PHYSICAL REVIEW B VOLUME 13, NUMBER 2 15 JANUARY 1976

Photoelectron valence-band spectra of PbF_2, SbF_3, and BiF_3

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(Received 6 August 1975)

The results of a photoelectron study of the molecular solids PbF_2, BiF_3, and SbF_3, taken with a helium discharge source, are compared with molecular-orbital calculations which use a geometry based on crystal data and which include a crystal potential. The features of the valence-band spectra for these solids are successfully interpreted in this way.

I. INTRODUCTION

Photoelectron spectroscopy (PES) has yielded much valuable information about the electronic structure of atoms, molecules, solids, and liquids. One of its greatest successes, in terms of quantitative agreement between the results of PES measurements and the predictions of a detailed theory, has been in the gas-phase studies of molecules and molecular-orbital (MO) theory.[1] Solid-state band-structure calculations have also been encouraged by the appearance of detailed photoelectron spectra from solid samples, but the agreement here has not always been as satisfactory. It is clearly reasonable to enquire whether concepts developed in molecular PES can be carried over profitably to the study of solids. This suggestion has been offered previously,[2,3] but only a few studies in this area have been reported.[4]

The application of MO theory to solids is expected to be most appropriate for those solids which may be classified as "molecular"; that is, those which may be regarded as a loosely bound collection of identifiable molecular units. In the case of naphthacene the crystal PES spectrum is almost identical to the gas-phase or molecular spectrum.[5] In general, for a wide variety of solids, molecular or otherwise, it should be instructive to conduct comparative investigations of the gas and solid-phase spectra of the same materials. Very few PES studies of this kind have been carried out to date.[6]

Investigations of the types outlined above have been restricted in part by the fact that MO calculations have not been generally available for molecules containing heavy atoms. This is due to the expense of performing *ab initio* linear-combination-of-atomic orbitals–self-consistent-field (LCAO-SCF) calculations on molecules containing a large number of electrons, and the inaccuracy of possible semiempirical valence-electron methods for such systems. However, a nonempirical valence-electron (NEVE) method,[7] developed for use with molecules containing heavy atoms, has recently been extended to accommodate atoms up to xenon (atomic number 54).

In this paper we report 40.81-eV PES measurements of the valence bands of the solids PbF_2, SbF_3, and BiF_3. Similar structure is exhibited in each spectrum. Solid-state band-structure calculations and resultant density-of-states predictions are not available for these samples. Nevertheless, their molecular structure invites comparison of the PES results with MO calculations. NEVE calculations have been made for the lightest molecule SbF_3 using a geometry based on crystal data and including a crystal potential. Satisfactory agreement is obtained with all the principal features of the experimental solid-phase spectrum.

II. EXPERIMENTAL RESULTS

The experimental details in regard to the spectrometer, photon sources, and sample preparation have been published in Ref. 8 and in references contained therein. Starting less than 5 sec after each sample evaporation, four 256-channel spectra were accumulated successively, with only one voltage sweep per spectrum (0.1s per channel). No evidence of sample charging due to the emission of electrons from the target was observed for these spectra. The spectrometer was calibrated for energy using the xenon $5p$ gas photolines.

Figure 1 shows the photoelectron spectra of PbF_2, SbF_3, and BiF_3 taken with an instrumental resolution [full width at half-maximum (FWHM)] of 0.3 eV. These spectra have been corrected for the transmission efficiency of the spectrometer,[9,10] but have not been smoothed or deconvoluted. The positions of the various peaks in the

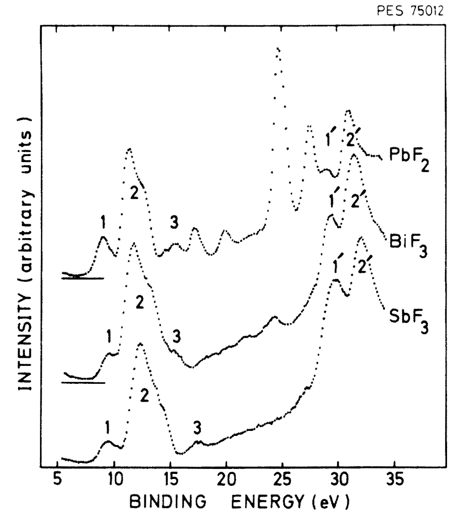

FIG. 1. Measured photoelectron spectra of solid PbF_2, BiF_3, and SbF_3 taken using He II (40.81 eV plus satellites) radiation. The peaks labeled 1′ and 2′ arise from He I (21.22 eV and satellites) radiation. Binding energies are referred to the vacuum level.

spectra, together with explanations of the origin of unnumbered peaks, are shown in Table I and Fig. 2. The majority of the unnumbered peaks arise from the outer 5*d* states of the heavy metal atom, being generated by the 40.81-, 48.37-, or 51.02-eV photon lines.

