Electronic structures of $\text{H}_2\text{O}\cdot\text{BF}_3$ and related $n\text{-}\nu$ addition compounds: A combined EELS-UPS study in vapor phase^{a)}

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The detailed electronic structure of the $n\text{-}\nu$ addition compound $\text{H}_2\text{O}\cdot\text{BF}_3$ has been investigated for the first time by a combined use of electron energy loss spectroscopy (EELS) and UV photoelectron spectroscopy (UPS) augmented by MO calculations. The calculated molecular orbital energies of $\text{H}_2\text{O}\cdot\text{BF}_3$ agree well with the UPS results and have been used to assign the electronic transitions obtained from EELS and to construct an orbital correlation diagram.

INTRODUCTION

Addition compounds between Lewis acids and Lewis bases constitute a limiting case of electron donor-acceptor interaction where the interaction energy is considerably higher than 10 kcal mol^{-1} . Adducts formed between BF_3 and electron donors such as H_2O are some of the most well-known examples of addition compounds coming under the category of $n\text{-}\nu$ complexes according to the classification of Mulliken.¹ Electronic structures of a few members of this important class of compounds have been investigated by quantum mechanical calculations and photoelectron spectroscopy.^{2,3} A complete understanding of the electronic structure of these addition compounds would however require a study of the electronic transitions of these compounds. Such a study poses severe experimental problems, since most of the electronic transitions would lie in the vacuum UV region and many of these compounds have very low vapor pressure. We have therefore investigated the detailed electronic structure of a typical addition compound, $\text{H}_2\text{O}\cdot\text{BF}_3$, in the vapor phase by employing electron energy loss spectroscopy (EELS) and ultraviolet photoelectron spectroscopy (UPS), augmented by *ab initio* MO calculations. The use of EELS has provided us ready access to the vacuum UV region.⁴ Based on the study, we have been able to construct a detailed energy level diagram of the $\text{H}_2\text{O}\cdot\text{BF}_3$ system. Electronic transitions of $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ and $\text{THF}\cdot\text{BF}_3$ are found to be similar to that of $\text{H}_2\text{O}\cdot\text{BF}_3$.

EXPERIMENTAL

Electron energy loss spectra were recorded with a home-built spectrometer consisting of a hemispherical sector electron monochromator (125 mm mean diameter), a collision chamber, a hemispherical electron energy analyzer (140 mm 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. Full details of the spectrometer have been provided elsewhere.⁴ For the purpose of this study an elastic electron beam of 45 V with 300 meV FWHM was employed. Ultraviolet photoelectron spectra were recorded with a home-built spectrometer consisting of a He(I) UV lamp, a 3 mm diam collision

chamber, and a channeltron electron multiplier. Differential pumping allowed for operation of the helium lamp at 1.5 Torr, a sample pressure of 0.1–0.5 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.

Samples of each complex were prepared on the vacuum line by cocondensing the donor with a small excess (5%–10%) of boron trifluoride at liquid nitrogen temperature in a glass ampoule with a Teflon tap. The mixture was carefully allowed to warm to room temperature, moderating the reaction (which was often vigorous) with cooling as necessary. Samples were admitted into the spectrometer by means of a needle valve. Usually the initial spectrum was contaminated with boron trifluoride; this rapidly pumped away to give the spectrum of the addition compound. Spectra of free water, diethyl ether, THF, and boron trifluoride were also recorded.

RESULTS AND DISCUSSION

The EEL spectrum of BF_3 has not been reported in the literature hitherto. The spectrum recorded by us is shown in Fig. 1. All the electronic transitions of BF_3 lie in vacuum UV region, above 7 eV, the bands at 7.9 and 9.9 eV being distinct. These bands along with the rest of the structure can be identified using the UPS data of Bassett and Lloyd⁵ and we shall examine the assignments later in the paper. The EEL spectrum of H_2O obtained by us was identical to that of Tam and Brion⁶ within the limits of the instrumental resolution; the most important transition for our purpose is that due to $1b_1(n_{\text{O}})-3sa_1$ at 7.4 eV. The $3a_1-3sa_1$ transition appears at 9.7 eV.

The EEL spectrum of $\text{H}_2\text{O}\cdot\text{BF}_3$ presented in Fig. 2 shows no evidence of bands due to H_2O and BF_3 as contaminants. In order to assign the bands in the EEL spectrum, we recorded the UV photoelectron spectrum of $\text{H}_2\text{O}\cdot\text{BF}_3$ shown in Fig. 3. This shows two sets of bands in the regions 10–12.5 and 13–15.5 eV, which can be readily assigned to the addition compound. We have assigned these on the basis of an *ab initio* molecular orbital calculation using the GAUSSIAN 80 program⁷ and STO-3G basis set, with full geometry optimization. The optimized geometry gave BF, OH, and BO distances of 1.334, 0.984, and 1.80 Å, respectively, and a point group of C_s . The FBO and BOH angles were 99.02° and 113.1°, respectively, with a dihedral angle 59.16° for FBOH and a tetrahedral arrangement for the F_3BO moiety.

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FIG. 1. EEL spectrum of free boron trifluoride.

