

A STUDY OF THE ELECTRONIC STRUCTURES OF $n-v$ ADDITION COMPOUNDS OF BH_3 BY A COMBINED USE OF UPS AND EELS*

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(Received 16 March 1988)

ABSTRACT

Orbital energies and electronic transition energies of $BH_3 \cdot H_2S$ and $BH_3 \cdot CO$ obtained from ultraviolet (HeI) photoelectron spectroscopy and electron energy loss spectroscopy are discussed in the light of quantum mechanical calculations. $BH_3 \cdot H_2O$ has been characterized, for the first time, by means of the HeI spectrum and the ionization energies assigned to the various orbitals based on calculations.

INTRODUCTION

Of the various types of electron donor-acceptor interactions, the two-way donor-acceptor, or $n-v$ (n = non-bonded orbital, v = vacant orbital), interaction is the strongest [1]. Addition compounds formed between Lewis acids and Lewis bases, such as $BH_3 \cdot NH_3$ and $BF_3 \cdot H_2O$, are well-known examples of $n-v$ donor-acceptor complexes. Thermodynamics of the $n-v$ complexes has been well documented and quantum chemical calculations with different approximations have been performed on some of the complexes to understand the nature of interaction and the magnitude of charge-transfer between the donor and the acceptor. Investigations of the experimental electronic structure of $n-v$ complexes have, however, been limited to ultraviolet photoelectron spectroscopic studies of a few complexes of BH_3 in order to obtain orbital energies [2,3]. There is no report in the literature on the electronic transitions of even the most well-known complexes of BH_3 , for example $BH_3 \cdot CO$. The only complete experimental study of an $n-v$ addition compound both in terms of orbital energies and electronic transitions is the one carried out recently by Durrant et al. [4] in this laboratory.

We have carried out an investigation of the vapour phase complexes of BH_3

*Contribution No. 526, dedicated on the occasion of his 75th birthday, to Professor K.S. Pitzer, a great Physical Chemist, who has inspired one of us (CNRR) in his formative years.

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with CO and H₂S by a combined use of ultraviolet photoelectron spectroscopy (UPS) and electron energy loss spectroscopy (EELS). While UPS directly provides the orbital energies, EELS gives electronic transition energies. In addition, we have carried out a preliminary UPS investigation of the complex between BH₃ and H₂O which has not been characterized hitherto.

EXPERIMENTAL

Electron energy loss spectra were recorded with a home-built spectrometer [5] consisting of a hemispherical electron monochromator (125 mm mean diameter), a collision chamber, a hemispherical electron energy analyzer (140 mm mean diameter), and a channeltron electron multiplier. By means of differential pumping, a sample pressure of 5×10^{-4} torr could be produced in the collision chamber, while the rest of the spectrometer remained at 2×10^{-6} torr. An electron beam of 45 V with 300 meV FWHM was employed in the present study. Ultraviolet photoelectron spectra were recorded with a home-built spectrometer [6] consisting of a HeI UV lamp, a 3 mm diameter collision chamber and a channeltron electron multiplier. Differential pumping allowed for operation of the helium lamp at 1.5 torr, a sample pressure of 0.1 to 0.5 torr and a pressure of 5×10^{-5} torr in the rest of the spectrometer. The resolution of the instrument was 80 meV FWHM at 19.7 eV.

In the case of BH₃·H₂S, samples of the complex were prepared in vacuum by co-condensation of the donor with a small excess of B₂H₆ at 77 K in a glass ampoule fitted with a teflon tap. In the case of BH₃·CO, one sample was prepared with a small excess of B₂H₆ and another with a small excess of CO. Samples of the complexes were gently warmed to room temperature and were admitted into the UP or EEL spectrometer by means of a needle valve. The initial spectrum was generally contaminated with the excess component (e.g. B₂H₆ or H₂S in the case of BH₃·H₂S), which rapidly pumped away to give the spectrum of the addition compound. The technique employed by us to obtain a nearly pure spectrum of the complex was similar to the one described in the literature [4,7]. HeI spectra of the complexes often contained the features of both the complex and the individual components. These spectra, when stripped off of the individual components, gave pure complex spectra.

