Microsolvation of the Be-F bond in complexes of BeF₂, BeF₃⁻¹, and BeF₄⁻² with nH₂O, for n = 1–6

Janet E. Del Bene a, Ibon Alkorta b and José Elguero b

aDepartment of Chemistry, Youngstown State University, Youngstown, OH, USA; bInstituto de Química Médica (IQM-CSIC), Madrid, Spain

ABSTRACT

Ab initio MP2/aug'-cc-pVTZ calculations have been carried out to determine the structures and binding energies of complexes of BeF₂, BeF₃⁻¹, and BeF₄⁻² with n H₂O molecules, with n = 1–6. For each series of complexes with BeF₂, BeF₃⁻¹, and BeF₄⁻², the binding energies increase as the number of water molecules increases, but the binding energies per intermolecular bond for complexes formed between BeF₂ and BeF₄⁻² and nH₂O decrease as the number of water molecules increases. The binding energies per bond of the BeF₃⁻¹ complexes show little dependence on the number of H₂O molecules present. Intermolecular O-H···F hydrogen bonds (HB) stabilise all complexes of H₂O with the beryllium bases except for BeF₂:1H₂O and BeF₂:2H₂O. Complexes of BeF₂ are also stabilised by O···Be beryllium bonds (BeB) and O-H···O hydrogen bonds. EOM-CCSD calculations have also been performed to determine the spin–spin coupling constants. The one-bond coupling constants ¹J(Be-F) increase as the Be-F distance decreases, and exhibit an excellent second-order correlation with that distance. ²hJ(O-F) coupling constants across O-H···F hydrogen bonds also exhibit a second-order dependence on distance. Coupling constants ¹beJ(O-Be) and ²hJ(O-O) are found in complexes with BeF₂ and exhibit a linear dependence on the Be-O and O-O distances, respectively.

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In this study we examine intramolecular Be-F bonds, as well as intermolecular Be···O beryllium bonds, and O-H···F and O-H···O hydrogen bonds. Our emphasis is on the structures and binding energies of these complexes, and on EOM-CCSD spin–spin coupling constants across the intermolecular and intramolecular bonds. Our work provides new insights into these bonds in charged and uncharged systems which should be of significant interest to the readers of Mol. Phys. We believe that it will be a very positive contribution to the literature on noncovalent bonds, particularly in related charged and uncharged systems.

1. Introduction

The solvation of ions by water through the formation of hydrogen bonds is of utmost importance for
understanding the structure of aqueous solutions and the role that these interactions play in biological processes [1]. The polar character of water leads to the dissociation of salts in aqueous solution and the dispersion of the resulting ions. The solvation of anions through hydrogen bonding in aqueous solution [2] has been investigated theoretically for a number of anions [3,4], including F⁻ and Cl⁻ [5–9], BF₄⁻ [10] and PF₆⁻ [11].

Among the myriad of possible anions, we have turned our attention to BeF₃⁻¹ and BeF₄⁻². These anions are isoelectronic with the neutral molecules BF₃ and CF₄, respectively, and share their planar D₃h and tetrahedral geometries, respectively. BeF₃⁻¹ has been observed in numerous X-ray structures of proteins, with 141 entries found in the PDB database, October-2020. BeF₄⁻² has only been observed in two systems, namely, PDB (1L5Y [1] and 1XHF [13]). BeF₃⁻¹ and BeF₄⁻² have been used to mimic transition state structures in phosphoryl transfer processes [14]. Moreover, the similarity in size and electronic characteristics of BeF₄⁻² and SO₄⁻² is responsible for the formation of tetrafluoroberyllates with crystal structures analogous to those of sulfates such as Langbeinite, Tutton’s salts [16]. In the Cambridge Structural Database [17], BeF₄⁻² appears in eight structures (KIPPEE [18], MOPGAZ [19], QQQBILD [20], QQQBLG [20], QQQBLJ [20], TGLYBE02 [21], TGLYBE20 [21], and XUGHAI [22]) with different protonated amines as counterions which form N–H···F hydrogen bonds. In addition, they are observed in four systems with metals as counterions (QQQGND [23], TITKEN [24], ZZZALG [25], ZZZALJ [25]). ¹⁹F-NMR spectroscopy has been used to identify BeF₂⁻², BeF₃⁻¹, BeF₂ and BeF⁺ in aqueous solutions [26–29] and the solid state [30]. Gas-phase theoretical studies have shown that beryllium dianions are metastable [31,32]. In the case of BeF₄⁻² a small barrier prevents its spontaneous dissociation into the more stable ions, BeF₃⁻¹ + F⁻ [32].