FIG. 2. EEL spectrum of the $\text{H}_2\text{O}\cdot\text{BF}_3$ addition compound.

FIG. 3. He(1) UPS spectra of the $\text{H}_2\text{O}\cdot\text{BF}_3$ addition compound, free H_2O (short dashes) and free BF_3 (long dashes). The peak marked with an asterisk in the spectrum of H_2O is a satellite due to n_{O} from He 1β radiation. Vertical lines at the top of the figure show the calculated orbital energies.

The calculated dissociation energy was $16.5 \text{ kcal mol}^{-1}$. The orbital energies obtained from the calculation are listed in Table I along with the observed vertical ionization energies. The calculated energies show good agreement with the UPS data, the first two bands at 10.7 and 11.1 eV being assigned to a composite of the first six fluorine lone pair orbitals. The major peak at 13.4 eV in the UPS is clearly due to the oxygen lone pair which is not involved in bond formation. In Table I we have shown the calculated orbital energies scaled to cor-

respond to the UPS data. These scaled values have been used to assign the electronic transitions found in the EEL spectrum.

Before we discuss the EEL spectrum of $\text{H}_2\text{O}\cdot\text{BF}_3$, we shall discuss the electronic transitions of BF_3 . The first ionization energy of BF_3 arising from the fluorine lone pair orbital is around 16 eV as found from UPS (Fig. 3). The EELS transitions of BF_3 are also associated with n_{F} . If we assign the first two transitions at 7.9 and 9.9 eV to $1a'_2-2a'_2$ and $1a'_2-3a'_1$, the transitions at 10.9, 11.7, 12.3, and 13.3 eV can also be rationalized as arising from n_{F} levels to the $2a'_2$ or $3a'_1$ upper states (Table II). The assignments of the transitions of BF_3 made here are similar to those of Planckaert *et al.*⁸ for BCl_3 . Although we have assigned the transitions to the $2a'_2$ and $3a'_1$ levels of BF_3 , it is to be noted that these upper states are likely to be essentially atomic in character.

TABLE I. Occupied orbital energies (in eV) for $\text{H}_2\text{O}\cdot\text{BF}_3$.

Assignment	STO-3G energy	Scaled energy ^a	Vertical I. E. (from UPS)
$14a'$	11.00	10.6	10.7
$7a''$	11.04	10.6	
$6a''$	11.18	10.8	
n_{F} $13a'$	11.46	11.2	11.4
$5a''$	11.47	11.2	
$12a'$	12.06	11.8	
n_{O} $11a'$	14.41	13.4	13.4
$4a''$	15.27	14.5	14.0–16.0
n_{F} $10a'$	15.65	14.6	
$9a'$	16.24	16.4	
σ_{BO} $8a'$	18.38	17.5	...
σ_{OH} $3a''$	19.54	19.2	...

^a See the text.

TABLE II. Electronic transitions of boron trifluoride from EELS.

Energy (eV)	Assignment
7.9	$1a'_2-2a'_2$
9.9	$1a'_2-3a'_1$
10.9	$1e''-3a'_1$
11.7	$1a'_2-2a'_2$
12.3	$2e'-2a'_2$
13.3	$1a'_2-3a'_1$

FIG. 4. MO energy level diagram for the $\text{H}_2\text{O} \cdot \text{BF}_3$ system. All of the levels below 10 eV are virtual.

The energy levels of BF_3 are depicted in Fig. 4.

The data obtained by us from EELS of $\text{BF}_3 \cdot \text{H}_2\text{O}$ can be supplemented by the optical spectrum reported by Scheffer and Hammaker.⁹ Although the optical spectrum is of the dihydrate, it is known that the second molecule of water is only bound by hydrogen bonding¹⁰ and should not seriously perturb the electronic structure of the $\text{H}_2\text{O} \cdot \text{BF}_3$ moiety. The optical spectrum shows bands in the near IR region at 1.1 and 1.3 and at 4.1 and 4.9 eV in the UV region. The UV band at 4.1 eV matches well with the 4.0 eV band found in EELS. The shoulder at 4.9 eV in the optical spectrum cannot be definitively identified in the EEL spectrum at the available resolution. Such low energy transitions occur in $\text{BF}_3 \cdot \text{H}_2\text{O}$ probably because of the strong interaction between the donor and the acceptor. Complexes with extensive charge transfer in the ground state are known to show electronic absorption bands at considerably longer wavelengths than the donor or the acceptor.

TABLE III. Electronic transition energies (in eV) for $\text{H}_2\text{O} \cdot \text{BF}_3$.

Assignment	Optical transitions	EELS transitions	Term value
$n_F - \sigma_{\text{BO}}^*$ 14a' - 15a'	1.1		
$n_F - \sigma_{\text{BO}}^*$ 6a'' - 15a'	1.3		
$n_O - \sigma_{\text{BO}}^*$ 11a' - 15a'	4.1	4.0	
$n_F - \sigma_{\text{BO}}^*$ 4a'' - 15a'	4.9		
$n_O - 3sa_1(R)$		6.1	7.3
$\sigma_{\text{BO}} - \sigma_{\text{BO}}^*$ 8a' - 15a'		7.9	
$n_F - R^a$		9.7	~1.0
$N_F - R^a$		10.8	~1.0
$\sigma_{\text{OH}} - 3sa_1(R)$		11.9	7.3

^a Likely to be the 3d level.