In order to obtain BH₃·H₂O in the vapour phase, B₂H₆ was introduced into the collision chamber contaminated with water vapour. HeI spectra were recorded until the pure B₂H₆ spectrum was obtained. The spectrum of the complex was present just prior to this stage.

RESULTS AND DISCUSSION

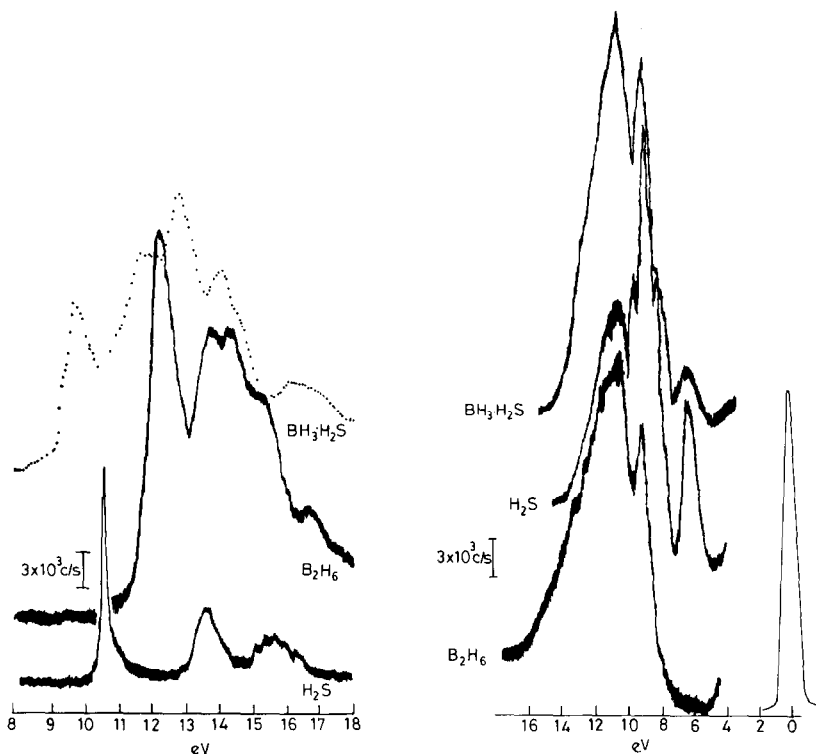
BH₃·H₂S

Figure 1 shows the HeI spectra of BH₃·H₂S, B₂H₆ and H₂S. H₂S has characteristic ionization energies (IE) of 10.4, 13.3 and 15.7 eV. The spectrum of

TABLE 1

Occupied Orbital energies of $\text{BH}_3 \cdot \text{H}_2\text{S}$

Assignment	STO-3G energies (eV)	Vertical IEs (eV) from UPS
n_s $11a'$	10.1	9.7
$\pi_{\text{B-H}}$ $3a''$	10.7	11.9
$\sigma_{\text{S-B}}$ $10a'$	10.8	12.8
$\pi_{\text{S-H}}$ $9a'$	13.4	14.1
$\pi_{\text{S-H}}$ $2a''$	16.3	16.6

Fig. 1. HeI spectra of B_2H_6 , H_2S and $\text{BH}_3 \cdot \text{H}_2\text{S}$.Fig. 2. Electron energy loss spectra of B_2H_6 , H_2S and $\text{BH}_3 \cdot \text{H}_2\text{S}$.

$\text{BH}_3 \cdot \text{H}_2\text{S}$ is distinctly different from that of H_2S or B_2H_6 . Table 1 lists the experimental vertical IEs of the complex obtained from UPS.

