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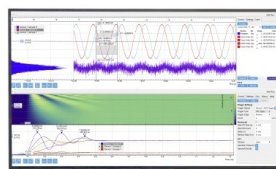
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An ultraviolet photoelectron spectroscopic study of BF_3 -donor complexes^{a)}

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He I spectra of strong $n-v$ type adducts of BF_3 with H_2O , CH_3OH , $(\text{C}_2\text{H}_5)_2\text{O}$, and CH_3CN as well as of weak complexes of BF_3 with NO and H_2S are reported along with assignments based on MO calculations. The energy of the fluorine orbitals of BF_3 is shown to be shifted in proportion to the strength of the donor-acceptor interaction. BF_3 seems to form a contact pair with CS_2 .

INTRODUCTION

Understanding the nature of interaction between electron donors and acceptors forming complexes has been a subject of considerable interest for some time.¹ UV photoelectron spectroscopy can provide direct information on the electron states of donor-acceptor complexes which throws much light on the nature of electronic interactions. While UV photoelectron spectroscopy has been employed to examine a few $n-v$ complexes between BH_3 and electron donors such as CO and substituted phosphines²⁻⁴ as well as some halogen-donor complexes,⁵ the technique has not been exploited to understand the nature of donor-acceptor interaction in a series of related complexes. We considered it most worthwhile to investigate adducts of varying interaction strengths formed by the classic Lewis acid, BF_3 . For this purpose, we have recorded the gas phase He I spectra of known stable addition compounds $\text{BF}_3 \cdot \text{H}_2\text{O}$, $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, $\text{BF}_3 \cdot \text{CH}_3\text{OH}$, and $\text{BF}_3 \cdot \text{CH}_3\text{CN}$ with dissociation energies of the order of 50 kJ mol^{-1} or higher. We have then studied the $\text{BF}_3 + \text{NO}$ and $\text{BF}_3 + \text{H}_2\text{S}$ systems as examples of weak complexes of BF_3 . Last, we have studied the $\text{BF}_3 + \text{CS}_2$ system where the interaction energy is in the range of thermal energy. We have carried out *ab initio* molecular orbital calculations in order to make spectral assignments and also to compare the relative stabilities of the complexes.

The results of the present study have shown that in the case of strong adducts such as $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ and $\text{BF}_3 \cdot \text{CH}_3\text{CN}$, the fluorine lone pair orbital energy is lowered considerably relative to that of free BF_3 . The shift is much smaller in weakly interacting complexes such as $\text{BF}_3 \cdot \text{NO}$ or $\text{BF}_3 \cdot \text{H}_2\text{S}$. $\text{BF}_3 \cdot \text{CS}_2$ seems to behave like a contact pair exhibiting a negligible shift in the n_F orbital energy.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

Ultraviolet photoelectron spectra were recorded with a homebuilt spectrometer⁶ consisting of a He I lamp, a 3 mm diameter collision chamber and a channeltron electron multiplier. Differential pumping allowed for operation of the He I 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 spectrom-

eter. The resolution of the spectrometer was 80 meV FWHM at 19.7 eV. Samples of the mixtures were prepared in vacuum by cocondensation of the donor with a small excess of the acceptor at 77 K in a glass ampoule fitted with a teflon tap. Samples of the donor-acceptor mixtures were gently warmed to room temperature and were admitted in to the ultraviolet photoelectron (UP) spectrometer by means of a needle valve. He I spectra of several mixtures of varying compositions were recorded in all the systems studied. The initial spectra generally contained features due to the excess components in addition to a few new bands. The positions of the new features did not vary with the composition but the intensities varied as expected. When the spectra were stripped off of the features due to monomers, we could get reproducible spectra which we attribute to the complexes. The spectra of the complexes were identical whether we started with excess donor or acceptor. Spectrum stripping was not necessary in some of the systems since we would get a nearly clean spectrum due to the pure complex devoid of features due to the individual components. The spectrum of $\text{BF}_3 \cdot \text{CH}_3\text{OH}$ shown in Fig. 1 is one such example.