To better understand the bonding in aqueous solution of the neutral molecule BeF₂ and the anions BeF₃⁻¹ and BeF₄⁻², we have now undertaken a detailed study of these species in complexes with nH₂O molecules, for n = 1–6. In this paper we report and discuss the equilibrium geometries of these complexes, the binding energies of these complexes, and their binding energies per intermolecular bond. We also examine the beryllium bonds and hydrogen bonds that bind the monomers together. In addition, we report EOM-CCSD intramolecular Be-F and intermolecular Be-O, O-F, and O-O coupling constants in these complexes. It is the purpose of this paper to report the results of this study.

2. Methods

The structures of the isolated monomers BeF₂, BeF₃⁻¹, and BeF₄⁻², and their complexes with nH₂O molecules for n = 1–6, were optimised at second-order Möller-Plesset perturbation theory (MP2) [33–36] with the aug-cc-pVTZ basis set [37]. This basis set was derived from the Dunning aug-cc-pVTZ basis set [38,39] by removing diffuse functions from H atoms. Frequencies were computed to establish that the optimised structures correspond to equilibrium structures on their potential surfaces. The binding energies of the complexes are given as –ΔE for the reaction that forms the complex from the corresponding isolated monomers. These calculations were carried out with the Gaussian-16 program [40].

The electron densities of the complexes have been analysed using the Atoms in Molecules (AIM) methodology [41–44] employing the AIMAll program [45]. The topological analysis of the electron density produces the molecular graph of each complex. This graph identifies the location of electron density features of interest, including the electron density (ρ) maxima associated with the various nuclei, and saddle points which correspond to bond critical points (BCPs) or ring critical points, the latter indicating a minimum electron density within a ring. The zero gradient line which connects a BCP with two nuclei is the bond path.

Spin–spin coupling constants for the complexes were evaluated using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI (configuration interaction)-like approximation [46,47] with all electrons correlated. For these calculations, the Ahlrichs qzp basis set [48] was placed on ¹⁷O and ¹⁹F, the Dunning cc-pVDZ basis set on ¹H atoms, and the hybrid basis set developed previously on ⁹Be [49]. All terms which contribute to the total coupling constant, namely, the paramagnetic spin orbit (PSO), diamagnetic spin orbit (DSO), Fermi contact (FC), and spin dipole (SD), have been evaluated. The EOM-CCSD calculations were performed using ACES II [50] on the HPC cluster Owens at the Ohio Supercomputer Center.

3. Results and discussion

Table 1 provides the symmetries of the complexes of BeF₂, BeF₃⁻¹, and BeF₄⁻² with nH₂O molecules, the complex binding energies and binding energies per bond, and the number and type of bonds found in these complexes. Complexes of BeF₂ with one and two H₂O molecules are stabilised by Be–O contacts. These interactions are known as beryllium bonds since the beryllium is the atom in the Lewis acid directly involved in the interaction [51,52]. In addition to beryllium bonds,
Figure 1. Complexes BeF$_2$:4H$_2$O, BeF$_3^{-1}$:4H$_2$O, and BeF$_4^{-2}$:4H$_2$O. The symmetries of these complexes are C$_2$, C$_{2v}$, and D$_{2d}$, respectively.

3.1. Binding energies

Table S1 of the Supplemental Data provides the structures, molecular graphs, and total energies of the complexes of BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ with nH$_2$O molecules. Table S2 provides simplified renderings of these complexes which illustrate the bonding patterns and the numbering system used for each. Examples of these renderings are shown in Figure 1 for complexes of BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ with 4 H$_2$O molecules.

