G.A. Yeo and T.A. Ford,
S. Afr. J. Chem., 2006, **59**, 129–134,
<http://journals.sabinet.co.za/sajchem/>.

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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Received 25 January 2006; revised and accepted 17 October 2006.

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 BF_3 and H_2O.[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 $BF_3.H_2O$ in argon[3] and neon[4] matrices have subsequently been reported, but a full assignment remains elusive. *Ab initio* computations of the spectrum of $BF_3.H_2O$, 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. $(NH_3)_2$ and $(PH_3)_2$,[6] and $H_2O.CO_2$ and $H_2S.CO_2$,[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 $BF_3.H_2O$ suggested that the H_2O molecule was coordinated with BF_3 with the H_2O angle bisector presenting virtually perpendicularly to the plane of BF_3.[1] However, some trial calculations at the MP2 level with larger basis sets showed that in each case the H_2O molecule adopted an eclipsed conformation relative to BF_3, 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 $BF_3.H_2O$ 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 $BF_3.H_2O$ using the largest basis set, in the expectation of removing the earlier ambiguities in the predicted[1,4,5] and experimental[1–4] vibrational assignments. These calculations form part of an ongoing theoretical study of the properties of the complexes of BF_3 with other oxygen bases, e.g. CO_2,[8] N_2O,[9] SO_2[10] and $(CH_3)_2O$.[11]

In view of the expected similarity between the complexes of BF_3 with H_2O and with its analogue H_2S, we have included parallel studies of the $BF_3.H_2S$ 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 BF_3 with a sulphur base which we have examined in this way, following an earlier study of $BF_3.(CH_3)_2S$.[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 option[15] in cases of slow convergence. Interaction energies were computed and corrected for basis set superposi-

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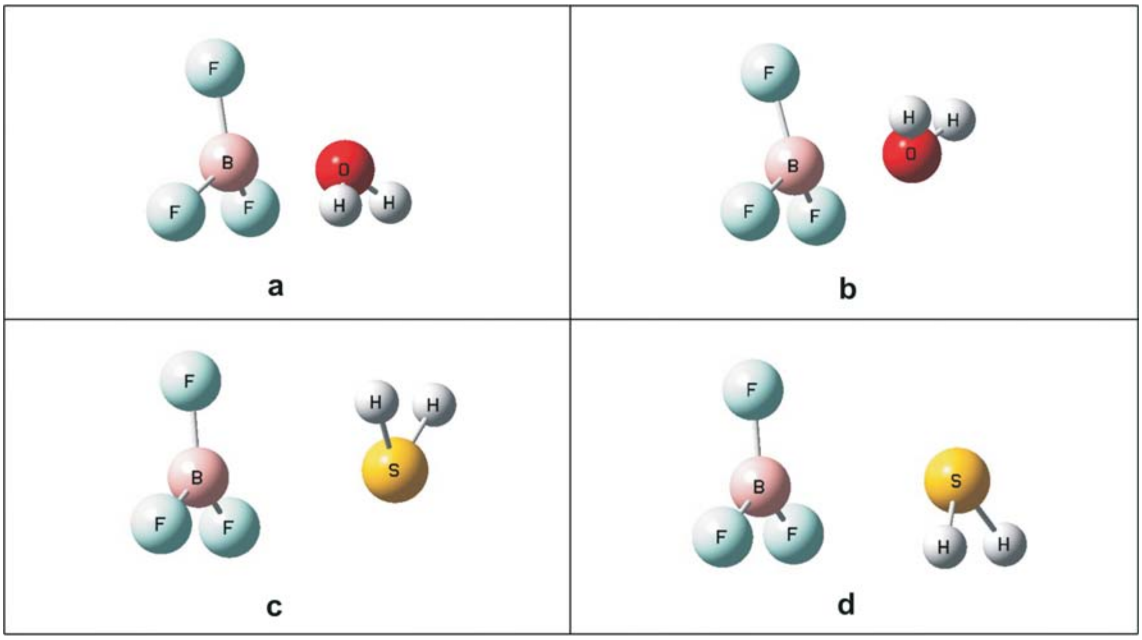

