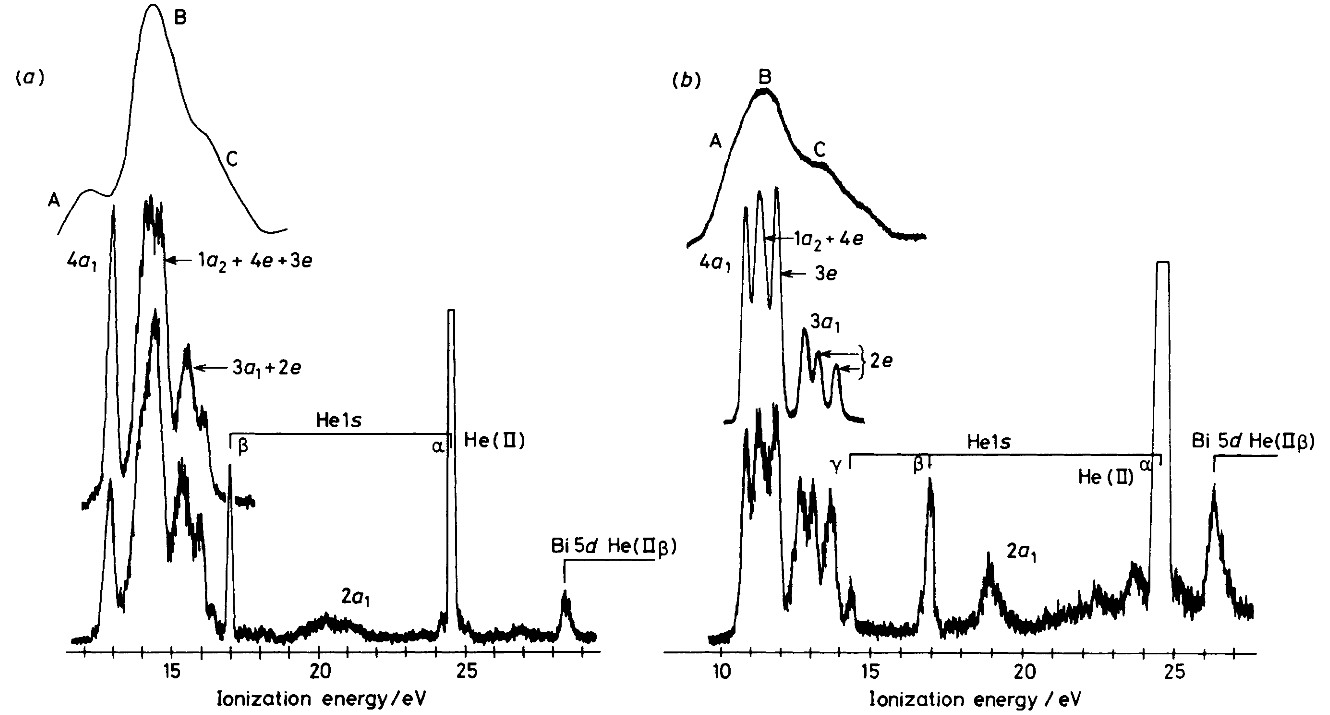

Figure 1. He(Iα)–He(IIα) photoelectron spectra of (*a*) BiF_3 and (*b*) $BiCl_3$: He(IIα) solid (upper spectrum), He(Iα) gas phase (middle spectrum), He(IIα) gas phase (lower spectrum)

