

## **The structure and harmonic vibrational frequencies of the weakly bound complexes formed by HF with CO, CO<sub>2</sub> and N<sub>2</sub>O**

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The structure and harmonic vibrational frequencies of several weakly bound complexes formed by HF are reported. The *ab initio* MP2 approach is used with large basis sets for the optimisation of geometries and the determination of harmonic frequencies. CO···HF and OC···HF are examined; both are found to be minima, with the latter being the dominant structure. The linear OCO···HF and *T* shaped OCO···FH are studied, but only the linear structure is a minimum. N<sub>2</sub>O···HF has two minima on the surface corresponding to bent NNO···HF and linear ONN···HF structures.

**Key words:** H-bonded complexes

### **1. Introduction**

Quantum chemistry is becoming an accepted tool for the study of the structure and properties of weakly bound complexes. Here we shall examine, using an efficient and reasonably accurate theoretical method, some complexes formed with hydrogen fluoride. Our purpose is to complement the recent advances made in microwave and infrared spectroscopy. Developments in microwave spectroscopy have resulted in a long list of structural data on a variety of weakly bound complexes between small molecules containing first row atoms [1, 2]. Legon and Millen [3] have recently reviewed the microwave data for hydrogen bonded complexes. High resolution vibrational spectroscopy on the other hand is more complicated and complete spectra over a wide range of frequencies are difficult to obtain. In this work we shall demonstrate that the *ab initio* calculated shifts

with respect to the monomer frequencies provide a good starting point for the search of the infrared spectrum. We will also demonstrate that our techniques can predict structures, binding energies and intermolecular frequencies to a reasonable degree of accuracy.

When HF combines with polar molecules such as HCN or H<sub>2</sub>O, there is a substantial shift in the HF vibrational frequency—for HCN it is  $-245\text{ cm}^{-1}$  [4] and for H<sub>2</sub>O it is  $-353\text{ cm}^{-1}$  [5]. We have examined these two complexes [6] and we have shown that it is essential to include electron correlation effects if reasonable agreement is to be obtained with experiment. MP2 calculations (Møller–Plesset second order [7]) with a double-zeta plus polarisation (DZP) basis set predict shifts within  $10\text{ cm}^{-1}$  of these values, but SCF calculations are in error by  $100\text{ cm}^{-1}$ . These MP2 DZP calculations are probably fortuitously good. For these calculations the geometries of the monomers and the complex were both optimised; we believe that this is the best way for the quantum chemist to proceed, if possible.

There has been much theoretical work on hydrogen bonded complexes, starting with Coulson's analysis of the various contributions to the binding energy [8]. Morokuma [9] and Kollman [10] examined by calculation these different contributions; namely, electrostatic (and exchange), induction, and dispersion. Buckingham and Fowler [11, 12] showed that the shape of these complexes could often be deduced from a knowledge of the permanent moments of the monomers forming the complex. Dykstra and coworkers [13–15] have performed extensive calculations to quantify further and also predict shifts and changes of monomer properties on the formation of these complexes. There has also been a recent review by van Lenthe et al. [16].

Since we prefer to perform separate calculations on the monomers and the complex, it is difficult to examine the various contributions to the interaction energy along the lines of Coulson. However, we directly calculate the new bond lengths and the new frequencies on the formation of the complex, and of course these are in practice what are observed. Our MP2 method is of sufficient accuracy that our interpretations and predictions will contribute to a greater understanding of these interesting systems.

The purpose here is to study theoretically a set of complexes formed by HF with molecules such that the strength of the H bond is less than 5 kcal/mole. We have chosen CO, CO<sub>2</sub> and N<sub>2</sub>O. We shall discuss our investigations, and compare with experiment, for each system separately, giving an overall summary at the end.

## 2. Computational details

For such weakly bound complexes, it is essential to include dispersion effects as they will form an important contribution to the intermolecular interactions. These effects are introduced through electron correlation. The other effects referred to earlier will all be included by the SCF method. Undoubtedly, the simplest way to include electron correlation effects is through Møller–Plesset perturbation

theory at second order. We have available in our quantum chemistry package, CADPAC [18], the ability to calculate gradients [19] (i.e. to optimise geometries) and to evaluate analytically second derivatives [20–22], at the MP2 level, using large basis sets. Our studies on the more strongly bound complexes referred to above [6] have demonstrated that such calculations present very useful results.