As reported in Table 1, the BeF$_2$:nH$_2$O complexes have binding energies which vary from 92 kJ/mol for the complex in which there is only one H$_2$O molecule and one beryllium bond, to 391 kJ/mol in the complex with 6 H$_2$O molecules which has two beryllium bonds, and four O-H···F and four O-H···O hydrogen bonds. The large binding energy of BeF$_2$:1H$_2$O is due to the strength of the O···Be beryllium bond. This is evident from the stability of this complex relative to the complexes BeF$_3^{-1}$:1H$_2$O, and BeF$_4^{-2}$:1H$_2$O which are stabilised by O-H···F hydrogen bonds with binding energies per bond of 33 and 65 kJ/mol, respectively. As expected, the binding energies of the BeF$_2$:nH$_2$O complexes increase as the number of H$_2$O molecules and the number of intermolecular bonds increase. However, as the number of H$_2$O molecules increases, the binding energy per bond of the complexes with BeF$_2$ decreases from 92 to 39 kJ/mol. Thus, although the binding energies of these complexes increase dramatically as the number of intermolecular bonds increases, the greater the number of intermolecular bonds the smaller the binding energy per bond. This situation arises because the Be···O bond is very strong, while the additional O-H···F hydrogen bonds are relatively weak. Nevertheless, there is a cooperative effect among these bonds which is suggested by the direction of electron flow in these complexes. For example, in the BeF$_2$:4H$_2$O complex illustrated in Figure 1, electron donation by O6 to O4-H occurs across the O4-H···O6 hydrogen bond. O4 is an electron donor to Be for the formation of the Be···O4 beryllium bond. Some of this electron density is distributed to F2, which is an electron donor to O6-H for the O6-H···F2 hydrogen bond. Thus, there is cyclic cooperativity of electron transfer among these bonds. A similar pattern of electron transfer is also observed in the complexes with BeF$_3^{-1}$ and BeF$_4^{-2}$.

Table 1. Symmetries, binding energies (−ΔE), binding energies per bond (−ΔE/bond, kJ mol$^{-1}$), and the number of hydrogen and beryllium bonds in the complexes of BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ with nH$_2$O molecules.

| Sym        | −ΔE | −ΔE/bond | No. of Be···O, O-H···F, and O-H···O bonds |
|------------|-----|----------|----------------------------------------|
| BeF$_2$    |     |          |                                        |
| with 1 H$_2$O | 91.9 | 1 / 0 / 0 | 91.9                                   |
| 2 H$_2$O   | 157.1 | 2 / 0 / 0 | 78.6                                   |
| 3 H$_2$O   | 222.1 | 2 / 1 / 1 | 55.5                                   |
| 4 H$_2$O A | 287.0 | 2 / 2 / 2 | 47.8                                   |
| 4 H$_2$O B | 281.1 | 2 / 2 / 2 | 46.8                                   |
| 6 H$_2$O   | 391.2 | 2 / 4 / 4 | 39.1                                   |
| BeF$_3^{-1}$ |     |          |                                        |
| with 1 H$_2$O | 65.8 | 0 / 2 / 0 | 32.9                                   |
| 2 H$_2$O A | 123.6 | 0 / 4 / 0 | 30.9                                   |
| 2 H$_2$O B | 111.9 | 0 / 4 / 0 | 28.0                                   |
| 3 H$_2$O   | 174.2 | 0 / 6 / 0 | 29.0                                   |
| 4 H$_2$O   | 209.0 | 0 / 8 / 0 | 26.1                                   |
| 5 H$_2$O   | 259.2 | 0 / 6 / 2 | 32.4                                   |
| 6 H$_2$O   | 597.9 | 0 / 12 / 0| 49.8                                   |
| BeF$_4^{-2}$ |     |          |                                        |
| with 1 H$_2$O | 129.7 | 0 / 2 / 0 | 64.9                                   |
| 2 H$_2$O   | 248.4 | 0 / 4 / 0 | 62.1                                   |
| 3 H$_2$O   | 442.3 | 0 / 8 / 0 | 55.3                                   |
| 4 H$_2$O   | 523.5 | 0 / 10 / 0| 52.4                                   |
| 5 H$_2$O   | 597.9 | 0 / 12 / 0| 49.8                                   |

a) Beryllium bonds are found only in the uncharged BeF$_2$:nH$_2$O complexes.
flow involving BeF$_2$ and the water molecules O$_5$H$_2$ and O$_7$H$_2$ also occurs in this complex.