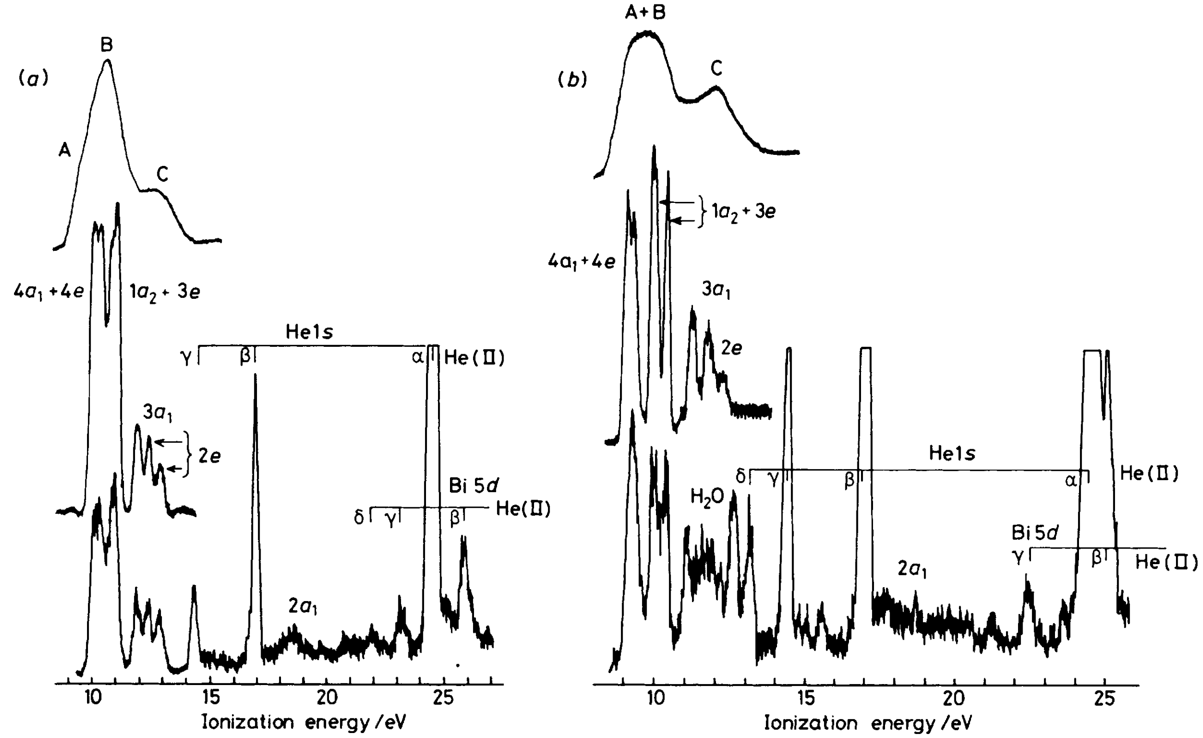

Figure 2. He(Iα)–He(IIα) photoelectron spectra of (*a*) $BiBr_3$ and (*b*) BiI_3: He(IIα) solid (upper spectrum), He(Iα) gas phase (middle spectrum), He(IIα) gas phase (lower spectrum)

interaction with states derived from ionization from halogen localized orbitals, the splitting being largest for the iodide. This effect results in a reduction of the observed $^2E_{\frac{3}{2}} - {}^2E_{\frac{1}{2}}$ splitting for $BiBr_3$ and BiI_3 (Table 1).

The halogen lone pair region of the heavier halides is also subject to marked spin-orbit coupling effects. Peel and Willett[5] concluded that it was necessary to reverse the $4e$, $1a_2$ orbital order deduced from molecular orbital calculations

