

UPS-EELS INVESTIGATION OF THE ELECTRONIC STRUCTURE OF $\text{BF}_3 \cdot \text{H}_2\text{S}$ *T. PRADEEP, C.S. SREEKANTH, M.S. HEGDE and C.N.R. RAO ¹*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*

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Orbital ionisation energies and electronic transitions of the 1 : 1 addition compound between BF_3 and H_2S have been investigated by ultraviolet photoelectron spectroscopy and electron energy loss spectroscopy. The $\sigma \rightarrow \sigma^*$ transition of the donor-acceptor bond is assigned to an energy loss feature at 9.4 eV.

1. Introduction

Addition compounds formed by BF_3 with electron donors have been of interest to chemists for many years and some of these compounds (e.g., $\text{BF}_3 \cdot \text{NH}_3$) are stable with high dissociation energies of the order of 50–100 kJ mol⁻¹ [1]. Although the structure and bonding of such compounds formed between Lewis acids and bases is of vital importance, there have been very few experimental investigations directed towards a complete description of the electronic structures. Reports in the literature are limited to photoelectron spectroscopic studies providing orbital energies of valence or core levels [2,3] and quantum chemical calculations [3–5]. The addition compound between BF_3 and H_2O is stable and has been studied recently [6]. The analogous addition compound between BF_3 and H_2S has, however, not been investigated and it has been suggested that this is unstable [4]. In this communication, we present the first experimental investigation of $\text{BF}_3 \cdot \text{H}_2\text{S}$ by making use of ultraviolet photoelectron spectroscopy (UPS) and electron energy loss spectroscopy (EELS). EELS provides information on electronic excitations, which is otherwise difficult to obtain for such species. Our experimental study combined with MO calculations has enabled us to establish the energy levels and electronic transitions of the $\text{BF}_3 \cdot \text{H}_2\text{S}$

complex. In particular we have assigned the $\sigma(\text{BS}) \rightarrow \sigma^*(\text{BS})$ transition of the donor-acceptor bond. For the purpose of comparison, we have carried out preliminary studies on $\text{BH}_3 \cdot \text{H}_2\text{S}$ which seems to show a $\sigma(\text{BS}) \rightarrow \sigma^*(\text{BS})$ transition with a comparable energy.

2. Experimental

A home-built ultraviolet photoelectron spectrometer consisting of a HeI UV lamp, a 3 mm diameter collision chamber and a channeltron electron multiplier was employed to determine orbital ionisation energies. Differential pumping allowed the operation of the HeI lamp at 1.5 Torr and maintenance of 5×10^{-5} Torr pressure in the rest of the spectrometer; the sample pressure was 0.1–0.5 Torr. The resolution of the spectrometer was 80 meV fwhm at 19.7 eV. The electron energy loss spectrometer is also home-built and consists of a hemispherical monochromator (125 mm mean diameter), a collision chamber, a hemispherical electron energy analyser (140 mm mean diameter), and a channeltron electron multiplier. Differential pumping allowed a sample pressure of 5×10^{-4} Torr while the rest of the spectrometer was maintained at 2×10^{-6} Torr. The resolution of the EEL spectrometer was 0.7% at the primary energy of 45 eV employed by us. The fwhm of the elastic peak was ≈ 300 meV.

In order to obtain the electron spectra of the addition compounds, BF_3 (B_2H_6) and H_2S were co-

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condensed at 77 K (with a small excess of the former) in a glass ampoule fitted with a teflon tap. The parent compound or the co-condensed mixture was admitted into the spectrometer by means of a needle valve. When the $\text{BF}_3 + \text{H}_2\text{S}$ or $\text{B}_2\text{H}_6 + \text{H}_2\text{S}$ is first admitted, the excess component generally contaminated the initial spectra, but is pumped away rapidly, finally giving the spectrum of the addition compound. These spectra, when stripped of the features due to the individual components, gave the spectrum of the 1:1 addition compound.

