

The Vibrational Spectra of the Boron Halides and their Molecular Complexes. Part 8. *Ab initio* Studies of the Complexes of Boron Trifluoride with Water and Hydrogen Sulphide

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ABSTRACT

The structures, interaction energies and vibrational spectra of the van der Waals complexes formed between boron trifluoride, as Lewis acid, and water and hydrogen sulphide, as Lewis bases, have been determined by means of *ab initio* calculations at the second-order level of Møller-Plesset perturbation theory, using a number of basis sets, including double- and triple-zeta, with polarization and diffuse functions. Two conformers, an eclipsed and a staggered species, have been examined for each complex. In the case of the boron trifluoride-water complex, the spectra computed using the largest basis set have been compared with the spectra obtained experimentally in nitrogen, argon and neon matrices at cryogenic temperatures.

KEYWORDS

Ab initio calculations, molecular complexes, boron trifluoride, water; hydrogen sulphide, molecular structures, interaction energies, vibrational spectra.

1. Introduction

Some years ago we reported the infrared spectrum of boron trifluoride and water co-condensed in nitrogen matrices at *ca.* 20 K, and interpreted the results in terms of a 1:1 molecular complex formed between BF₃ and H₂O.¹ A partial assignment of the spectrum of this complex in argon matrices had been reported by Hunt and Ault,² but these authors were unable to locate all of the fundamentals of the aggregate. In order to assist with the assignment of our spectra, we supplemented our experimental measurements with an *ab initio* calculation, at the restricted Hartree-Fock (RHF) level and with a small (4-31G) basis set.¹ This calculation enabled us to make tentative assignments of eight of the nine intramolecular modes of the complex, and of the two highest-frequency intermolecular modes. Experimental spectra of BF₃·H₂O in argon³ and neon⁴ matrices have subsequently been reported, but a full assignment remains elusive. *Ab initio* computations of the spectrum of BF₃·H₂O, at the RHF and second-order Møller-Plesset (MP2) levels of theory, using six different basis sets,⁵ and at the RHF, MP2, QCISD and CCSD(T) levels with the 6-311+G(d,p) basis set,⁴ have helped to clarify our understanding of the spectrum of this species, but several questions still remain. Our recent experience with some weakly-bound molecular complexes, e.g. (NH₃)₂ and (PH₃)₂,⁶ and H₂O·CO₂ and H₂S·CO₂,⁷ has taught us that for such aggregates the preferred structure may be a function of the basis set used, and the use of different basis sets sometimes leads to quite different optimized structures. Our original RHF/4-31G computation for BF₃·H₂O suggested that the H₂O molecule was coordinated with BF₃ with the H₂O angle bisector presenting virtually perpendicularly to the plane of BF₃.¹ However, some trial calculations at the MP2 level with larger basis sets showed that in each case the H₂O

molecule adopted an eclipsed conformation relative to BF₃, but in some cases a staggered conformation was also found to be a stationary point. In an attempt fully to characterize the true structure and vibrational spectrum of the BF₃·H₂O complex, we have undertaken a systematic reinvestigation of this adduct, at the correlated (MP2) level of theory. We employed a range of basis sets featuring both double- and triple-zeta bases, with and without polarization and diffuse functions, in order to explore the effect of these various features of the basis sets on the optimized geometry. We have also recalculated the vibrational spectrum of BF₃·H₂O using the largest basis set, in the expectation of removing the earlier ambiguities in the predicted^{1,4,5} and experimental¹⁻⁴ vibrational assignments. These calculations form part of an ongoing theoretical study of the properties of the complexes of BF₃ with other oxygen bases, e.g. CO₂,⁸ N₂O,⁹ SO₂¹⁰ and (CH₃)₂O.¹¹

In view of the expected similarity between the complexes of BF₃ with H₂O and with its analogue H₂S, we have included parallel studies of the BF₃·H₂S complex, under the same computational conditions, in order to confirm their similarities and to reveal whatever differences may exist among their properties. This complex is the second adduct of BF₃ with a sulphur base which we have examined in this way, following an earlier study of BF₃·(CH₃)₂S.¹¹