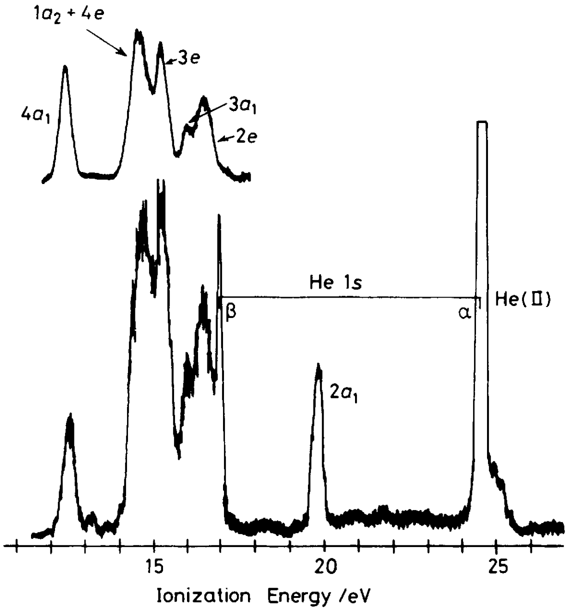

Figure 3. He(Iα)-He(IIα) photoelectron spectra of gas-phase SbF_3: He(Iα) (upper spectrum), He(IIα) (lower spectrum)

Table 1. Ionization potentials[a] and assignments for bismuth trihalides and antimony trifluoride

	BiF_3	$BiCl_3$	$BiBr_3$	BiI_3	SbF_3
$4a_1$	12.96 (12.81)[b]	10.98	10.15	9.09	12.66
$1a_2$	14.14	11.44	10.86	9.96	14.70
$4e$	14.14	11.44	10.44	9.28	14.70
$3e\ {}^2E_{\frac{3}{2}}$	14.55	11.96	10.86	9.96	15.39
${}^2E_{\frac{1}{2}}$			11.07	10.30	
$3a_1$	15.40	12.77	11.99	11.11	16.10
$2e\ {}^2E_{\frac{3}{2}}$	15.40	13.19	12.51	11.61	16.64
${}^2E_{\frac{1}{2}}$	15.99	13.79	12.97	11.90	
$2a_1$	20.45	18.98	18.53	17.8	18.90
$5d^{-1}\ {}^2D_{\frac{5}{2}}$	35.90	33.86	33.43	32.66	
${}^2D_{\frac{3}{2}}$			36.42		

[a] All values in eV. [b] Low ionization energy shoulder.

to obtain a good fit to their spectra of $AsBr_3$ and AsI_3, although Berkosky *et al.*[3] obtained a good fit to the photoelectron spectra of the phosphorous halides using the $4e$, $1a_2$ orbital order. The detailed pattern will clearly depend on the form of the molecular orbital wavefunction used to deduce the magnitude of the first- and second-order spin-orbit effects. For the bismuth halides, as already commented, the energy separation of the halogen lone pair features is the lowest for the group and second-order spin-orbit coupling effects will play an important part. It is therefore likely that it will not be possible to associate final ionized states unambiguously with particular orbitals. Bearing these comments in mind the following suggestions are made as to the detailed assignments. The halogen lone pair regions of the $BiBr_3$ and BiI_3 photoelectron spectra split into two regions which on intensity grounds are each associated with three final ionized states. Assuming a similar electronic configuration to that deduced for the chloride, where spin-orbit coupling effects are small, the first feature in the spectra of both the bromide and iodide will correspond to states formed as a result of spin-orbit coupling between ionized states formed by ionization from the near degenerate group of $4e$, $1a_2$, and $4a_1$ orbitals. Since the second-order coupling between the ${}^2E_{\frac{1}{2}}$, $1a_2^{-1}$ and $4a_1^{-1}$ states will be large, the most reasonable assignment would appear to be that given in Table 1, *i.e.* that the ${}^2E_{\frac{1}{2}}$ $1a_2^{-1}$ state is to be associated with the second halogen lone pair feature, the first feature being associated with the ${}^2E_{\frac{3}{2}}$ $4e^{-1}$ and ${}^2E_{\frac{1}{2}}$ $4e^{-1}$, $4a_1^{-1}$ states, although of course the ${}^2E_{\frac{1}{2}}$ states will not be pure. The second halogen lone pair feature is then to be associated with the ${}^2E_{\frac{3}{2}}$ $3e^{-1}$ and ${}^2E_{\frac{1}{2}}$ $1a_2^{-1}$, $3e^{-1}$ states. The splitting in this feature for the iodide spectrum is associated with first-order spin-orbit splitting for the $3e^{-1}$ state.