The binding energies of the BeF$_3$$^{-1}$:nH$_2$O complexes vary from 66 kJ mol$^{-1}$ for BeF$_3$$^{-1}$:1H$_2$O to 259 kJ mol$^{-1}$ for BeF$_3$$^{-1}$:5H$_2$O. What is more significant is the small variation in the binding energy per intermolecular bond, which ranges from 33 kJ mol$^{-1}$ for the complex with one H$_2$O, to 26 kJ mol$^{-1}$ when 4 H$_2$O molecules are present. The binding energies per intermolecular bond do not decrease as the number of intermolecular bonds increases, as observed for the BeF$_2$:nH$_2$O complexes. Rather, the two complexes with the greatest binding energies per bond are BeF$_3$$^{-1}$:1H$_2$O and BeF$_3$$^{-1}$:5H$_2$O at 33 and 32 kJ mol$^{-1}$, respectively. Moreover, the binding energies per bond of the BeF$_3$$^{-1}$:nH$_2$O complexes are less than the binding energies per bond of the BeF$_4$$^{-2}$:nH$_2$O complexes, which vary from 65 kJ mol$^{-1}$ for BeF$_4$$^{-2}$:1H$_2$O to 50 kJ mol$^{-1}$ for BeF$_4$$^{-2}$:6H$_2$O. Figure 2 presents a plot of the binding energies per bond versus the number of bonds for the three series of complexes. From Figure 2 it can be seen that the binding energies per bond for the complexes of BeF$_3$$^{-1}$ with H$_2$O are almost independent of the number of bonds that stabilise these complexes, but the correlation coefficient for a linear dependence is only 0.160. The binding energies of the complexes of BeF$_4$$^{-2}$ with water increase linearly as the number of bonds increases, with a correlation coefficient of 0.998. The complexes of BeF$_2$ with H$_2$O show a second order dependence on the number of bonds, with a correlation coefficient of 0.991.

It is informative to compare the binding energies per bond for corresponding complexes in the two series of complexes BeF$_2$:nH$_2$O and BeF$_4$$^{-2}$:nH$_2$O which have the same number of H$_2$O molecules. When more than two H$_2$O molecules are present, the binding energies per bond of the complexes with BeF$_4$$^{-2}$ are greater than the binding energies of the corresponding BeF$_2$ complexes. This is as expected, since the number of intermolecular bonds in corresponding complexes is greater in the BeF$_4$$^{-2}$ complexes as can be seen in Table 1, and the O\cdots F bonds are charged hydrogen bonds. In contrast, the binding energies per bond of the BeF$_2$ complexes with one and two H$_2$O molecules are greater than the binding energies per bond of the corresponding complexes of BeF$_4$$^{-2}$, even though there are more bonds in the latter complexes. The large binding energies of the BeF$_2$ complexes may be attributed to the presence of strong O\cdots Be beryllium bonds.

As noted in the Introduction, BeF$_4$$^{-2}$ is a metastable ion in gas phase, [29] since it is 259.8 kJ mol$^{-1}$ less stable than the sum of the energies of BeF$_3$$^-$ and F\(^-\) in agreement with analogous dianion beryllium derivatives. The effect of microsolvation on the stability of BeF$_4$$^{-2}$ can be estimated from the energies of the complexes BeF$_4$$^{-2}$:nH$_2$O with n = 0–3, with the assumption that in the formation or dissociation of these complexes, BeF$_3$$^-$ and F\(^-\) are bonded to the same number of water molecules. The reaction for the formation of BeF$_4$$^{-2}$:2nH$_2$O is then given as

$$\text{BeF}_3\prescript{-1}{}\text{nH}_2\text{O} + \text{F}^{-1}\text{nH}_2\text{O} \rightarrow \text{BeF}_4\prescript{-2}{}\text{2nH}_2\text{O}. \hspace{1cm} (1)$$

That solvation significantly stabilises BeF$_4$$^{-2}$ can be seen in Figure 3, which is a plot of the binding energies of these complexes versus the number of water molecules.
The correlation coefficient of the second-order trendline is 1.000, or more precisely, 0.999996.

### 3.2. Structures

The unique intramolecular Be-F distances, intermolecular Be-O distances across beryllium bonds, and O-F and O-O distances across hydrogen bonds are given in Table 2. Solvation of the BeF2, BeF3⁻¹, and BeF4⁻² molecules with nH2O molecules has a significant effect on the length of the Be-F bond. The Be-F distance of 1.39 Å in the isolated BeF2 molecule (exp. 1.386 Å [53]) increases to between 1.43 Å in the complex with one H2O molecule and 1.53 Å in the complex with six H2O molecules. Thus, for these complexes the overall tendency is for the Be-F distance to increase as the number of H2O molecules increases.