The basis sets used in this study are Dunning's [23] 5s4p contraction for C, O and F for the CO/HF systems, and his 5s3p contraction for C, N, O and F for the CO<sub>2</sub>/HF and N<sub>2</sub>O/HF systems, with his 3s contraction for H. These are augmented by two sets of polarisation functions on each atom ( $d_C$ : 1.2, 0.4;  $d_N$ : 1.35, 0.45;  $d_O$ : 1.35, 0.45;  $d_F$ : 2.0, 0.67;  $p_H$ : 1.5, 0.5). Thus the basis set for each calculation has triple-zeta plus double polarisation quality (TZ2P). This leads to 96 basis functions for the CO/HF system and to 113 for the CO<sub>2</sub>/HF and N<sub>2</sub>O/HF systems.

In spite of the use of these large basis sets, it is important to include the effects of the basis set superposition error (BSSE). We have used the counterpoise method of Boys and Bernardi [34], where the error is computed by performing calculations on the monomers in the presence of the basis set for the other partner in the complex. No geometry reoptimisation was attempted with BSSE.

### 3. The H-bonded complexes between CO and HF

This system was first detected by Legon et al. [24] with microwave spectroscopy. Their results were consistent with a linear complex in the form OC · · · HF (carbon atom closer to HF), and this was later confirmed by the high quality Approximate Coupled-Cluster Doubles (ACCD) calculations of Benzel and Dykstra [25, 26]. In the infrared spectrum, the HF stretching and H-bond bending frequencies have been determined experimentally by Kyro et al. [27].

The monomer geometries were optimised at the MP2 level, and the resulting molecular properties are reported in Table 1. For HF the now expected [28] 0.001 Å agreement with experiment for  $r_e$  is achieved, and the value for the harmonic frequency is within 10 cm<sup>-1</sup> of the value deduced from experiment.

**Table 1.** Properties of the monomers calculated at the MP2/TZ2P level<sup>a</sup>

	Energy	$r_e$	$\omega_e$	$\mu_e$	$Q_e$
HF	-100.340809	0.9179	4147 <sup>b</sup>	1.884	2.46
Expt. <sup>c</sup>		0.9168	4138	1.826	2.36
CO	-113.161462	1.1365	2123	-0.260	-1.73
Expt. <sup>c</sup>		1.1283	2170	-0.122	-1.94

<sup>a</sup> Energies are in hartree, bond lengths in Å, frequencies in cm<sup>-1</sup>, dipole moments in debye and quadrupole moments calculated relative to the center of mass are in Buckingham. Positive  $\mu$  indicates a positive carbon end for CO

<sup>b</sup> 3006 cm<sup>-1</sup> for DF

<sup>c</sup> All experimental data from [9] except for  $Q_e$  for CO from [10]

The dipole and quadrupole moments are in good agreement with experiment also. For CO, the error in  $r_e$  is 0.008 Å, to be expected with this method for multiple bonds. The dipole moment has the correct sign, unlike the SCF value [29]. The harmonic frequency is in error by 2.5% or 47 cm<sup>-1</sup>.

The calculated structures, binding energies and harmonic vibrational frequencies for the complexes OC ··· HF and CO ··· HF are given in Table 2. Both complexes correspond to minima on the potential energy surface (with five frequencies less than 1 cm<sup>-1</sup>). This is in agreement with other theoretical calculations [30, 31], although only OC ··· HF has been detected experimentally.

The well depths calculated as the difference in energy between the complexes and the monomers, for OC ··· HF and CO ··· HF are 1426 cm<sup>-1</sup> and 560 cm<sup>-1</sup> respectively. These are in good agreement with the TZP/ACCD values of 1066 and 603 cm<sup>-1</sup> [30], and with the MP3/6-311++G\*\*(2d) values of 1171 and 643 cm<sup>-1</sup> [31]. We note that MP2 favours the OC ··· HF structure more strongly than the other methods probably due to the overestimation of the O<sup>+</sup>C<sup>-</sup> dipole moment. The MP2/TZ2P equilibrium well depths are reduced to 1258 cm<sup>-1</sup> and 399 cm<sup>-1</sup> when basis set superposition error is taken into account at the MP2 level. For OC ··· HF and OC ··· DF, the  $D_0$  calculated by including the zero point vibrational energy, are 642 cm<sup>-1</sup> and 760 cm<sup>-1</sup> respectively. These values may be compared with those of Legon et al. [24], who obtained 987 cm<sup>-1</sup> and 1024 cm<sup>-1</sup> by fitting experimental data to a pseudodiatom model [1]. These experimental values are between the calculated  $D_e$  and  $D_0$ , probably because the vibrational energy is only included in an average manner in the experimental fit. For the complex CO ··· HF the calculated value for  $D_0$  is negligible at 10 cm<sup>-1</sup>, whereas for CO ··· DF,  $D_0$  has a value of 89 cm<sup>-1</sup>. Although the MP2 method overestimates the CO dipole moment in favour of the OC ··· HF arrangement, it is clear from these calculations that OC ··· HF is the dominant structure. This is in agreement with the experimental interpretation. However, we suggest that