2. Computational Details

The calculations were carried out using the Gaussian-98 program,¹² at the MP2 level of theory.¹³ Full geometry optimizations were carried out, using the VERYTIGHT convergence criterion,¹² mainly with the Berny algorithm,¹⁴ but with the Murtagh-Sargent option¹⁵ in cases of slow convergence. Interaction energies were computed and corrected for basis set superposi-

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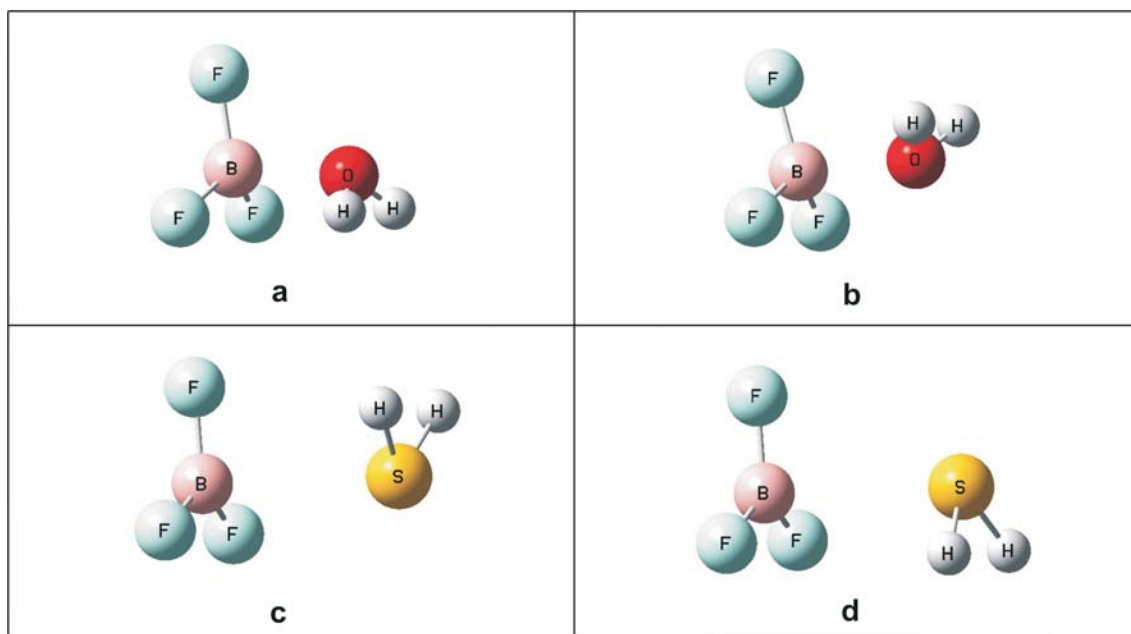


Figure 1 The optimized structures of the BF₃.H₂O and BF₃.H₂S complexes determined using the 6-311++G(d,p) basis set: (a) eclipsed BF₃.H₂O (energy minimum); (b) staggered BF₃.H₂O (saddle point); (c) staggered BF₃.H₂S (energy minimum); (d) eclipsed BF₃.H₂S (saddle point).

tion error (BSSE),¹⁶ using the Boys-Bernardi full counterpoise method,¹⁷ and for zero-point energy differences. We employed eight basis sets, 6-31G, 6-31++G, 6-31G(d,p), 6-31++G(d,p), 6-311G, 6-311++G, 6-311G(d,p) and 6-311++G(d,p). This range of bases allowed us to examine the effect of adding first diffuse functions, then polarization functions, then both augmentations on all atoms, to the standard double-zeta 6-31G basis, and then repeating the stepwise augmentation strategy starting with the triple-zeta 6-311G basis set.

3. Results and Discussion

3.1. Molecular Structures

The effect of changing the basis set on the calculated properties of the various species is illustrated by reference to the minimized energies of the BF₃ monomer. The energies are plotted as a function of the basis set in Supplementary Material, Fig. SM1. The greatest effect on the energy of improving the basis set is achieved by the addition of polarization functions, followed by substitution of double-zeta by triple-zeta, and the least significant influence is the addition of diffuse functions.