This is not the case for the Be-F distances in the complexes of BeF3⁻¹ with H2O. These distances increase or decrease slightly as the number of H2O molecules increases, and appear to be almost independent of the number of H2O molecules in the complex. Thus, the shortest Be-F distance of 1.46 Å and the longest distance of 1.50 Å are found in the complexes BeF3⁻¹:1H2O and BeF3⁻¹:5H2O, respectively. These distances lie between the shortest and longest Be-F distances in the complexes with BeF2. The longest Be-F distances are found in the complexes with BeF4⁻². These distances range from 1.58 Å in the complexes BeF4⁻²:1H2O and BeF4⁻²:5H2O to 1.63 Å in the complex BeF4⁻²:1H2O. Thus, the longest and the shortest Be-F distances are found in the same complex, namely, BeF4⁻²:1H2O.

O-H···F hydrogen bonds are found in all of the complexes of BeF2, BeF3⁻¹, and BeF4⁻² with H2O, except for BeF2:1H2O and BeF2:2H2O. The longest O-F distances are found in the complexes BeF3⁻¹:nH2O which have the smallest binding energies per bond. These distances

![Figure 3. -ΔE for Equation (1) as function of the number of interacting H2O molecules with BeF4⁻².](image-url)
range from 2.82–2.95 Å. The shortest distances are found in the complexes with BeF$_2$, which range from 2.62–2.67 Å, while longer distances between 2.66 and 2.81 Å are found in the complexes with BeF$_4$.$^2$.

The complexes BeF$_2$:1H$_2$O and BeF$_2$:2H$_2$O are stabilised solely by beryllium bonds. When two intermolecular bonds form at the same site, it is expected that these bonds should lengthen, that is, the Be-O distance in BeF$_2$:2H$_2$O is greater than that distance in BeF$_2$:1H$_2$O. When more than two H$_2$O molecules are present, there are two types of intermolecular interactions, the Be⋯O beryllium bond and the O-H⋯F hydrogen bond. As noted above, there is a cooperative effect among these bonds such that the beryllium bonds are strengthened by the presence of hydrogen bonds. As a result, the average Be-O distance should decrease as the number of water molecules and therefore the number of hydrogen bonds increases. This is illustrated in Figure 4 by the second-order trendline which has a correlation coefficient of 0.994. It should be noted that the average Be-O distance is identical to the individual Be-O distance except for complexes with $n = 3$ and 4 B.

The majority of the O-H⋯F hydrogen bonds in the complexes of BeF$_2$, BeF$_3$.$^1$, and BeF$_4$.$^2$ with H$_2$O are nonlinear, with deviations from linearity between 15 and 25°. There are three unique exceptions, two in the BeF$_3$.$^1$:2H$_2$O complex and one in the BeF$_4$.$^2$:1H$_2$O complex. The O6-H⋯F2 and O8-H⋯F4 hydrogen bonds in the BeF$_3$.$^1$ complex deviate from linearity by 2 and 8°, respectively, while in the BeF$_4$.$^2$ complex the deviation from linearity is 10°. As noted above, the BeF$_2$:nH$_2$O complexes are also stabilised by Be⋯O beryllium bonds and O-H⋯O hydrogen bonds. The Be-O distances across the beryllium bonds range from 1.68 Å for the O4⋯' Be bond in BeF$_2$:4H$_2$O B to 1.78 Å for the O4⋯' Be bond in BeF$_2$:3H$_2$O and the O5⋯' Be bond in BeF$_2$:4H$_2$O. O-H⋯O hydrogen bonds are found in complexes of BeF$_2$ containing 3, 4, and 6 H$_2$O molecules. These hydrogen bonds have short O-O distances between 2.63 and 2.69 Å and are nonlinear by 16 to 20°. An O-H⋯O hydrogen bond is also found in the BeF$_3$.$^1$:5H$_2$O complex. This O8-H⋯O6 hydrogen bond has a long O-O distance of 2.99 Å and is nonlinear by 10°.

Those water molecules involved in two simultaneous O-H⋯F hydrogen bonds show smaller H-O-H angles than in the isolated molecule (104.1°). The maximum effect is reached in the BeF$_4$.$^2$:4H$_2$O complex where the H-O-H angle is only 95.7°. The energetic penalty of this deformation is compensated by the large binding energies found in the complexes.