Figure 1 The optimized structures of the $BF_3.H_2O$ and $BF_3.H_2S$ complexes determined using the 6-311++G(d,p) basis set: (**a**) eclipsed $BF_3.H_2O$ (energy minimum); (**b**) staggered $BF_3.H_2O$ (saddle point); (**c**) staggered $BF_3.H_2S$ (energy minimum); (**d**) eclipsed $BF_3.H_2S$ (saddle 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 BF_3 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 $BF_3.H_2O$,[1] at the RHF/4-31G level, we found that the angle, Θ, between the C_2 axis of H_2O and the C_3 axis of BF_3 was close to 180°, indicating that coordination involved mainly the axial ($3a_1$) non-bonding orbital of H_2O. 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 $BF_3.H_2O$ and $BF_3.H_2S$ adducts for each basis set studied. For $BF_3.H_2O$ 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 H_2O molecule at the B atom virtually perpendicular to the BF_3 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 H_2O 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 $BF_3.H_2O$ to be separated reliably. The optimized structures of the eclipsed and staggered species of $BF_3.H_2O$, determined with the 6-311++G(d,p) basis set, are illustrated in Figs 1(a) and 1(b).

For the $BF_3.H_2S$ 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 H_2O molecule, has an average value of about 122°, while the corresponding angle

Table 1 Intermolecular structural parameters [a] of some $BF_3.H_2O$ and $BF_3.H_2S$ complexes, computed with a variety of basis sets.

Basis set	$BF_3.H_2O$		$BF_3.H_2S$			
	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 $BF_3.H_2S$ averages approximately 110° (eclipsed) and 113° (staggered). This results in the amplitude of the torsional motion which interconverts the two conformers in $BF_3.H_2S$ being larger than that in $BF_3.H_2O$, enabling the conformers to be more clearly differentiated. Figures 1(c) and 1(d) show the optimized eclipsed and staggered structures of $BF_3.H_2S$, computed with the largest basis set.

The difference in the conformational preferences of the two complexes may be rationalized as follows. In the $BF_3.H_2O$ 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 $BF_3.H_2S$ 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 $BF_3.H_2O$ 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 $BF_3.H_2S$, 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 $2b_1$ non-bonding orbital of H_2S in the interaction, relative to the $5a_1$ 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 $BF_3.H_2O$ complex may now be compared with those of Ball[5] 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 $BF_3.H_2O$[21–23] and $BF_3.H_2S$[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 $BF_3.H_2O$ and $BF_3.H_2S$ 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^{-1} [23] and –71.7 kJ mol^{-1} [25] but these calculations were performed with much smaller basis sets. Jacox *et al.* did not report the interaction energies.[4] For staggered $BF_3.H_2S$, 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 $BF_3.H_2S$ has been reported previously as –22 kJ mol^{-1} [23] 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 $BF_3.H_2O$ is bound by about 70 kJ mol^{-1} (60 kJ mol^{-1} with zero-point energy correction), eclipsed $BF_3.H_2S$ by 12 kJ mol^{-1} (8 kJ mol^{-1}) and staggered $BF_3.H_2S$ by 10 kJ mol^{-1} (5 kJ mol^{-1}). These relative values for interaction of BF_3 with a hard (H_2O) and a soft (H_2S) base are quite consistent with chemical intuition.

Comparison of our computed fully-corrected interaction energy of the BF_3 complex with H_2O with those with other oxygen donor bases, CO_2,[8] N_2O,[9] SO_2[10] and $(CH_3)_2O$[11] recalculated under the same conditions[26] (–4.556, –3.450, –8.844 and

Table 2 Interaction energies of some $BF_3.H_2O$ and $BF_3.H_2S$ complexes, corrected for BSSE and for zero-point energy differences, computed with a variety of basis sets.