The effect of basis set on the optimized geometries is illustrated in the Supplementary Material, Table SM1, where the computed bond lengths and angles of the three monomers are listed for each basis set, along with the experimental structural parameters.^{18–20} The individual percentage errors are all within 5%, with the exception of the HOH bond angle, which is overestimated by 6.19% (6-31+G) and 6.33% (6-311+G). The inclusion of polarization functions is found to have a strong positive influence in reducing the errors between the computed and experimental geometrical parameters.

In our earlier study of BF₃.H₂O,¹ at the RHF/4-31G level, we found that the angle, Θ , between the C₂ axis of H₂O and the C₃ axis of BF₃ was close to 180°, indicating that coordination involved mainly the axial ($3a_1$) non-bonding orbital of H₂O. The direction of the deviation of the angle Θ from linearity determines whether the conformation of each complex is eclipsed or staggered; in either case the point group of the complex is expected to be C_s. Supplementary Material Table SM2 reports

the minimized energies and Hessian indices of the BF₃.H₂O and BF₃.H₂S adducts for each basis set studied. For BF₃.H₂O the results obtained with the 6-31G, 6-31++G, 6-311G and 6-311++G basis sets failed unambiguously to identify the preferred species. In these cases, optimization starting with either the eclipsed or the staggered conformation led to essentially the same structure, with coordination of the H₂O molecule at the B atom virtually perpendicular to the BF₃ pseudo-plane, as we found at the RHF/4-31G level.¹

With the 6-31G and 6-31++G basis sets, this converged structure turned out to be a first-order saddle point on the potential energy surface, while in the 6-311G and 6-311++G cases it represented a true minimum. It was only on the introduction of polarization functions, in the 6-31G(d,p), 6-31++G(d,p), 6-311G(d,p) and 6-311++G(d,p) bases, that the eclipsed and staggered conformations could be clearly distinguished. For all four of these bases the eclipsed structure was found to be the minimum and the staggered a first-order saddle point. The imaginary mode representing the reaction coordinate in these four cases was the torsional mode of the H₂O molecule about the B...O axis. It appears, therefore, that only those basis sets which include polarization functions have sufficient directional properties to enable the two conformers of BF₃.H₂O to be separated reliably. The optimized structures of the eclipsed and staggered species of BF₃.H₂O, determined with the 6-311++G(d,p) basis set, are illustrated in Figs 1(a) and 1(b).

For the BF₃.H₂S complex, the preferred structure determined using the double-zeta basis sets oscillated between eclipsed [6-31++G and 6-31++G(d,p)] and staggered [6-31G and 6-31G(d,p)]. For the four triple-zeta results the staggered conformer was consistently found to be a true minimum. For this complex even the four bases which did not include polarization functions were able to discriminate between the two structural possibilities. This is probably because, even though the differences between the optimized eclipsed and staggered energies for each basis set are quite similar in both complexes, in those cases where the two conformers are clearly distinguished, the angle B...OX, where X is the centre of mass of the H₂O molecule, has an average value of about 122°, while the corresponding angle

Table 1 Intermolecular structural parameters^a of some BF₃·H₂O and BF₃·H₂S complexes, computed with a variety of basis sets.

Basis set	BF ₃ ·H ₂ O		BF ₃ ·H ₂ S			
	Eclipsed		Eclipsed		Staggered	
	R/pm	Θ/deg	R/pm	Θ/deg	R/pm	Θ/deg
6-31G	–	–	–	–	300.33	119.20
6-31++G	–	–	282.54	113.16	–	–
6-31G(d,p)	180.25	117.35	–	–	304.46	115.60
6-31++G(d,p)	177.76	125.37	292.84	107.30	–	–
6-311G	–	–	–	–	312.94	122.39
6-311++G	–	–	–	–	270.65	106.08
6-311G(d,p)	183.61	120.71	–	–	310.28	115.97
6-311++G(d,p)	181.57	125.71	–	–	290.87	100.94

^a R is the B...O or B...S separation; Θ is the B...OX or B...SX angle, where X is the centre of mass of the electron donor molecule.

in BF₃·H₂S averages approximately 110° (eclipsed) and 113° (staggered). This results in the amplitude of the torsional motion which interconverts the two conformers in BF₃·H₂S being larger than that in BF₃·H₂O, enabling the conformers to be more clearly differentiated. Figures 1(c) and 1(d) show the optimized eclipsed and staggered structures of BF₃·H₂S, computed with the largest basis set.