In order to assign the IEs to various molecular levels, we have carried out ab initio calculations with the STO-3G basis set using the GAUSSIAN 80 program [8] with full geometry optimization. The optimized geometry gave B-H,

S-H and B-S distances of 1.15, 1.33 and 2.02 Å with a point group of C_s . The H-S-H and H-B-H angles were 93.95° and 115.46° with a tetrahedral arrangement for the H_3BS moiety. The calculated dissociation energy of $BH_3 \cdot H_2S$ (into BH_3 and H_2S) was 122 kJ mol⁻¹, a value which is rather high. The dissociation energy of $BH_3 \cdot H_2O$ calculated with the same basis set [9] is much higher (165 kJ mol⁻¹) indicating that $BH_3 \cdot H_2S$ is a weaker complex than $BH_3 \cdot H_2O$. MP3/6-31G* calculations [10] yield dissociation energies of 33 and 61 kJ mol⁻¹, respectively, for $BH_3 \cdot H_2S$ and $BH_3 \cdot H_2O$. These values seem to be more realistic. In any case, the calculations clearly show $BH_3 \cdot H_2S$ to be a sufficiently stable molecular complex, but weaker than $BH_3 \cdot H_2O$.

Table 1 gives assignments of the experimental IEs from UPS to the various orbitals, the ordering corresponding to that obtained from our STO-3G calculations. It is important to note that the orbital which is involved in B-S bonding is \bar{n}_s .

Figure 2 shows the EEL spectrum of $BH_3 \cdot H_2S$ along with the spectra of H_2S and B_2H_6 . The EEL spectrum of B_2H_6 shows bands at 6.8, 9.1 and 10.6 eV which exactly correspond to the UV absorption bands reported in the literature [11,12]. The EEL spectrum of H_2S shows bands at 6.3, 8.3, 8.9, 9.6 and 10.8 eV. The EEL spectrum of $BH_3 \cdot H_2S$ has bands at 6.1, 8.7 and 10.5 eV, respectively. Of the three bands, the lowest energy transition around 6 eV corresponds to an $n-\pi^*$ excitation. The more important transition is the one from $\sigma(BS)$ to $\sigma^*(BS)$ found around 10.5 eV. Assignments of the electronic transitions are listed in Table 2. Figure 3 gives the MO diagram for $BH_3 \cdot H_2S$ using the experimental orbital energies of the complex as well as of H_2S and theoretically calculated energies of BH_3 . Experimental electronic transition energies have been employed to fix the positions of the unoccupied states.

$BH_3 \cdot CO$

Of the various addition compounds of BH_3 , the most exhaustively studied one is probably $BH_3 \cdot CO$. Extensive quantum chemical calculations have been carried out on this complex by several workers [13-15]. The experimental dissociation energy of this complex is 79 kJ mol⁻¹. The HeI spectrum of

TABLE 2

Electronic transitions in $BH_3 \cdot H_2S$

Assignment	Transition energies (eV) from EELS
$11a' \rightarrow 4a''$	6.1
$3a'' \rightarrow 4a''$	8.7
$10a' \rightarrow 12a'$	10.5