Hartree-Fock energies of the complexes were computed in the frame work of the SCFLCAOMO (self-consistent-field linear combination of atomic orbitals molecular orbital) method using the GAUSSIAN 86 program.⁷ The split valence 3-21G basis set was used in all the computations. Monomer geometries were fully optimized and used as input for the calculations on the complexes. Geometries of the complexes were also optimized.

While it is known that one-to-one correspondence does not exist between observed and calculated ionization energies (IEs), the possibility of enhanced relaxation effects cannot be ignored in interpreting UP spectra. It is to be noted that the experimental shifts in the IEs between the free molecules and adducts are dominated by electrostatic effects⁸ and that Koopman's approximation is generally adequate to describe UV photoelectron spectra. Much of the photoelectron spectra of intermolecular complexes in the literature are interpreted based on this assumption.

RESULTS AND DISCUSSION

In Fig. 1 we show the He I spectra of the adducts of BF_3 with CH_3OH and H_2O along with the spectra of free BF_3 , H_2O , and CH_3OH . The spectra of the addition compounds show features distinctly different from those of the free do-

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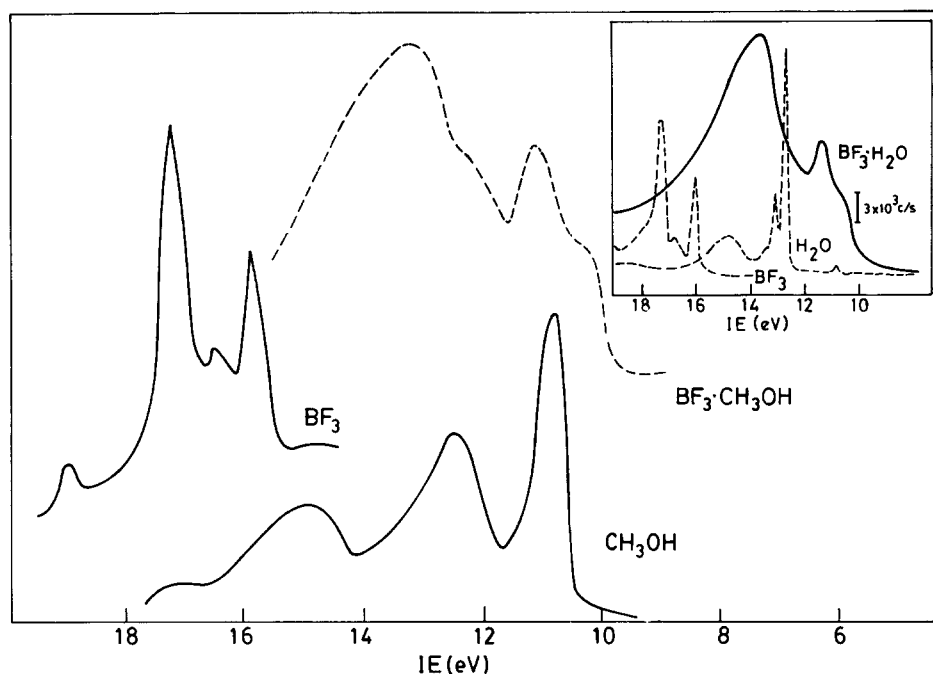


FIG. 1. He I spectra of BF₃, CH₃OH, and BF₃·CH₃OH. The spectra of BF₃, H₂O, and BF₃·H₂O are shown in the inset.

nor and acceptor molecules. Thus, the spectrum of BF₃·CH₃OH shows no band in the region where BF₃ has its characteristic features. Furthermore, there are new features not present in the spectra of the free donor molecules including some at ionization energies lower than those of the donors. We sought to assign the bands in He I spectra of the addition compounds based on self-consistent-field molecular orbital (SCFMO) calculations performed for the BF₃·H₂O adduct. Calculations with the 3-21G basis set give an optimized geometry with a C_s point group on OH, BF, and BO distances of 0.96, 1.36, and 1.65 Å, respectively, and FBO and BOH angles of 105.7° and 119.4° respectively. The F₃BO moiety is nearly pyramidal and the FBOH dihedral angle is 103.4°. The computed dissociation energy of the complex is 144 kJ mol⁻¹. An STO-3G calculation gives a dissociation energy of 67 kJ mol⁻¹ with a BO distance of 1.8 Å.