The difference in the conformational preferences of the two complexes may be rationalized as follows. In the BF₃·H₂O complex, the eclipsed conformer is stabilized by an electrostatic attraction between the partially positively-charged hydrogen atoms and the fractionally negatively-charged fluorine atoms which straddle the symmetry plane. The closest approach of these two pairs of atoms is achieved when the complex adopts the eclipsed conformation. In the BF₃·H₂S complex, on the other hand, the partial positive charge on the hydrogen atoms is reduced, due to the lower electronegativity of sulphur compared with oxygen, and the average distance between the hydrogens and the out-of-plane fluorines is substantially increased. This diminishes the electrostatic H...F attraction, and the steric effect becomes dominant. The repulsion of the H and F atoms is maximized when the complex is in the staggered conformation.

The intermolecular structural parameters of the two complexes are collected in Table 1, for those species for which the eclipsed and staggered conformers could be distinguished, and which were found to be true minima. For the eclipsed BF₃·H₂O complex the smaller basis sets underestimate the van der Waals bond length, but have little effect on the angle Θ. In the case of eclipsed BF₃·H₂S, a larger B...S separation is again found with the larger basis set, and the angle Θ is found to be smaller, implying a coordination angle closer to perpendicular, and therefore a greater involvement of the 2b₁ non-bonding orbital of H₂S in the interaction, relative to the 5a₁ orbital. For the staggered conformer, the triple-zeta bases predict a longer van der Waals bond length than the corresponding double-zeta, but the basis sets containing diffuse functions suggest substantially shorter B...S distances. The 6-311++G and 6-311++G(d,p) basis sets also yield noticeably smaller Θ angles.

Our calculations for the BF₃·H₂O complex may now be compared with those of Ball⁵ and Jacox *et al.*⁴ Ball's calculations were all carried out at the RHF level, except for one performed with the MP2/6-311++G(d,p) combination, in which he failed correctly to predict the C_s symmetry of the complex, through not using a sufficiently stringent convergence criterion. Our 6-311++G(d,p) structural parameters are mostly in qualitative agreement with his results, after allowing for the slightly different basis set, and the lower symmetry of Ball's structure.

He also neglected to consider a staggered conformer as a possibility.⁵ Jacox and her co-workers employed, in addition to the RHF and MP2 theoretical models, the QCISD and CCSD(T) theories, also with the 6-311++G(d,p) basis.⁴ This set of calculations did converge in the correct point group, with comparable structural results to ours and Ball's,⁵ but again a staggered conformer was not included.

In summary, the complex of boron trifluoride with water adopts exclusively the eclipsed conformation, but the preferred conformation for the complex with hydrogen sulphide is the staggered. We are not aware of any gas phase microwave studies on either of these complexes with which to compare our structural results. However, Rao *et al.* have investigated BF₃·H₂O^{21–23} and BF₃·H₂S^{22–24} by means of both electron energy loss and ultraviolet photoelectron spectroscopy, and the symmetries of the complex molecular orbitals derived from these studies are consistent with a C_s structure.