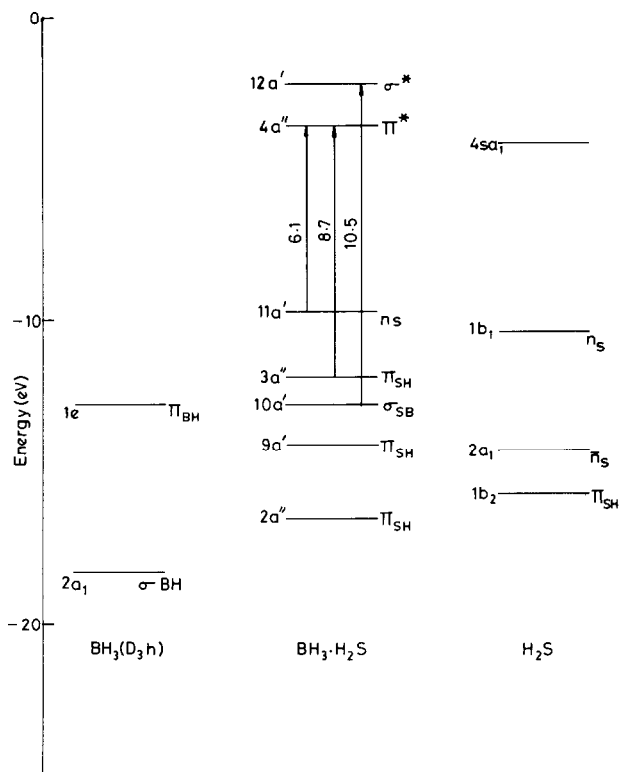
Fig. 3. MO diagram of BH₃·H₂S

TABLE 3

Occupied orbital energies of BH₃·CO

Assignment	4-31G energies (eV) ^a	Vertical IEs (eV) from UPS
π _{B-H} 2e	12.6	{ 11.9 12.5
σ _{B-C} 7a ₁	15.6	14.1
π _{C-O} 1e	19.1	17.0
n _O 6a ₁	21.6	18.7

^aThe corresponding values from W.C. Ermler et al. [13] are 12.8, 15.4, 19.9 and 21.8 eV respectively.

BH₃·CO has been reported in the literature [3]. The first peak in the spectrum due to the 2e (π_{BH}) orbital appears as a doublet at 11.9 and 12.5 eV due to Jahn-Teller splitting in the ionic state. The assignments of the other levels are straight-forward and are listed in Table 3. We have recorded the EEL spec-

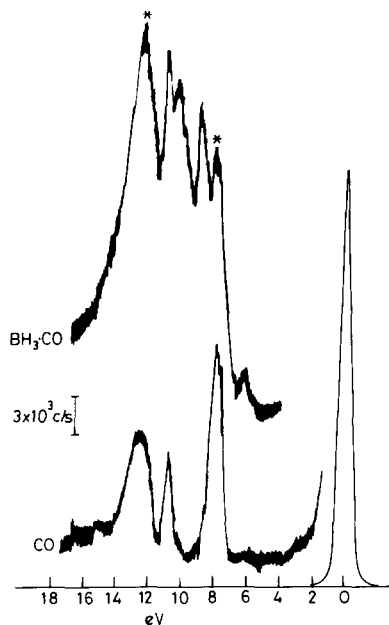


Fig. 4. Electron energy loss spectra of CO and $\text{BH}_3 \cdot \text{CO}$. The peaks with asterisks are probably due to CO impurity.

TABLE 4

Electronic transitions in $\text{BH}_3 \cdot \text{CO}$

Assignment	Transition energies (eV) from EELS
$2e \rightarrow 3e$	6.5
$2e \rightarrow 4e$	9.0
$7a_1 \rightarrow 8a_1$	10.4
$1e \rightarrow 3e$	11.2

trum of $\text{BH}_3 \cdot \text{CO}$ shown in Fig. 4. The spectrum shows fairly sharp features corresponding to transitions at 6.5, 9.0, 10.4 and 11.2 eV, besides peaks at 8.3 and 12.5 eV. We consider the last two to arise from CO formed by dissociation of the complex; part of the justification for this is that we are unable to assign them to any meaningful transition of the complex. The transition energies and their assignments are given in Table 4. The first two transitions at 6.5 and 9.0 eV correspond to $\pi \rightarrow \pi^*$ transitions. The transition at 10.4 eV is from $\sigma(\text{BC})$ to $\sigma^*(\text{BC})$.

$BH_3 \cdot H_2O$

Although this complex has been described in theoretical calculations [16,17], experimental investigations have been difficult due to the hydrolysis of diborane. Figure 5 shows the HeI photoelectron spectrum which, we feel, can be attributed to the $BH_3 \cdot H_2O$ complex. The reason that we have been able to obtain the spectrum is that most of the water is destroyed by reaction with B_2H_6 leaving a few molecules of H_2O in the vapour phase to form the complex, under the experimental conditions employed here. Furthermore, the HeI spectrum shows two bands at 9.7 and 10.6 eV which are much lower than the lowest IEs of water (12.6 eV) and B_2H_6 (11.9 eV). We therefore feel that the five features in the HeI spectrum at 9.7, 10.6, 11.8, 13.2, and 14.4 eV are all due to the complex. Ab-initio calculations using the 3-21G basis set [8] enabled us to assign these ionization energies to various orbitals. As mentioned earlier, ab-initio calculations predict $BH_3 \cdot H_2O$ to be a stable complex; our 3-21G calculations yield a dissociation energy of 94 kJ mol^{-1} for the staggered configuration. The optimized geometry gave O-H, B-H and B-O distances of 0.96, 1.20 and 1.71 Å. The H-B-H, H-O-B and H-O-H angles are 115.28, 114.98 and 113.22° with a point group of C_s and a tetrahedral arrangement for the OBH_3