3. Results and discussion

HeI photoelectron spectra of BF_3 and H_2S are shown in fig. 1 along with the spectrum which we ascribe to the 1:1 addition compound. The spectrum of the addition compound is distinctly different from that of BF_3 or H_2S , suggesting complex formation. Ab initio molecular orbital calculations with the STO-3G basis set and full geometry optimisation using the GAUSSIAN 80 program [7] showed $\text{BF}_3 \cdot \text{H}_2\text{S}$ to be a stable compound with a dissociation energy of 16 kJ mol⁻¹. In the optimal geometry, the BF_3 moiety is nearly planar, with a F-B-F angle of 119.5°, and a B-S distance of 2.6 Å. It appears that

the pyramidal geometry is unstable [4]. It is to be noted that BF_3 forms a stable addition compound with dimethylsulphide with a dissociation energy of 14 kJ mol⁻¹ [8].

In table 1 we list the experimentally observed ionisation energies and orbital assignments based on our calculations. The first feature in the HeI spectrum of the addition compound at 11.6 eV corresponds to the sulphur lone pair. The $\sigma(\text{BS})$ orbital formed by the interaction between the donor and the acceptor has an ionisation energy of 16.1 eV.

Fig. 2 shows the electron energy loss (EEL) spectra of BF_3 , H_2S and the addition compound. The EEL spectrum of H_2S shows bands at 6.3, 8.3, 8.9, 9.6 and 10.8 eV due to $1b_1 \rightarrow 4s_{a_1}$, $1b_1 \rightarrow 4p_{a_1}$, $1b_1 \rightarrow 3d$, $3a_1 \rightarrow 4s_{a_1}$ and $1b_1 \rightarrow R$ transitions, respectively. The EEL spectrum of BF_3 shows peaks at 8.2, 10.1, 13.0 and 14.0 eV which are assigned to $1a_2' \rightarrow 2a_2''$, $1a_2' \rightarrow 3a_1'$, $1a_2'' \rightarrow 3a_1'$ and $2e' \rightarrow 3a_1'$ transitions, respectively. These transition energies of BF_3 vary slightly from those reported earlier [6], where the $1a_2' \rightarrow 2a_2''$ transition energy was given as 7.9 eV. It is possible that the spectrum reported earlier was slightly contaminated due to the presence of water vapour.

The main features in the EEL spectrum of the addition compound are at 5.1, 7.8, 9.4, 11.0, 12.3, and 13.4 eV. These transitions could be readily assigned by making use of the orbital energies obtained from the HeI spectrum. The first three transitions of

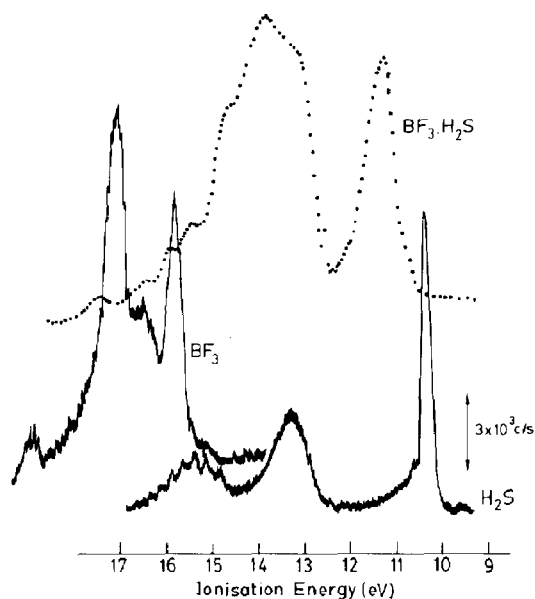


Fig. 1. HeI spectra of BF_3 , H_2S and $\text{BF}_3 \cdot \text{H}_2\text{S}$.

Table 1
Orbital ionisation energies of $\text{BF}_3 \cdot \text{H}_2\text{S}$ from the HeI spectrum

Assignment	Vertical IE (eV)
$17a'$ n(S)	11.6
$16a''$ $\pi(\text{SH})$	13.4
$8a''$ n(F) } $15a'$ n(F) } $7a'$ n(F) }	14.2
$6a''$ n(F) } $14a'$ n(F) }	14.8
$5a''$ $\pi(\text{SH})$	15.7
$13a'$ $\sigma(\text{BS})$	16.1
$12a''$ $\pi(\text{BF})$ } $4a''$ $\pi(\text{BF})$ }	16.6