3.2. Interaction Energies

The computed interaction energies of the BF₃·H₂O and BF₃·H₂S complexes which were found to be energy minima are presented in Table 2. Those structures for which it was not possible to distinguish between the eclipsed and staggered species are excluded. Our binding energies are substantially larger than the 40 kJ mol⁻¹ determined by Ball,⁵ even though Ball's interaction energies were not corrected for either BSSE or zero-point energy differences. Other estimates of the binding energy are –144 kJ mol⁻¹²³ and –71.7 kJ mol⁻¹²⁵ but these calculations were performed with much smaller basis sets. Jacox *et al.* did not report the interaction energies.⁴ For staggered BF₃·H₂S, addition of polarization functions, e.g. 6-31G(d,p) *versus* 6-31G, led to a reduction in the strength of binding. Where all four triple-zeta basis sets predicted the same (staggered) conformer, inclusion of diffuse functions caused an increase and polarization functions a decrease in the energy of interaction. The binding energy of BF₃·H₂S has been reported previously as –22 kJ mol⁻¹²³ and +384.3 kJ mol⁻¹.²⁵ Clearly the energy of interaction is very sensitive to the basis set employed. Insofar as mean values of this property are meaningful, our results indicate that eclipsed BF₃·H₂O is bound by about 70 kJ mol⁻¹ (60 kJ mol⁻¹ with zero-point energy correction), eclipsed BF₃·H₂S by 12 kJ mol⁻¹ (8 kJ mol⁻¹) and staggered BF₃·H₂S by 10 kJ mol⁻¹ (5 kJ mol⁻¹). These relative values for interaction of BF₃ with a hard (H₂O) and a soft (H₂S) base are quite consistent with chemical intuition.

Comparison of our computed fully-corrected interaction energy of the BF₃ complex with H₂O with those with other oxygen donor bases, CO₂,⁸ N₂O,⁹ SO₂,¹⁰ and (CH₃)₂O¹¹ recalculated under the same conditions²⁶ (–4.556, –3.450, –8.844 and

Table 2 Interaction energies of some BF₃·H₂O and BF₃·H₂S complexes, corrected for BSSE and for zero-point energy differences, computed with a variety of basis sets.

Basis set	BF ₃ ·H ₂ O		BF ₃ ·H ₂ S			
	Eclipsed		Eclipsed		Staggered	
	a	b	a	b	a	b
6-31G	–	–	–	–	–10.561	–5.596
6-31++G	–	–	–14.291	–9.128	–	–
6-31G(d,p)	–71.100	–60.732	–	–	–6.990	–2.759
6-31++G(d,p)	–79.577	–69.215	–10.443	–6.253	–	–
6-311G	–	–	–	–	–7.821	–3.661
6-311++G	–	–	–	–	–16.619	–11.418
6-311G(d,p)	–62.385	–53.192	–	–	–5.350	–1.656
6-311++G(d,p)	–66.333	–56.699	–	–	–10.593	–6.878

a, Corrected for BSSE only.

b, Corrected for BSSE and zero-point energy differences.

Table 3 Computed wavenumbers of the eclipsed ¹¹BF₃·H₂O complex.

Symmetry species	Mode	Approximate description	6-311++G(d,p) (this work)	4-31G (ref. 1)	6-311++G(d,p) (ref. 4)	6-311++G(d,p) (ref. 5)
a'	ν ₁	ν _s (H ₂ O)	3818.0	3951	3818	3818
	ν ₂	δ(H ₂ O)	1631.6	1870	1632	1632
	ν ₃	ν _a (BF ₃)	1321.7	1404	1322	1323
	ν ₄	ν _s (BF ₃)	834.6	959	835	835
	ν ₅	gearing libration	608.4	722	608	607
	ν ₆	δ _s (BF ₃)	605.1	544	606	606
	ν ₇	δ _a (BF ₃)	456.3	430	456	456
	ν ₈	ν(B...O)	278.3	321	278	278
	ν ₉	antigearing libration	238.7	287	240	240
a''	ν ₁₀	ν _a (H ₂ O)	3930.4	4117	3930	3930
	ν ₁₁	ν _a (BF ₃)	1294.9	1441	1295	1295
	ν ₁₂	gearing libration	727.8	894	728	728
	ν ₁₃	δ _a (BF ₃)	455.4	557	455	455
	ν ₁₄	antigearing libration	273.0	459	273	273
	ν ₁₅	B...O torsion	39.2	224	36	35

–130.554 kJ mol^{–1}, respectively), reveals a general trend of increasing interaction energy with increasing gas phase basicity²⁷ and decreasing ionization energy.²⁸

3.3. Vibrational Spectra

Since the structural and energetic results reported above indicate that, among the eight basis sets which we have examined, it is the 6-311++G(d,p) basis which yields the most consistent and reliable data, we will confine our discussion of the vibrational spectra to those derived using that basis set only. The performance of this basis set in reproducing the experimental wavenumbers of the ¹¹BF₃, H₂O and H₂S monomers^{19,29–33} is recorded in the Supplementary Material, Table SM3.