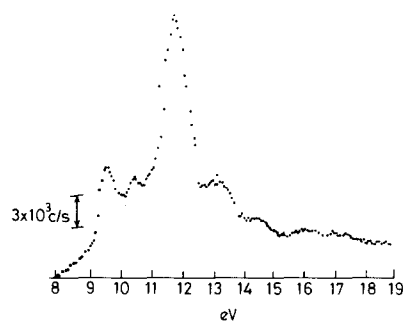


Fig. 5. HeI spectrum of $BH_3 \cdot H_2O$

TABLE 5

Occupied orbital energies of $BH_3 \cdot H_2O$

Assignment	3-21G energies (eV)	Vertical IEs (eV) from UPS
$\pi_{B-H} 7a'$	11.7	9.7
$\pi_{B-H} 2a''$	11.8	10.6
$\sigma_{B-O} 6a'$	15.2	11.8
$n_O 5a'$	17.5	13.2
$n_O + \sigma_{B-O} 4a'$	20.2	14.4

moiety. Experimental IE's and calculated orbital energies of $\text{BH}_3 \cdot \text{H}_2\text{O}$ are listed in Table 5 along with the assignments. Further studies on this complex are now in progress.

ACKNOWLEDGEMENT

The authors are thankful to the Department of Science & Technology, Government of India, for support of this research.

REFERENCES

- 1 R.S. Mulliken and W.B. Person, *Molecular Complexes*, Wiley-Interscience, New York, 1969.
- 2 I.H. Hillier in H. Ratajczak and W.J. Orville-Thomas (Eds.), *Molecular Interactions*, Wiley, New York, 1981, Vol. 2.
- 3 D.R. Lloyd and N. Lymnagh, *J. Chem. Soc. Faraday Trans. 2*, 68 (1972) 947.
- 4 M.C. Durrant, M.S. Hegde and C.N.R. Rao, *J. Chem. Phys.*, 85 (1986) 6356.
- 5 M.S. Hegde, V. Jayaram, P.V. Kamath and C.N.R. Rao, *Pramana - J. Phys.*, 24 (1985) 293.
- 6 V. Jayaram and M.S. Hegde, *Proc. Ind. Acad. Sci. (Chem. Sci.)*, 97 (1986) 617.
- 7 P.V. Kamath, M.S. Hegde, and C.N.R. Rao, *J. Phys. Chem.*, 90 (1986) 990.
- 8 J.S. Binkley, R.A. Whiteside, R. Krishnan, R. Seeger, DeFrees, H.B. Schlegel, S. Topiol, L.R. Kahn and J.A. Pople, *QCPE*, 13, 406.
- 9 Carnegie-Mellon Quantum Chemistry Archive, 2nd edn., July 1981.
- 10 J.D. Madhura, J. Chandrasekhar and W.L. Jorgenson, unpublished results.
- 11 E. Blum and G. Herzberg, *J. Phys. Chem.*, 41 (1937) 91.
- 12 W.C. Price, *J. Chem. Phys.* 16 (1948) 894.
- 13 W.C. Ermler, F.D. Glasser and C.W. Kern, *J. Am. Chem. Soc.*, 98 (1976) 3799.
- 14 S. Kato, H. Fujimato, S. Yamabe and K. Fukui, *J. Am. Chem. Soc.*, 96 (1974) 2024.
- 15 H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, 98 (1976) 7208.
- 16 O. Eisenstein, H.B. Schlegel and M.M. Kayser, *J. Org. Chem.*, 47 (1982) 2886.
- 17 T. Clark, D. Wilhelm and P.V.R. Schleyer, *J. Chem. Soc. Chem. Commun.*, 11 (1983) 606.