The He I spectrum of the adduct between BF₃ and

(C₂H₅)₂O shows features similar to those of BF₃·CH₃OH. In Table I we list the observed ionization energies of BF₃·H₂O, BF₃·CH₃OH, and BF₃·(C₂H₅)₂O systems with the orbital assignments. The most noteworthy feature is that in all these oxygen donor systems, the nonbonding fluorine orbitals *n*_F have the lowest ionization energies giving rise to the first two peaks in the He I spectra. The oxygen nonbonding orbital ionization energy is around 13 eV. We could assign a weak feature around 15.9 eV in the spectrum of BF₃·(C₂H₅)₂O complex to the σ_{BO} orbital. We could not resolve a similar feature in the spectrum of BF₃·CH₃OH.

The He I spectrum of the mixture of BF₃ and CH₃CN containing some proportion of the addition compound BF₃·CH₃CN is shown in Fig. 2. The spectrum of BF₃·CH₃CN obtained after stripping bears some similarity to that of BF₃·CH₃OH giving rise to low IE features due to the fluorine lone pair orbitals. Based on SCFMO calculations the different spectral bands are assigned in Table II. In

TABLE I. Occupied orbital energies and assignments of the addition compounds of BF₃ with H₂O, CH₃OH, and (C₂H₅)₂O.

BF ₃ ·H ₂ O						
<i>I</i> _v (eV)	Scaled (0.9ε)3-21G energy	Scaled (0.9ε)STO-3G energy ^a	MO	BF ₃ ·CH ₃ OH <i>I</i> _v (eV)	BF ₃ ·(C ₂ H ₅) ₂ O <i>I</i> _v (eV)	Assignment
10.7	13.9–14.3	9.9–10.1	7 <i>a</i> '', 14 <i>a</i> ', 6 <i>a</i> ''	10.7	9.9	<i>n</i> _F
11.4	14.5–14.8	10.3–10.8	13 <i>a</i> ', 12 <i>a</i> ', 5 <i>a</i> ''	11.3	10.6	<i>n</i> _F
13.4	15.8	13.0	11 <i>a</i> '	12.7	12.6	<i>n</i> _O
14.0–16.0	17.1	13.7	4 <i>a</i> ''	13.4	14.0	π _{BF₃}
	17.4	14.1	10 <i>a</i> '	...	15.9 ^b	σ _{BO}
	17.9	16.5	9 <i>a</i> '	...	16.5 ^b	π _{BF₃}

^a From Ref. 9.

^b Weak features.

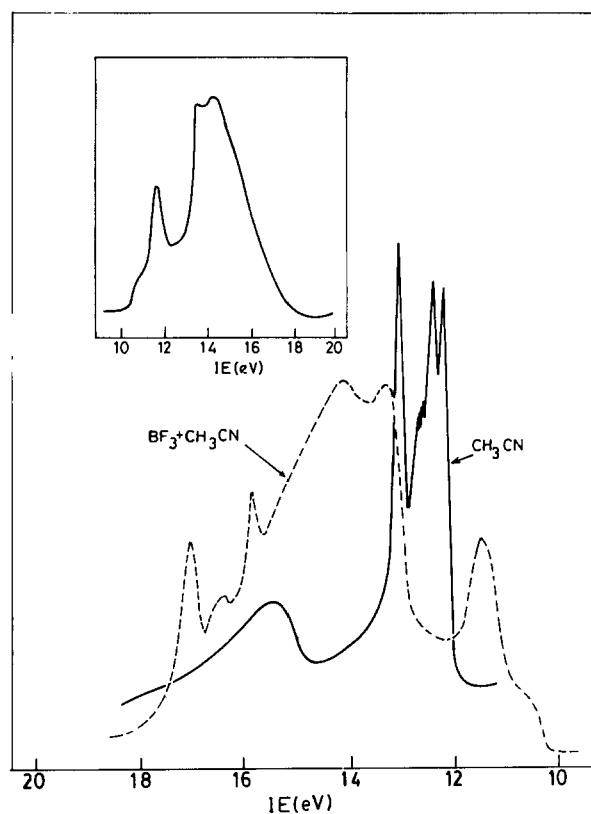


FIG. 2. He I spectra of CH_3CN and a $\text{BF}_3 + \text{CH}_3\text{CN}$ mixture. The spectrum of the "pure" $\text{BF}_3 \cdot \text{CH}_3\text{CN}$ complex is shown in the inset.