The computed wavenumbers of ¹¹BF₃·H₂O derived using the 6-311++G(d,p) basis set are listed in Table 3, along with those determined earlier^{1,4,5}. Discounting our early effort at the RHF level with a small basis set,¹ our present 6-311++G(d,p) results are in good agreement with those of Jacox *et al.*⁴ and Ball.⁵ The wavenumbers determined experimentally in nitrogen,¹ argon^{2,3} and neon⁴ matrices are listed in Table 4. This table indicates a number of mis-assignments in our preliminary analysis.¹ The band at 1725 cm^{–1} is clearly at too high a wavenumber to be the H₂O bending mode, ν₂, although we cannot suggest an alternative interpretation. The band at 460 cm^{–1} must be assigned to the

Table 4 Experimental wavenumbers of the ¹¹BF₃·H₂O complex.

Symmetry species	Mode	Wavenumber/cm ^{–1}			
		N ₂ ^a	Ar ^b	Ar ^c	Ne ^d
a'	ν ₁	3590		3555.1	3548.7
	ν ₂	1725			
	ν ₃	1225	1241	1283.9 ^e 1251.9	1303.8
	ν ₄	863		874.5	875.9
	ν ₅	625		654.9	
	ν ₆	460		691.5 ^e 664.0	
	ν ₇	385			455.3
	ν ₈				
	ν ₉				
a''	ν ₁₀	3660		3730.0	3712.5
	ν ₁₁	1240	1313 ^e 1285	1314.6 ^e 1264.7	1323.0
	ν ₁₂	818		851.5	
	ν ₁₃	460			
	ν ₁₄				
	ν ₁₅				

^a Ref. 1; ^b Ref. 2; ^c Ref. 3; ^d Ref. 4; ^e Bands due to ¹⁰BF₃·H₂O.

Table 5 Computed (using the 6-311++G(d,p) basis set) and experimental intramolecular wavenumber shifts of the BF₃ and H₂O fragments of the eclipsed ¹¹BF₃·H₂O complex.

Fragment	Monomer mode	Complex mode	Wavenumber shift/cm ⁻¹			
			Computed	Experimental		
				N ₂ ^a	Ar ^b	Ne ^c
BF ₃	ν_1	ν_4	-39.3			
	ν_2	ν_6	-90.2	-28		
	$\nu_3(a')$	ν_3	-112.3	-215	-209	-124.5
	$\nu_3(a'')$	ν_{11}	-139.1	-200	-165	-143.7
	$\nu_4(a')$	ν_7	-18.5	-19		-23.6
	$\nu_4(a'')$	ν_{13}	-19.4	-19		
H ₂ O	ν_1	ν_1	-66.5	-45		
	ν_2	ν_2	3.0			
	ν_3	ν_{10}	-72.4	-67		

^a Ref. 1; ^b Ref. 2; ^c Ref. 4.

two components of the antisymmetric BF₃ bending vibration, ν_7 and ν_{13} , heavily overlapped. The 625 cm⁻¹ band must therefore be the out-of-plane BF₃ bending mode, ν_6 , while the band observed at 385 cm⁻¹ must be assigned to one of the intermolecular modes, although no predicted mode appears sufficiently close to this observed band to be a credible candidate. The remaining assignments are in reasonable agreement with those reported earlier.²⁻⁴