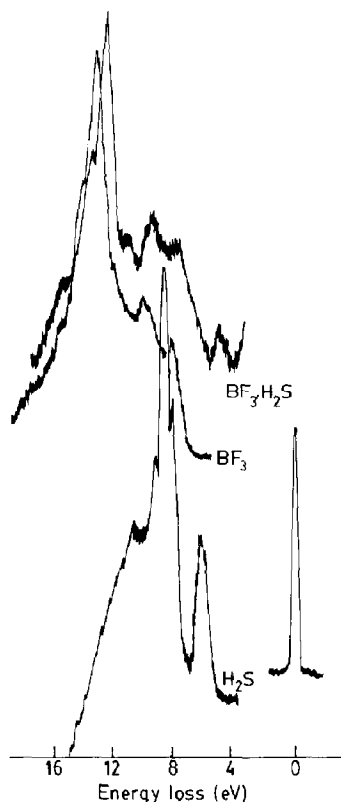


Fig. 2. Electron energy loss spectra of BF_3 , H_2S and $\text{BF}_3 \cdot \text{H}_2\text{S}$.

$\text{BF}_3 \cdot \text{H}_2\text{S}$ at 5.1, 7.8, and 9.4 eV arise from excitations to the σ^* (BS) level (table 2). The 5.1 eV transition is due to the $n \rightarrow \sigma^*$ excitation of the sulphur lone pair. Of particular interest is the transition at 9.4 eV due to the $\sigma(\text{BS}) \rightarrow \sigma^*(\text{BS})$ transition which is characteristic of the donor-acceptor bond in the addition compound. The higher energy transitions of $\text{BF}_3 \cdot \text{H}_2\text{S}$ at 11.0, 12.3 and 13.4 eV seem to arise

Table 2
Electronic transitions of $\text{BF}_3 \cdot \text{H}_2\text{S}$ from EELS

Energy (eV)	Assignment
5.1	$17a' \rightarrow 18a'$, $n \rightarrow \sigma^*$
7.8	$8a'' \rightarrow 18a'$, $n \rightarrow \sigma^*$
9.4	$13a' \rightarrow 18a'$, $\sigma \rightarrow \sigma^*$
11.0	$16a' \rightarrow 9a''$, $\pi \rightarrow \pi^*$
12.3	$6a'' \rightarrow 9a''$, $n \rightarrow \pi^*$ (R)
13.4	$5a'' \rightarrow 9a''$, $\pi \rightarrow \pi^*$ (R)

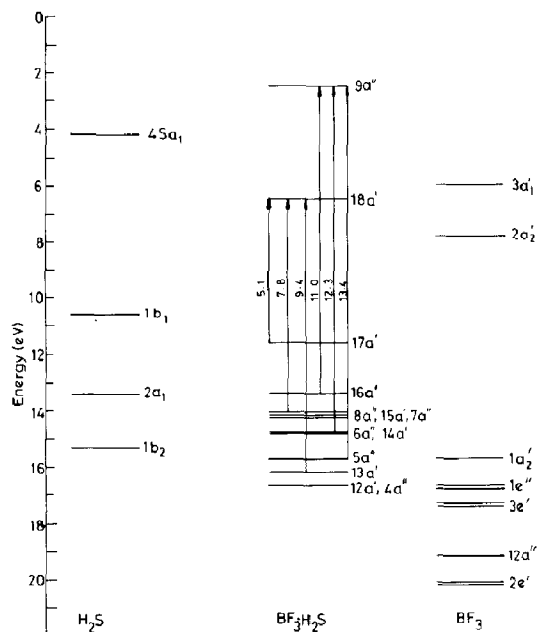


Fig. 3. MO diagram for the $\text{BF}_3 \cdot \text{H}_2\text{S}$ system.

from excitations to an unoccupied π^* level from the $16a'$, $6a''$ and $5a''$ levels, respectively. Table 2 lists the observed transition energies and their assignments.

The HeI spectrum of $\text{BH}_3 \cdot \text{H}_2\text{S}$ gave ionisation energies of 9.7 and 12.8 eV for the $n(\text{S})$ and $\sigma(\text{BS})$ orbitals. In the EEL spectrum we find bands at 6.1, 8.7 and 10.5 eV of which the last is due to the $\sigma(\text{BS}) \rightarrow \sigma^*(\text{BS})$ transition. We are now carrying out further experimental and theoretical investigations of the addition compounds of BH_3 .

Based on the experimental orbital ionisation energies of BF_3 , H_2S and the addition compound, we have drawn an approximate MO energy level diagram in fig. 3. In this figure, we have shown the levels due to two unoccupied states by making use of the electronic transition energies obtained from EELS.

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