**Table 2.** Properties of the complexes calculated at the MP2/TZ2P level<sup>a</sup>

	OC ··· HF	OC ··· DF	CO ··· HF	CO ··· DF
$r_e$ (CO)	1.134		1.137	
$r_e$ (HF)	0.924		0.919	
$r_e$ (H-bond) <sup>b</sup>	2.067		2.085	
Energy	-213.508768		-213.504824	
$D_e$	1258		399	
$D_0$	642	760	10	89
$\omega$ (CO)	2150	2150	2122	2122
$\omega$ (HF)	3993	2896	4127	2991
“shear”	511	374	293	213
“stretch”	140	138	102	100
“bend”	98	96	56	55

<sup>a</sup> Energies are in hartree, bond lengths in Å, binding energies and frequencies in cm<sup>-1</sup>

<sup>b</sup> This is the C-H distance in OC ··· HF and O-H in CO ··· HF

CO $\cdots$ DF is bound, and we predict the inter- and intramolecular frequencies for this complex (see Table 2).

For OC $\cdots$ HF, the HF bond length has increased by 0.006 Å, and the frequency changed by  $-154\text{ cm}^{-1}$ . The CO frequency has changed by  $+27\text{ cm}^{-1}$ . Kyro et al. [27] report  $\Delta\nu$ , the change in the fundamental for HF, to be  $-117\text{ cm}^{-1}$  in the gas phase and Andrews et al. [32] get  $\Delta\nu$  to be  $165\text{ cm}^{-1}$  in an argon matrix. The discrepancy between our calculated value and experiment for this shift is considerably different to HCN $\cdots$ HF, where good agreement is found [6]. It may be that MP2 overestimates the shift in this case, or that anharmonic effects are more significant for OC $\cdots$ HF, or both. The CO shift of  $27\text{ cm}^{-1}$  is in very good agreement with the Ar-matrix value of  $24\text{ cm}^{-1}$  [32] and Botschwina's  $27\text{ cm}^{-1}$  [33].

From the calculated intermolecular frequencies of Table 2, only the H-bond bending and stretching frequencies for OC $\cdots$ HF can be compared with values estimated (i.e. not directly measured) from experimental data. These estimated values are  $75 \pm 12\text{ cm}^{-1}$  [27] and  $125\text{ cm}^{-1}$  [24] respectively, and compare well with the calculated  $98\text{ cm}^{-1}$  and  $140\text{ cm}^{-1}$  harmonic frequencies. The frequencies of the "shear" mode and the CO stretch have not yet been observed in the gas phase.

#### 4. The CO $_2\cdots$ HF complex

This complex is of interest because of the importance of CO $_2$  and HF in the atmosphere. Furthermore there is interest in CO $_2$  and HF lasers, and also CO $_2\cdots$ HF is used as a catalyst in several organic chemistry reactions [35].

The spectroscopic studies of Baiocchi et al. [35] and more recently by Lovejoy et al. [36] as well as by other workers [37, 38] suggests that CO $_2\cdots$ HF has a linear equilibrium geometry, although vibrational averaging will cause deviations from linearity. Nesbitt also observed a surprisingly low frequency  $\nu_6$  intermolecular CO $_2$  bend which appears to be the reason behind apparent bent geometries in upper vibrational states.

The interaction potentials between CO $_2$  and HF have been investigated repeatedly theoretically. Electrostatic models based on a distributed multipole analysis [39, 40] and distributed polarisability analysis [41] give the structure for the CO $_2\cdots$ HF complex [11, 12, 42–44] in agreement with experiment. SCF calculations using various basis sets (3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*) give the same predicted structure; that CO $_2\cdots$ HF is a linear complex [45–48].

We performed calculations at a higher level of theory than has been done previously. We also carried out a more complete search of the potential energy surface of this system, looking for any other stationary points, and we also calculated the harmonic vibrational frequencies of the complex to characterize the stationary points and to account for frequency changes upon complexation and the low CO $_2$  bending frequency in CO $_2\cdots$ HF.

In Table 3, the monomer properties of CO<sub>2</sub> and HF are reported. For CO<sub>2</sub>,  $r_e$  is calculated to be 0.009 Å longer than the experimental value; this is in line with our experience of MP2 for doubly bonded systems [22]. The accuracy of the harmonic frequencies  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  is again high, being in error by  $-50\text{ cm}^{-1}$  ( $-7.4\%$ ),  $-29\text{ cm}^{-1}$  ( $-2.1\%$ ) and  $-19\text{ cm}^{-1}$  ( $-0.8\%$ ) respectively, compared to best experimentally deduced values [49].