The valence-band region is of major interest, and it may be seen that the three fluorides exhibit very similar spectral features in this region. While it seems reasonable to suggest that the broad and intense feature numbered 2 is predominantly fluorine 2*p* in character because of its position and intensity[11,12] and that the peaks numbered 1 may be associated with the metal-atom outer *p* level, more detailed analysis of the results is clearly desirable.

The possibility that various features of the spectra might not be due to intrinsic band structure but rather to final-state or electron-transport effects was investigated and rejected. For example, the peaks numbered 1 lie at smaller binding energies than the main peaks (numbered 2) and cannot be caused by the various processes known to generate lower kinetic-energy satellite structure, such as characteristic energy loss, shake up or shake off, configuration interaction, etc. Wertheim *et al.*[13] have interpreted structure in the valence bands of transition-metal compounds in terms of a multiplicity of final states generated by the crystal field. In the present work this requires a transition from an initial $F^- 2p^6$ to a final $F^- 2p^5$ ion configuration. In crystal symmetries of lower order than tetrahedral there may be up to three final states of the $2p^5$ configuration. This interpretation normally suggests an intensity ratio of 1 : 2 for crystal-field split peaks at variance with the present experimental findings. A further possible mechanism is exchange splitting which has been successfully used to explain structure in the 4*f* photoelectron spectra of the rare-earth trifluorides.[14] However, in the present case this would produce two peaks of equal intensity and consequently is not an acceptable mechanism.

TABLE I. Tabulation of the centroid binding energies and FWHM of the measured photoelectron valence bands shown in Fig. 1. The binding energies are referred to the vacuum level.

	Band 1		Band 2		Band 3
Sample	Binding energy (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)	Binding energy (eV)
PbF_2	9.0	1.4	11.8	2.5	15.5
BiF_3	9.6	(1.8)	12.2	3.0	15.5
SbF_3	9.6	1.9	12.9	3.1	17.6

III. MO CALCULATIONS

The present fluorides, in crystalline form, are molecular in character,[15] and are appropriate samples to investigate the relationship between MO calculations and solid-state PES spectra. While the corresponding gas-phase spectra do not appear to have been measured, gas-phase spectra for other group-IV*A* and -V*A* fluorides have been reported: SiF by Westwood[16] and NF_3, PF_3, and AsF_3 by Potts *et al.*[17] Although these spectra were taken at 21.22 eV photon energy, and hence do not explore the same depth of structure as does the present solid-phase work, the gas-phase spectra all show structure reminiscent of the present results (see Fig. 2). In particular, there is an isolated band at small values of ionization potential (IP) corresponding to a largely non-

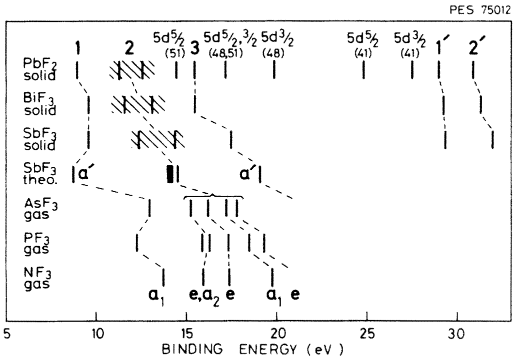

FIG. 2. Summary and designation of the principal features of the spectra shown in Fig. 1. In addition gas phase photoelectron data from Ref. 17 is presented for NF_3, PF_3, and AsF_3.

TABLE II. Calculated MO eigenvalues and corresponding compositions for SbF_3 as well as calculated net atomic charges for Sb and F.

Symmetry[a]	Eigenvalues (eV)		Composition
	Calculation I[b]	Calculation II[c]	
a'	-10.14	-8.72	Sb localized (92% Sb)
a''	-14.82	-14.03	F localized [(19–100)% F]
a'	-15.02	-14.11	
a'	-15.06	-14.14	
a''	-15.06	-14.15	
a''	-15.09	-14.18	
a'	-15.10	-14.18	
a''	-15.19	-14.30	Sb-F
a'	-15.47	-14.66	
a'	-20.14	-19.07	Bonding (38% Sb)
Atom	Net atomic charges		
Sb	0.81	1.02	
F	$-0.26, -0.27$	$-0.32, -0.35$	

[a] C_{3v} symmetry in gas phase is reduced to C_s in crystal.
[b] MO calculation for isolated molecule.
[c] MO calculation including crystal potential.

bonding a_1 molecular orbital of heavy-atom s-p hybrid character, which may be regarded as arising from the "lone-pair" on this atom, and a series of closely spaced, intense bands at greater IPs corresponding to a number of orbitals with predominantly fluorine $2p$ character.