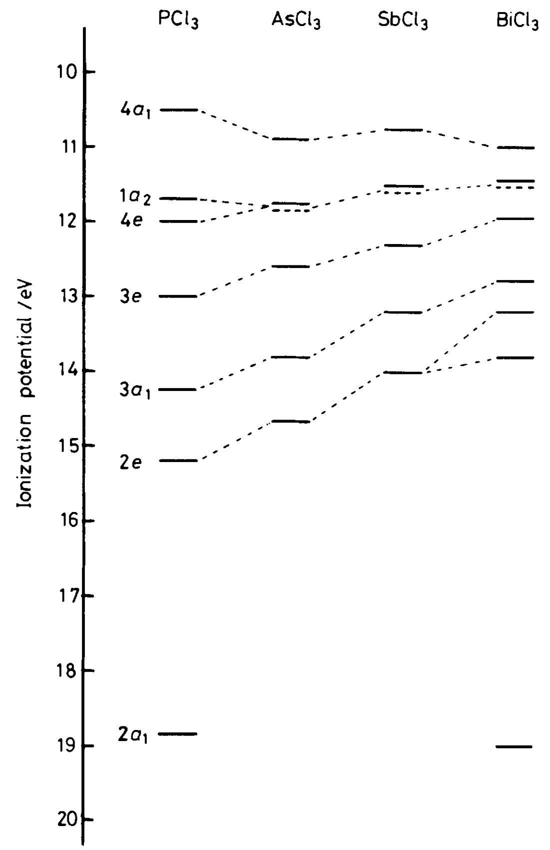

Figure 4. Correlation of valence-shell ionization potentials for the Group 5B trichlorides

The Fluorides.—The spectra of BiF_3 and SbF_3 [Figures 1(*a*) and 3] bear a marked resemblance to that of $BiCl_3$ [Figure 1(*b*)] and similar assignments have been assumed. The most notable difference is in the He(I)–He(II) relative intensity change of the $4a_1^{-1}$ band. The large apparent reduction in the relative intensity of the $4a_1^{-1}$ band compared to other fluorine lone pair features in the He(II) spectrum indicates that the $4a_1$ orbital can no longer be associated with the halogen localized orbitals but as for the lighter Group 5B fluorides has gained considerable Sb–Bi valence p_z character due to the lowering in the halogen valence p orbital energy for the fluorides. A further point associated with this band is the development of a low ionization energy shoulder in the $4a_1^{-1}$ spectrum of BiF_3 and of a low ionization energy asymmetry in the $4a_1^{-1}$ feature of SbF_3. Since both features are assigned to ionization from singly degenerate orbitals such substructure is difficult to explain. The most likely explanation appears to be that the low energy feature is a ' hot band '. The higher

Table 2. Binding energies[a] for condensed spectra from He(IIα) spectra

Feature	BiF_3	$BiCl_3$	$BiBr_3$	BiI_3
Valence band edge	0	0	0	0
A	1.21	1.17	1.14	—
B	3.35	2.04	1.60	1.40 (A + B)
C	5.05 5.57	3.48 4.71	3.80	3.52
D[b]	—	9.20	9.93 13.12	10.38
E[c]	—	—	24.61	24.74

[a] All values in eV referred to valence band edge. [b] D corresponds to Bi $6s^{-1}$ ionization. [c] E corresponds to Bi $5d^{-1}$ ionization $^2D_{\frac{5}{2}}$ state.

temperature required to vaporize BiF_3 compared to that required for other bismuth halides will result in a larger number of vibrational states being populated. The observed photoelectron envelope will then be the sum of the Franck–Condon envelopes from the various possible vibrational levels. Such a process could conceivably give rise to the observed low energy shoulder (Table 1).