the optimized structure (C_{3v} point group), the BNCC skeleton is linear with BN, CN, and CC distances of 1.76, 1.13, and 1.46 Å, respectively and with FBN and CCH angles of 102.4° and 109.6°, respectively. The FBNF and HCCH dihedral angles are both 120.0° and the calculated dissociation energy is 82 kJ mol^{-1} .

The feature at 15.3 eV in the He I spectrum of the $\text{BF}_3 \cdot \text{CH}_3\text{CN}$ adduct has some contribution from the donor-acceptor bond. Thus, σ_{BN} ionization energy is comparable to that of σ_{BO} in the $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ adduct (15.9 eV). What is interesting is that, in all these addition compounds, viz., $\text{BF}_3 \cdot \text{H}_2\text{O}$, $\text{BF}_3 \cdot \text{CH}_3\text{OH}$, $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, and $\text{BF}_3 \cdot \text{CH}_3\text{CN}$, with comparable dissociation energies, the fluorine lone pair orbital energies are significantly reduced (to 10–11 eV) on adduct formation. The first orbital of BF_3 due to n_{F} is associated with a very high ionization energy (15.9 eV).

TABLE II. Occupied orbital energies and assignments of $\text{BF}_3 \cdot \text{CH}_3\text{CN}$.

I_v (eV)	Scaled (0.9ϵ) 3-21G energy	MO character	MO
10.9	13.3	$n_{\text{F}}, \sigma_{\text{CN}}$	14e, 13e
11.6	13.6	n_{F}	1a ₂
13.4	14.1–14.2	n_{F}	12e, 11e, 12a ₁
14.3	14.6	n_{F}	10e, 9e
15.3	16.7–17.0	$\pi_{\text{BF}_2}, \pi_{\text{BF}_2}, \sigma_{\text{BN}}$	8e, 7e, 6e

In Fig. 3 we have shown the He I spectra of free NO and of the $\text{BF}_3 + \text{NO}$ mixture. Free NO shows the first peak at 10 eV along with the expected vibrational structure; the band at 17 eV due to π_{NO} also shows extensive vibrational structure. We could obtain a good spectrum of $\text{BF}_3 \cdot \text{NO}$ after applying the stripping procedure. The first feature in the spectrum of the adduct at 11.4 eV is clearly due to the valence orbital of NO (compared to 10 eV in free NO). From MO calculations, we find that the boron atom is bonded to the nitrogen atom of NO with a BN distance of 2.5 Å. The BF_3 moiety is nearly planar and the FBN and BNO angles are 91.2° and 168.4°, respectively while the FBNO dihedral is 120.0°. The calculated dissociation energy of the complex is 16 kJ mol^{-1} , a value much lower to that in the addition compounds of BF_3 with $(\text{C}_2\text{H}_5)_2\text{O}$ and CH_3CN . The fluorine orbitals in $\text{BF}_3 \cdot \text{NO}$ are shifted by 2.5 eV compared to free BF_3 , unlike in $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ and such complexes. In Table III, we list the calculated orbital energies with the observed ionization energies of the $\text{BF}_3 \cdot \text{NO}$ complex. $\text{BF}_3 \cdot \text{NO}$ is indeed a novel example of a weakly interacting 1:1 donor-acceptor complex, being specially attractive because the donor is a simple diatomic molecule.