### 3.3. Spin–spin coupling constants

Table S3 of the Supporting Information provides the PSO, DSO, FC, and SD components of the coupling constants $^1$J(Be-F), $^2$hJ(O-F), $^{1be}$J(Be-O), and $^{2b}$J(O-O) for the complexes of BeF$_2$, BeF$_3$.$^1$, and BeF$_4$.$^2$ with nH$_2$O molecules. It is apparent that the one-bond coupling constants $^1$J(Be-F) are dominated by the FC term, with the PSO term making contributions ranging from 2 to 5 Hz. Since the FC term is negative and the PSO term positive, the FC term overestimates the absolute value of
$^{1}J(\text{Be-F})$. The variation of coupling constants $^{2}hJ(O-F)$ across the O-H···F hydrogen bonds in the complexes of BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ with nH$_2$O molecules follows a different and unusual pattern. When the beryllium base is BeF$_2$, the FC term which is negative is the dominant contributor to $^{2}hJ(O-F)$, with the PSO term making a smaller positive but non-negligible contribution. However, in the complexes BeF$_3^{-1}$:nH$_2$O, both the PSO and FC terms are positive, but it is the PSO term that dominates $^{2}hJ(O-F)$ in the complexes with 1 and 2 H$_2$O molecules. When more than 2 H$_2$O molecules are present, the PSO and FC terms make similar contributions to $^{2}hJ(O-F)$, and this coupling constant is positive. For the complexes of BeF$_4^{-2}$ with one or two H$_2$O molecules, the PSO and FC term have similar magnitudes but opposite signs, so that $^{2}hJ(O-F)$ absolute values are less than 1 Hz. For the BeF$_4^{-2}$:4H$_2$O complex, the PSO term is positive and dominant, and $^{2}hJ(O-F)$ is positive with a value of 3.1 Hz. The coupling constants $^{1}J(\text{Be-O})$ and $^{2}hJ(O-O)$ are both dominated by the FC terms which are positive, and these two coupling constants are also positive.

### 3.4. $^{1}J(\text{Be-F})$

The one-bond coupling constants $^{1}J(\text{Be-F})$ in the complexes of BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ with H$_2$O are always negative since the magnetogyric ratio of $^{9}$Be is negative. For the complexes with BeF$_2$, they range from $-40$ Hz in BeF$_2$:2H$_2$O at a Be-F distance of 1.53 Å, to $-70$ Hz at a Be-F distance of 1.43 Å in BeF$_2$:1H$_2$O. The values in the complexes BeF$_3^{-1}$:nH$_2$O range from $-49$ to $-61$ Hz at Be-F distances of 1.50 and 1.46 Å, respectively, both found in the complex BeF$_3^{-1}$:2H$_2$O B. In the complexes with BeF$_4^{-2}$, $^{1}J(\text{Be-F})$ is reduced in absolute value, and ranges from $-27$ to $-37$ Hz at Be-F distances of 1.63 and 1.58 Å, respectively, in BeF$_4^{-2}$:1H$_2$O. The variation of $^{1}J(\text{Be-F})$ for BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ complexes with nH$_2$O molecules is illustrated in Figure 5 which is a plot of $^{1}J(\text{Be-F})$ versus the Be-F distance. The correlation is excellent, with a second-order trendline that has a correlation coefficient of 0.977. The significant overlap of these coupling constants for the complexes with BeF$_2$ and BeF$_3^{-1}$ is evident in this figure.

### 3.5. $^{2}hJ(O-F)$

Coupling constants $^{2}hJ(O-F)$ across the O-H···F hydrogen bonds are also given in Table 3. These coupling constants are negative in the complexes with BeF$_2$, ranging from $-11$ Hz at an O-F distance of 2.67 Å in BeF$_2$:6H$_2$O, to $-16$ Hz at an O-F distance of 2.61 Å in the BeF$_2$:4H$_2$O A complex. Complexes with BeF$_3^{-1}$ with H$_2$O have positive values of $^{2}hJ(O-F)$, and these are smaller than the absolute values of the coupling constants for the BeF$_2$ complexes. $^{2}hJ(O-F)$ ranges from 5.5–7 Hz at O-F distances of 2.83 and 2.89 Å in the complexes BeF$_3^{-1}$:2H$_2$O A and BeF$_3^{-1}$:2H$_2$O B, respectively. The complexes with BeF$_4^{-2}$ have much smaller values of $^{2}hJ(O-F)$ of $-0.7$, 0.6, and 3.1 for the complexes with 1, 2, and 4 H$_2$O molecules at O-F distances of 2.66, 2.68, and 2.74 Å, respectively. It should be noted that although these distances are shorter
Table 3. Coupling constants $^1J$(Be-F), $^2hJ$(O-F), $^1beJ$(Be-O), and $^2hJ$(O-O) (Hz) for BeFx−y:nH2O complexes.