A marked difference is noted between the $2e^{-1}$ and $3a_1^{-1}$ features of BiF_3 and SbF_3. This is assumed to be due to the large spin-orbit splitting of the $2e^{-1}$ band for BiF_3. Thus for SbF_3 a simple assignment of the 16.10 and 16.64 eV features to $3a_1^{-1}$ and $2e^{-1}$ ionization is possible, whereas for BiF_3 spin-orbit splitting reverses the relative intensity of these bands and they are now assigned to the $3a_1^{-1}$ $^2E_{\frac{1}{2}}$ and $2e^{-1}$ $^2E_{\frac{3}{2}}$ states 15.40 eV and to the $2e^{-1}$ $^2E_{\frac{1}{2}}$ state 15.99 eV.

Inner Valence Shell Ionizations.—Weak bands in the 18 to 20 eV region of the He(II) spectra are assigned to ionization from the $2a_1$ orbitals. For SbF_3 (Figure 3) this feature appears to be anomalously enhanced. No features have been associated with ionization from the $1a_1$ and $1e$ orbitals. These orbitals are expected to have a low photoelectron cross-section being largely halogen valence s in character.

In addition to ionization from the valence orbitals indicated in the electronic configuration, it might be expected from a consideration of the valence d shell ionization potentials of related halides that ionization from the $5d^{-1}$ shell of bismuth will be observed in the 32 to 35 eV region;[11] although this region is overlapped by the He(Iα) valence shell spectrum it has been possible to identify features on the He(IIα), He(IIβ), or He(IIγ) lines which could be assocated with this ionization (Figures 1—3). Because of overlap problems it was in general only possible to identify the $^2D_{\frac{5}{2}}$ state. However, for $BiBr_3$ both states were observed indicating a spin-orbit splitting of 2.99 eV in close agreement with the reported splitting for solid BiI_3.[12] In all cases the sharp nature of these features indicated their atomic character. The chemical shift observed for the fluoride, chloride, bromide, and iodide (Table 1) is similar to that observed for other related inorganic halides[11] and reflects the increasing ionic character of the lighter halides.

Spectra of Solids.—He(IIα) spectra of the condensed bismuth halides are shown in Figures 1 and 2 and the binding energies relative to the top of the valence band are given in Table 2. Although it is frequently possible to give an absolute calibration of spectra recorded by continuous deposition by use of internal gas calibrants,[8] shifts with respect to the gas-phase calibrant (He) suggested that for the more ionic molecules surface charging effects were affecting calibrations and the top of the valence band has therefore been adopted as a reference level. For BiI_3 charging effects appear to be absent and an absolute value of 30.97 eV was obtained for the $^2D_{\frac{5}{2}}$ level giving a relaxation energy of 1.69 eV from the gas-phase level. This must, however, be considered as a lower limit because of the possibility of charging.

Spectra of BiI_3 and BiF_3 are in close agreement with those already reported for these molecules.[12-14] The spectrum of solid SbF_3 has previously been analysed by reference to calculation of molecular ionization potentials.[14] This close relationship between the band structure of the solids and the electronic structure of the molecules is shown by Figures 1 and 2 where the He(IIα) spectra of the condensed solids are shown with the same energy dispersion but with the solid spectra drawn to show the strong correlation between gas-phase and solid features. The agreement is clearly close in all cases, the spectra of the solid representing a slightly broadened molecular spectrum. Thus the $4a_1$ feature which is separate from the halogen lone pair region in gas-phase BiF_3 but not in the heavier halides is also separate in the spectrum of solid BiF_3 but not in spectra of the condensed heavier halides. This close correspondence suggests the following direct relationship between the solid state features and molecular orbitals: A = $4a_1$, B = $3e$, $4e$, $1a_2$, C = $2e$, $3a_1$. The nomenclature for the solid spectra is that given in Figures 1 and 2 and in Table 2.

It thus appears that although exhibiting some band structure effects the electron-density distribution indicated by the photoelectron spectra shows that these solids are perhaps best thought of as molecular solids.

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