Another example of a weakly interacting complex of BF_3 that we have studied is $\text{BF}_3 \cdot \text{H}_2\text{S}$. The first two features in the He I spectrum of the complex are at 11.6 and 13.4 eV, associated with the sulfur orbitals, $17a'$ (n_{S}) and $16a'$ (π_{SH}), respectively. Features due to fluorine lone pair orbitals appear only at 14.2 and 14.8 eV. In the optimal geometry (C_s ,

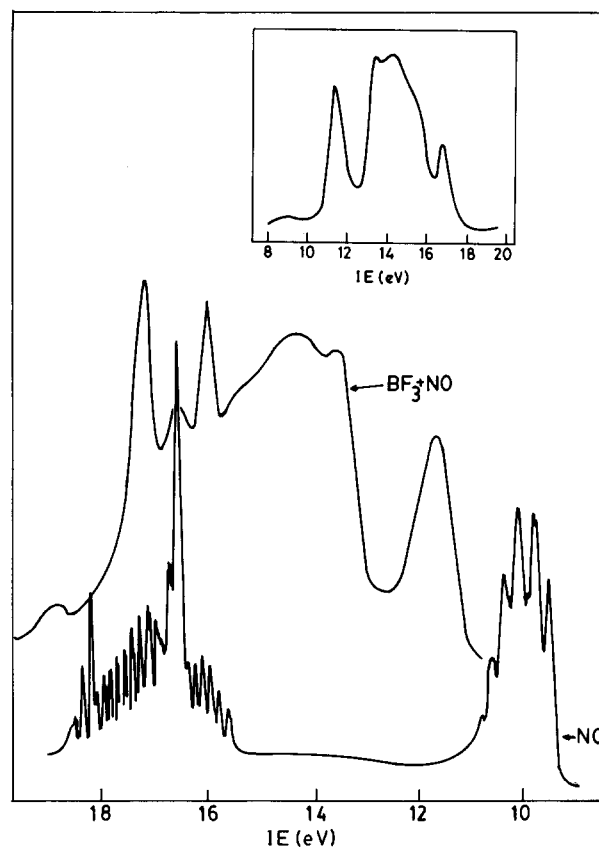


FIG. 3. He I spectra of NO and a $\text{BF}_3 + \text{NO}$ mixture. The spectrum of the $\text{BF}_3 \cdot \text{NO}$ complex is shown in the inset.

TABLE III. Occupied orbital energies and assignments of BF₃·NO.

I_v (eV)	Scaled (0.9 ϵ) 3-21G energy	MO character	MO
11.4	11.4	σ_{NO}	17a'
13.4	15.6	n_F	7a''
14.2	15.9	π_{NO}	6a''
15.3	16.1-16.4	n_F	16a', 5a'', 4a'', 15a'
16.8	16.3	π_{NO}	14a'

point group) predicted by MO calculations, the BF₃ part is nearly planar and the BS distance is 3.0 Å. The computed dissociation energy is 22 kJ mol⁻¹, comparable to that of the BF₃·NO complex.

We have examined the He I spectrum of the BF₃ + CS₂ system in order to see whether a complex is indeed formed. Our MO calculations show that the interaction energy of the 1:1 complex is very low (2 kJ mol⁻¹). The dissociation energy of the 2:1 complex (BF₃)₂·CS₂, is equally low. In the optimized geometry of the 1:1 complex (point group C_{3v}), the structural parameters of the donor and acceptor molecules are not affected to any significant extent. The BF₃ moiety remains planar with a linear BSCS arrangement and a large BS distance of 3.3 Å.

In accordance with the results of the MO calculations, the He I spectrum (Fig. 4) shows the first three features at 11.5, 13.5, and 14.5 eV, all ascribable to the valence orbitals of CS₂. The fourth feature due to the nonbonding fluorine orbital is at 15.8 eV which is close to that of free BF₃ (Table