| BeFx:nH2O   | $^1J$(Be-F) | $^2hJ$(O-F) | $^1beJ$(Be-O) | $^2hJ$(O-O) |
|-------------|-------------|-------------|--------------|-------------|
| BeF2        | −90.1       | −70.1       | 6.3          | 3.3         |
| with 1 H2O  | −70.1       | 6.3         | 3.3          | 3.3         |
| 2 H2O       | −52.9       | −15.2       | 3.3          | 6.7         |
| 3 H2O       | −51.3       | −15.2       | 5.5          | 6.7         |
| 4 H2O A     | −46.1       | −15.5       | 5.4          | 6.5         |
| 4 H2O B     | −46.4       | −13.0       | 7.1          | 5.6         |
| 6 H2O       | −39.8       | −10.9       | 3.4          | 4.9         |

| BeF3−1:nH2O | BeF3−1      | BeF3−2      | BeF4−2      |
|-------------|-------------|-------------|-------------|
| BeF3−1     | −53.1       | −51.6       | −31.7       |
| with 1 H2O | −57.9       | −55.7       | −27.2       |
| 2 H2O A   | −50.2       | −49.1       | −37.1       |
| 2 H2O B   | −61.0       | −53.9       | −32.5       |
| 3 H2O     | −51.5       | −62.0       | −31.6       |
| 4 H2O     | −57.0       | −64.0       | −32.7       |

BeF3−2:nH2O

| with 1 H2O | −57.9       | −62.0       | −31.6       |
| 2 H2O     | −31.6       | −32.7       | −31.6       |

a) Small SD terms have been estimated from the SD terms computed for other complexes in this set. See Table S3.

than the distances in the complexes with BeF3−1, $^2hJ$(O-F) values are much smaller in the complexes with BeF4−2 compared to those in the BeF3−1 complexes. Figure 6 provides a plot of $^2hJ$(O-F) versus the O-F distance for the O-H···F hydrogen bonds in these complexes. The linear trendlines have correlation coefficients greater than 0.990 for the complexes with BeF2 and BeF4−2, but only 0.595 for the BeF3−1 complexes. However, it should be noted that for this group of complexes, $^2hJ$(O-F) varies by only 1.5 Hz as the O-F distance varies by 0.129 Å. Thus, the coupling constants for the BeF3−1 complexes are almost independent of the O-F distance.

3.6. $^1beJ$(Be-O) and $^2hJ$(O-O).

There are two coupling constants that are unique to the BeF2:nH2O complexes. The first and more interesting coupling constant is $^1beJ$(Be-O) across the Be···O beryllium bond. This coupling constant ranges from 3.3 Hz at Be-O distances of 1.77 and 1.78 Å in BeF2:2H2O and BeF2:3H2O, respectively, to 7.1 Hz at a Be-O distance of 1.68 Å in BeF2:4H2O B. Thus, in these complexes $^1beJ$(Be-O) varies by less than 4 Hz as the Be-O distance varies by 0.095 Å. Figure 7 provides a plot of $^1beJ$(Be-O) versus the Be-O distance. There is a linear dependence of this coupling constant on the Be-O distance, with a correlation coefficient of 0.992.

O-H···O hydrogen bonds are also present in these complexes when three or more H2O molecules interact with BeF2. $^2hJ$(O-O) values vary between 5 and 7 Hz as the O-O distance varies between 2.69 and 2.63 Å in the

![Figure 6](image)

$^2hJ$(O-F) versus the O-F distance for complexes of BeF2, BeF3−1, and BeF4−2 with nH2O.
complexes with six and three H$_2$O molecules, respectively. These are relatively short distances for O-H⋯O hydrogen bonds. Figure S1 of the Supporting Information provides a plot of $2h_J(O-O)$ versus the O-O distance. The correlation coefficient is 0.992. It should be noted that there is also an O6-H⋯O8 hydrogen bond in the complex BeF$_3^{-1}$:5H$_2$O. This hydrogen bond has a much longer O-O distance of 2.985 Å, but no coupling constants were computed for this complex.