TABLE IV. EELS transition energies (in eV) for $\text{Et}_2\text{O} \cdot \text{BF}_3$ and $\text{THF} \cdot \text{BF}_3$.

Assignment	$\text{Et}_2\text{O} \cdot \text{BF}_3$	$\text{THF} \cdot \text{BF}_3$
$n_O - \sigma_{\text{BO}}^*$	4.3	4.3
$n_O - 3sa_1$	6.2	6.1
$\sigma_{\text{BO}} - \sigma_{\text{BO}}^*$	8.0	8.0
$n_F - R$	9.9	9.7
$n_F - R$	10.8	10.7

We have assigned the electronic transitions of $\text{H}_2\text{O} \cdot \text{BF}_3$ by making use of the energies of the occupied levels obtained from UPS and MO calculations. The transitions at 1.1 and 1.3 eV are clearly molecular electronic transitions originating from the n_F orbitals. Assigning them to transitions from HOMO to LUMO, the energy of the σ_{BO}^* (15a') orbital works out to be 9.5 eV. The transitions at 4.1 and 4.9 eV can also be assigned to this σ_{BO}^* level from n_F (11a', 4a''). The transition at 6.1 eV is, however, best assigned to the $n_O - 3sa_1$ transition, the upper state corresponding to that in water. This Rydberg transition gives a term value of 7.3 eV. The EELS transition at 7.9 eV can be assigned to the $\sigma_{\text{BO}} - \sigma_{\text{BO}}^*$ transition (8a' - 15a'). The transition at 9.7 and 10.7 eV are also Rydberg transitions originating from the n_F orbitals and these give term values around 1 eV. We would like to assign the last transition at 11.9 eV to the $\sigma_{\text{OH}} - 3sa_1(R)$ transition. If we make use of the term value of 7.3 eV for the $n_O - 3sa_1$ transition, the energy of the σ_{OH} orbital works out to be 19.2 eV (see Table I). This is comparable to the corresponding level (18.5 eV) in free water.¹¹ The electronic transitions of $\text{H}_2\text{O} \cdot \text{BF}_3$ are listed in Table III.

In Fig. 4 we have shown the orbital correlation diagram of $\text{BF}_3 \cdot \text{H}_2\text{O}$ constructed on the basis of EELS and UPS data. The most obvious feature of the correlation diagram is the increase in the energies of all of the water orbitals and a corresponding decrease of all the boron trifluoride levels except the one involved in bond formation. This effect, which is observed in similar systems,^{2,12} is a result of the net transfer of electron density from the donor to the acceptor, resulting in deshielding and shielding of the nuclei, respectively. The previous studies did not include the virtual levels and it is interesting that with the exception noted above these behave in a very similar way to the occupied levels. In fact, our calculations indicate a net transfer of 0.2 of an electron from H_2O to BF_3 . The diagram also brings home the importance of symmetry considerations in chemical bond formation. Thus the BO bond is formed from the more tightly bound of the two oxygen lone pairs, since its symmetry rather than that of the HOMO of water matches the LUMO of BF_3 .

EEL spectra of $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$ and $\text{THF} \cdot \text{BF}_3$ are very similar to that of $\text{H}_2\text{O} \cdot \text{BF}_3$. In the absence of UPS data no detailed analysis of these systems is possible; however, the EELS transitions and their tentative assignments are given in Table IV.

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- ¹R. S. Mulliken, *J. Chim. Phys.* **61**, 1, 20 (1964).
- ²I. H. Hillier, in *Molecular Interactions*, edited by H. Ratajczak and W. J. Orville-Thomas (Wiley, New York, 1981), Vol. 2.
- ³H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.* **98**, 7208 (1976).
- ⁴M. S. Hegde, V. Jayaram, P. V. Kamath, and C. N. R. Rao, *Pramana* **24**, 293 (1985).
- ⁵P. J. Bassett and D. R. Lloyd, *J. Chem. Soc. A* **1971**, 1551.
- ⁶W. C. Tam and C. E. Brion, *J. Electron Spectrosc.* **3**, 263 (1974).
- ⁷J. 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.
- ⁸A. A. Planckaert, P. Sauvageau, and C. Sandorfy, *Chem. Phys. Lett.* **20**, 170 (1973).
- ⁹E. R. Scheffer and E. M. Hammaker, *J. Am. Chem. Soc.* **72**, 5607 (1950).
- ¹⁰N. N. Greenwood and B. S. Thomas, in *Comprehensive Inorganic Chemistry*, edited by J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson (Pergamon, London, 1975), Vol. 1, p. 963.
- ¹¹M. B. Robin and N. A. Kuebler, *J. Electron Spectrosc.* **1**, 13 (1972).
- ¹²M. Barber, J. A. Cornor, M. F. Guest, I. H. Hiller, M. Schwarz, and M. Stacey, *J. Chem. Soc. Faraday Trans. 2* **69**, 551 (1973).