Basis set	$BF_3.H_2O$		$BF_3.H_2S$			
	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 $^{11}BF_3.H_2O$ 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	$\nu_s(H_2O)$	3818.0	3951	3818	3818
	ν_2	$\delta(H_2O)$	1631.6	1870	1632	1632
	ν_3	$\nu_a(BF_3)$	1321.7	1404	1322	1323
	ν_4	$\nu_s(BF_3)$	834.6	959	835	835
	ν_5	geared libration	608.4	722	608	607
	ν_6	$\delta_s(BF_3)$	605.1	544	606	606
	ν_7	$\delta_a(BF_3)$	456.3	430	456	456
	ν_8	$\nu(B\ldots O)$	278.3	321	278	278
	ν_9	antigeared libration	238.7	287	240	240
a″	ν_{10}	$\nu_a(H_2O)$	3930.4	4117	3930	3930
	ν_{11}	$\nu_a(BF_3)$	1294.9	1441	1295	1295
	ν_{12}	geared libration	727.8	894	728	728
	ν_{13}	$\delta_a(BF_3)$	455.4	557	455	455
	ν_{14}	antigeared 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 basicity[27] 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 $^{11}BF_3$, H_2O and H_2S monomers[19,29–33] is recorded in the Supplementary Material, Table SM3.

The computed wavenumbers of $^{11}BF_3.H_2O$ 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 neon[4] 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 H_2O bending mode, ν_2, although we cannot suggest an alternative interpretation. The band at 460 cm^{-1} must be assigned to the

Table 4 Experimental wavenumbers of the $^{11}BF_3.H_2O$ 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]	1303.8
				1251.9	
	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]	1314.6 [e]	1323.0
			1285	1264.7	
	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 $^{10}BF_3.H_2O$.

Table 5 Computed (using the 6-311++G(d,p) basis set) and experimental intramolecular wavenumber shifts of the BF_3 and H_2O fragments of the eclipsed $^{11}BF_3.H_2O$ 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		
	ν_3(a′)	ν_3	−112.3	−215	−209	−124.5
	ν_3(a″)	ν_{11}	−139.1	−200	−165	−143.7
	ν_4(a′)	ν_7	−18.5	−19		−23.6
	ν_4(a″)	ν_{13}	−19.4	−19		
H_2O	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 BF_3 bending vibration, ν_7 and ν_{13}, heavily overlapped. The 625 cm^{-1} band must therefore be the out-of-plane BF_3 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 BF_3 and H_2O molecules, while the corresponding experimental shifts are also included.[1,2,4] The two antisymmetric BF_3 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. N_2 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 BF_3 fragment is considerably larger than the experimental value in N_2. Inspection of the forms of the normal modes, however, reveals that ν_6 of $BF_3.H_2O$ is not a pure BF_3 bending vibration. As a result of the proximity of the ν_5 geared libration (H_2O 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 H_2O 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 BF_3 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 H_2O bending vibration, which is typical of water acting as a Lewis base.

The corresponding calculated wavenumbers of $^{11}BF_3.H_2S$, along with the experimental values for the two antisymmetric BF_3 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 H_2S bending mode, in contrast to the H_2O bending vibration in $BF_3.H_2O$. This finding serves to emphasize the difference in the ways in which the electron donors are bound to the BF_3 fragment. Again, the computed antisymmetric BF_3 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 6 Computed (using the 6-311++G(d,p) basis set) and experimental wavenumbers of the staggered $^{11}BF_3.H_2S$ 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	ν(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	

[a] In Ar; ref. 2.

Table 7 Computed (using the 6-311++G(d,p) basis set) and experimental intramolecular wavenumber shifts of the BF_3 and H_2S fragments of the staggered $^{11}BF_3.H_2S$ 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	
	ν_3(a′)	ν_2	−26.8	−129
	ν_3(a″)	ν_{11}	−16.7	−180
	ν_4(a′)	ν_6	−4.4	
	ν_4(a″)	ν_{12}	−0.6	
H_2S	ν_1	ν_1	−8.2	
	ν_2	ν_3	−33.5	
	ν_3	ν_{10}	−7.8	

[a] In Ar; ref. 2.

4. Conclusions

The preferred conformation calculated for the $BF_3.H_2O$ 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 $BF_3.H_2O$ 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.

Acknowledgements

This material is based upon work supported by the National Research Foundation under Grant Number 2053648. Any opinion, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Research Foundation. The authors also acknowledge the financial assistance of the University of KwaZulu-Natal Research Fund, through its support of the Centre for Theoretical and Computational Chemistry, and the expert technical assistance of Mr Kishore Singh.

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