The intermolecular coupling constants $2h_J(O-F)$ across O-H⋯F hydrogen bonds, $2h_J(O-O)$ across O-H⋯O hydrogen bonds, and $1be_J(Be-O)$ across Be⋯O beryllium bonds exhibit a linear dependence on the corresponding intermolecular distance. The linear dependence indicates that these bonds are traditional intermolecular bonds, that is, the degree of atom sharing between the two bonded molecules is extremely small as compared to other interactions that present proton shared or transferred bonds [54–56].

4. Conclusions

Ab initio MP2/aug-cc-pVTZ calculations have been carried out to determine the structures and binding energies of complexes of BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ with n H$_2$O molecules, with n = 1–6. EOM-CCSD calculations have then been performed on these complexes to determine the spin–spin coupling constants $1J(Be-F)$ in BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ complexes, $2h_J(O-F)$ across O-H⋯F hydrogen bonds in these same complexes, and $1be_J(Be-O)$ across Be⋯O beryllium bonds and $2h_J(O-O)$ across O-H⋯O hydrogen bonds in complexes with BeF$_2$. (a) The one-bond coupling constants $1J(Be-F)$ increase as the Be-F distance decreases, and exhibit an excellent second-order correlation with that distance.

The intermolecular O-H⋯F hydrogen bonds stabilise all complexes of H$_2$O with the beryllium bases except for BeF$_2$:1H$_2$O and BeF$_2$:2H$_2$O. All of the complexes with BeF$_2$ are also stabilised by Be⋯O beryllium bonds as well as O-H⋯O hydrogen bonds in complexes with more than 2 H$_2$O molecules. These hydrogen bonds have short O-O distances.

2. Intramolecular Be-F distances increase as the number of H$_2$O molecules increases in complexes with BeF$_2$, but tend to decrease as the number of H$_2$O molecules increases in complexes with BeF$_4^{-2}$. Be-F distances exhibit little dependence on the number of H$_2$O molecules present. The smallest binding energies are found for the BeF$_3^{-1}$ complexes.

3. Intermolecular O-H⋯F hydrogen bonds stabilise all complexes of H$_2$O with the beryllium bases except for BeF$_2$:1H$_2$O and BeF$_2$:2H$_2$O. All of the complexes with BeF$_2$ are also stabilised by Be⋯O beryllium bonds as well as O-H⋯O hydrogen bonds in complexes with more than 2 H$_2$O molecules. These hydrogen bonds have short O-O distances.

4. There are four coupling constants of interest in these complexes, namely, $1J(Be-F)$ in BeF$_2$, BeF$_3^{-1}$, and BeF$_4^{-2}$ complexes, $2h_J(O-F)$ across O-H⋯F hydrogen bonds in these same complexes, and $1be_J(Be-O)$ across Be⋯O beryllium bonds and $2h_J(O-O)$ across O-H⋯O hydrogen bonds in complexes with BeF$_2$. (a) The one-bond coupling constants $1J(Be-F)$ increase as the Be-F distance decreases, and exhibit an excellent second-order correlation with that distance.
(b) Coupling constants $2hJ(O-F)$ across O-H···F hydrogen bonds exists in complexes with all of the beryllium bases with two exceptions. These coupling complexes for the bases $\text{BeF}_2$ and $\text{BeF}_4^{-2}$ exhibit an excellent linear correlation with the O-F distance. $2hJ(O-F)$ coupling constants for $\text{BeF}_3^{-1}$ are also linearly dependent on the O-F distance, but with significantly greater scatter.

(c) Coupling constants $1\text{be}J(\text{Be-O})$ across Be···O beryllium bonds and $2hJ(O-O)$ across O-H···O hydrogen are found in complexes with $\text{BeF}_2$. These coupling constants exhibit an excellent linear dependence on the Be-O and O-O distances, respectively.

5. The linear distance dependence of the intermolecular coupling constants indicates that the intermolecular bonds are traditional bonds with very little atom-shared character.

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Data availability statements

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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ORCID

Janet E. Del Bene http://orcid.org/0000-0002-9037-2822
Ibon Alkorta http://orcid.org/0000-0001-6876-6211
José Elguero http://orcid.org/0000-0002-9213-6858

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