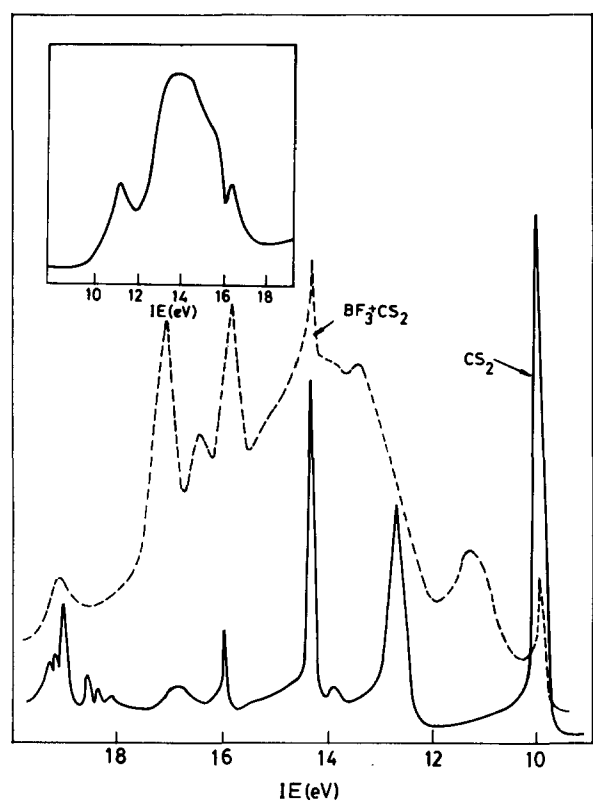


FIG. 4. He I spectra of CS₂ and a BF₃ + CS₂ mixture. The spectrum of the complex is shown in the inset.

TABLE IV. Occupied orbital energies and assignments of BF₃·CS₂.

I_v (eV)	Scaled (0.9 ϵ) 3-21G energy	MO character	MO
11.5	9.4	n_S	18e, 17e
13.5	13.3	π_{CS}, σ_{CS}	16e, 15e
14.5	14.5	π_{CS}	16a ₁
15.5	15.8	n_F	1a ₂
16.4	16.3-16.4	n_F	14e, 13e, 12e
	16.8	σ_{CS}	11e, 15a ₁

IV). These spectral features in conjunction with results from the calculations show that BF₃·CS₂ is a contact pair¹ or a van der Waals complex.

The present study of the complexes of BF₃ with several acceptors of varying interaction strengths reveals an interesting general feature. The magnitude of the shift in the fluorine ionization energy of BF₃ in the 1:1 complex depends on the strength of the donor-acceptor interaction. Thus, the shifts are large in the addition compounds of BF₃ with H₂O, CH₃OH, (C₂H₅)₂O and CH₃CN, and rather small in the weak complexes BF₃·NO and BF₃·H₂S. It is close to zero in the contact pair BF₃·CS₂. In Fig. 5 we have plotted the shift of the n_F orbital in the complex relative to free BF₃ against the dissociation energy of the 1:1 adduct. The plot is nearly linear showing a proportionality. The linearity confirms that the shift in the n_F orbital is determined by the magnitude of the electron donation by the donor which in turn also determines the dissociation energy of the complex. Although we do not have experimental dissociation energies for all these complexes, the correlation of the observed shifts in the n_F IEs with the theoretical dissociation energies is still significant. Chemical intuition as well as known trends in the dissociation energies of adducts of these donors with other acceptors predict the same order of interaction strengths as found in our calculations.

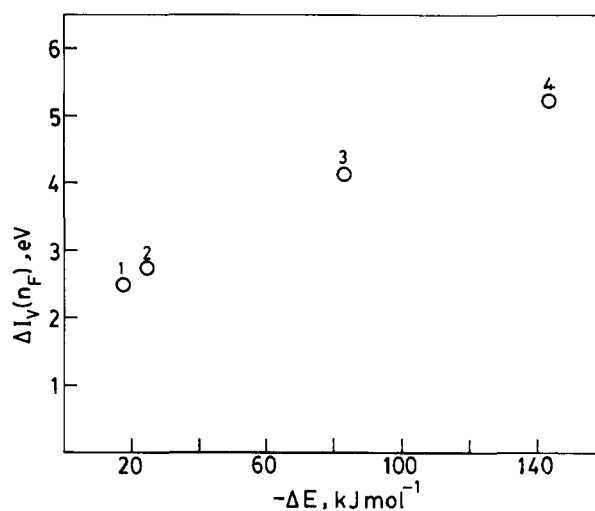


FIG. 5. Plot of the experimentally observed shift in the ionization energy of the fluorine lone pair orbital, $\Delta I_v(n_F)$, against the calculated dissociation energy of the adduct, ΔE : (1) BF₃·NO; (2) BF₃·H₂S; (3) BF₃·CH₃CN; (4) BF₃·H₂O.

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