It is the shifts of the monomer modes on complexation which provide the most characteristic computational measure of the strength of interaction, for comparison with experimental data. These shifts, for the 6-311++G(d,p) basis set, are presented in Table 5, for both the BF₃ and H₂O molecules, while the corresponding experimental shifts are also included.^{1,2,4} The two antisymmetric BF₃ stretching modes consistently undergo the largest perturbations on complexation. The computed shifts are substantially smaller than the experimental ones, except those in neon.⁴ However, it is well known that *ab initio* calculations for isolated 1:1 (gas phase) complexes do not account for the strong matrix effects experienced by molecules trapped in, e.g. N₂ and Ar. In neon matrices the perturbations are smaller, and agreement between the calculated and the experimental shifts is much improved. On the other hand, our calculated shift of -90.2 cm⁻¹ for the symmetric bending mode of the BF₃ fragment is considerably larger than the experimental value in N₂. Inspection of the forms of the normal modes, however, reveals that ν_6 of BF₃·H₂O is not a pure BF₃ bending vibration. As a result of the proximity of the ν_5 geared libration (H₂O wagging) mode at 608.4 cm⁻¹ (see Table 3), these two vibrations are strongly coupled with one another, and the out-of-plane bending also involves a large amplitude displacement of the H₂O fragment. This coupling has the effect of lowering the wavenumber of ν_6 and raising that of ν_5 , so that the vibration nominally assigned to the out-of-plane BF₃ bending mode is artificially low, and its shift is exaggerated. All the calculated shifts are to the red, with the exception of that of the H₂O bending vibration, which is typical of water acting as a Lewis base.

The corresponding calculated wavenumbers of ¹¹BF₃·H₂S, along with the experimental values for the two antisymmetric BF₃ stretching motions,² are given in Table 6. These wavenumbers lead to the computed and experimental shifts reported in Table 7. All the wavenumber shifts are to lower values, including that of the H₂S bending mode, in contrast to the H₂O bending vibration in BF₃·H₂O. This finding serves to emphasize the difference in the ways in which the electron donors are bound to the BF₃ fragment. Again, the computed antisymmetric BF₃

Table 6 Computed (using the 6-311++G(d,p) basis set) and experimental wavenumbers of the staggered ¹¹BF₃·H₂S complex.

Symmetry species	Mode	Approximate description	Computed	Experimental ^a
a'	ν_1	$\nu_s(H_2S)$	2808.7	
	ν_2	$\nu_a(BF_3)$	1407.2	1321
	ν_3	$\delta(H_2S)$	1199.8	
	ν_4	$\nu_s(BF_3)$	858.4	
	ν_5	$\delta_s(BF_3)$	620.3	
	ν_6	$\delta_a(BF_3)$	470.4	
	ν_7	geared libration	238.9	
	ν_8	$\nu(B...S)$	92.0	
	ν_9	antigeared libration	81.2	
a''	ν_{10}	$\nu_a(H_2S)$	2828.3	
	ν_{11}	$\nu_a(BF_3)$	1417.3	1270
	ν_{12}	$\delta_a(BF_3)$	474.2	
	ν_{13}	geared libration	261.1	
	ν_{14}	antigeared libration	91.3	
	ν_{15}	B...S torsion	45.2	

^aIn Ar; ref. 2.

stretching shifts substantially underestimate the experimental ones,² but this is simply due to the neglect of the perturbing effect of the argon matrix in the theoretical calculations.

Table 7 Computed (using the 6-311++G(d,p) basis set) and experimental intramolecular wavenumber shifts of the BF₃ and H₂S fragments of the staggered ¹¹BF₃·H₂S complex.

Fragment	Monomer mode	Complex mode	Wavenumber shift/cm ⁻¹	
			Computed	Experimental ^a
BF ₃	ν_1	ν_4	-15.5	
	ν_2	ν_5	-75.0	
	$\nu_3(a')$	ν_2	-26.8	-129
	$\nu_3(a'')$	ν_{11}	-16.7	-180
	$\nu_4(a')$	ν_6	-4.4	
	$\nu_4(a'')$	ν_{12}	-0.6	
H ₂ S	ν_1	ν_1	-8.2	
	ν_2	ν_3	-33.5	
	ν_3	ν_{10}	-7.8	

^aIn Ar; ref. 2.

4. Conclusions

The preferred conformation calculated for the $\text{BF}_3\cdot\text{H}_2\text{O}$ complex is the eclipsed, while that for the H_2S analogue is the staggered. The order of the energies of interaction of the complexes of BF_3 with the hard oxygen base H_2O and the soft sulphur base H_2S is in accordance with predictions based on conventional wisdom. The computed vibrational spectrum of $\text{BF}_3\cdot\text{H}_2\text{O}$ correlates, with the reservations noted above, with those observed in nitrogen, argon and neon matrices, and the computations have assisted in the re-assignment of a number of the observed bands.

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