Antimony trifluoride (SbF_3) was chosen for detailed study because, of the three samples, its metal atom is the lightest. The SbF_3 molecule is pyramidal, with C_{3v} symmetry. Crystalline SbF_3 is orthorhombic, with four clearly identifiable molecules per unit cell, each molecule having C_s symmetry. This arises from the fact that, in the crystal, the SbF_3 molecular units differ from a perfect pyramidal shape only in the small displacement of one fluorine atom.[15]

Two NEVE molecular-orbital calculations have been performed. The first was for an isolated SbF_3 molecule with a geometry based on the crystal data; that is, with C_s molecular symmetry. The second calculation included in addition a crystal potential determined for the crystal coordinates and calculated by the Ewald method.[18] The crystal potential is incorporated in the self-consistent-field calculation according to the description given by Roby *et al.*[19]

The valence MO eigenvalues for the two calculations are given in Table II, together with details of the atomic compositions, which are similar in the two cases. The effect of the crystal potential is to increase the ionicity of the molecule as shown by the calculated atomic charges determined from the orbital population analysis. In addition, the eigenvalues are uniformly more positive by about 1 eV in the crystal calculation than in the isolated molecule calculation. The order of occupied MOs is the same in both calculations.

IV. DISCUSSION

On the basis of Koopmans's approximation[20] the bands in the photoelectron spectrum of solid SbF_3 can be correlated with the calculated ionization potentials as follows.

The first band (see Figs. 1 and 2) measured at 9.6 eV binding energy is well separated from the bands at larger values of IP and clearly may be identified with the first (a') MO at 8.72 eV. It is assigned therefore, to $5s$-$5p$ electrons very largely localized on the antimony atoms. Band broadening is considerable in the solid; this band has a FWHM of 1.9 eV, which may be compared with a FWHM of 0.6 eV for the first band of the experimental PES gas-phase spectrum of AsF_3.[17]

The broad, intense structure near 13 eV in the experimental spectrum may be readily identified with two groups of MO states: first, the six MOs, with energy eigenvalues from -14.03 to -14.18 eV, which are of fluorine $2p$ character and essentially localized and nonbonding; and second, the eighth and ninth MOs at -14.30 and -14.66 eV, which are of Sb-F bonding character although largely fluorine $2p$ in composition. The latter two orbitals may be identified with the shoulder apparent on the high binding-energy side of the experimental band. The experimental peak at 17.6 eV may then be identified with the tenth (a') MO calculated at 19.07 eV and of Sb(5s)-F(2p) character.

The photoelectron spectrum of solid SbF_3 is

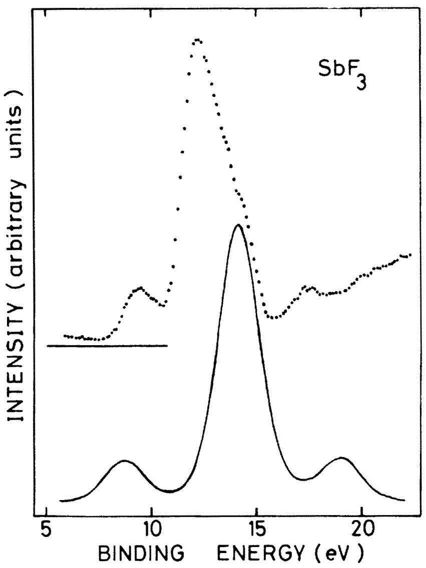

FIG. 3. 40.81-eV photoelectron spectrum of SbF_3 (dotted line) compared with the result of a molecular-orbital calculation (II—see Table II) (solid line).

therefore interpreted in terms of a molecular model, and the eigenvalues of calculation II are the basis of the calculated spectrum shown in Fig. 3. Koopmans's theorem is assumed, and each ionization potential is given the same intensity and is represented by a Gaussian function with a FWHM of 2 eV, to represent the several processes (such as intramolecular vibration and electron energy loss) that lead to band broadening in the solid-state spectrum. The agreement between the experimental and theoretical spectra is most illuminating, particularly in view of the relatively severe assumptions made; for example, the use of Koopmans's theorem, which neglects relaxation effects. As is not uncommon, the ordering of the MOs agrees precisely with the experimental results, though the binding-energy values show some disagreement.

Although we cannot at present perform similar calculations for molecular PbF_2 and BiF_3, their photoelectron spectra are clearly interpretable in the same terms as that of SbF_3. Hence the first band in each case may be associated with the lone pair 6*p* electrons of the central heavy atom. The most intense band is mainly of fluorine nonbonding character with a higher-energy shoulder arising from the metal-fluorine bonding orbitals. The remaining band in each case may be associated with metal 6*s* electrons. The consequent explanation of these features suggests that MO theory may provide a fruitful alternative viewpoint for examining the structure of a variety of solids.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the technical support of Miss M. Sierzputowski and Mr. G. J. Newton, and the Australian Research Grants Committee.

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