Two stationary points were located on the potential energy surface, corresponding to the linear OCO...HF and to the *T*-shaped OCO...FH structures shown in Fig. 1. Properties of the structures are given in Table 4. Calculation of the harmonic vibrational frequencies characterize the linear configuration as a minimum on the surface and the *T*-shaped configuration as a transition state with imaginary frequencies of  $i137\text{ cm}^{-1}$  and  $i65\text{ cm}^{-1}$  (rotational frequencies all being less than  $1\text{ cm}^{-1}$ ). Such a *T*-shaped stationary point has only been investigated once before by Reed et al. [50], in some SCF calculations, but the character of the point was not determined.

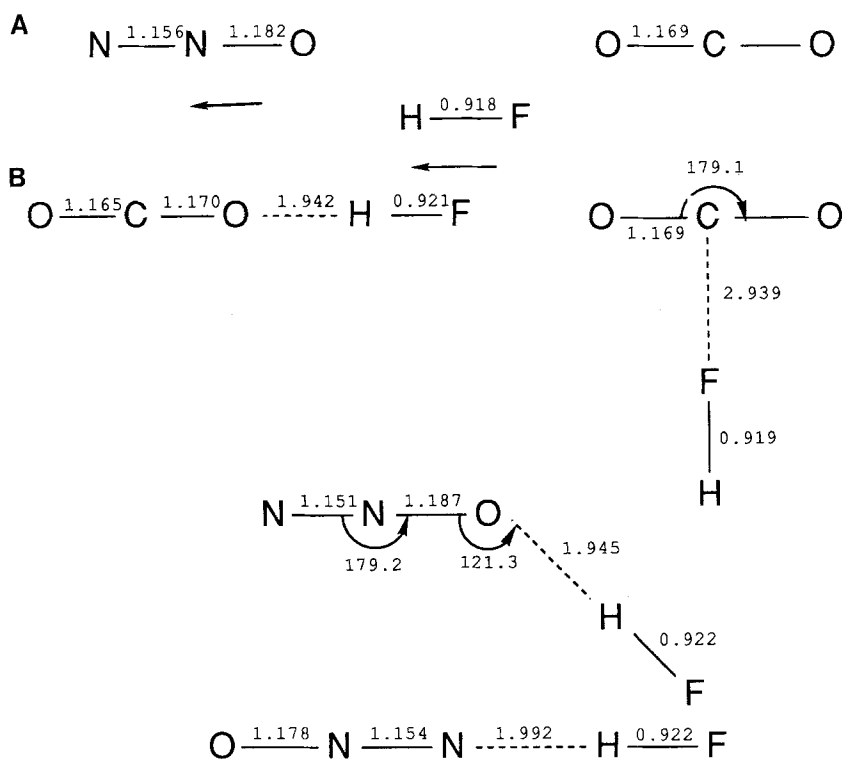
The linear minimum has a well depth  $D_e$  of  $1125\text{ cm}^{-1}$ , but this is reduced to  $847\text{ cm}^{-1}$  when the BSSE of  $278\text{ cm}^{-1}$  is deducted. The latter value is again so large that our final value of  $D_0$ ,  $392\text{ cm}^{-1}$ , could be uncertain by as much as  $300\text{ cm}^{-1}$ . A previous MP2 study with a 6-31G\* basis set [50], keeping the internal monomer geometries fixed at the SCF 6-31G\* level, gave an optimized  $R_{\text{OH}}$  value of 2.03 Å and a  $D_e$  value of 3.26 kcal/mol. Our full optimisation at the MP2/TZ2P level gave an  $R_{\text{OH}}$  of 1.942 Å and a  $D_e$  of 3.22 kcal/mol. The greater flexibility in the TZ2P basis set yields better monomer values, so we expect the same to be true for the complex. Klemperer's experiments [35] found  $R_{\text{OH}}$  to be 1.91 Å but this was obtained by arranging the complex in its linear equilibrium structure and keeping the distance between the monomer centre of masses fixed at the vibrationally averaged distance found from the experiment. Our calculation, though, is in reasonable agreement with this value. Experimentally the well depth is not known. We calculated the equilibrium dipole moment to be 2.775 D as compared to the experimentally vibrationally averaged value of 2.247 D. The equilibrium monomer geometries have not changed significantly upon complexation ( $R_{\text{HF}}$  has increased by 0.002 Å), thus demonstrating that this is a weaker complex than CO...HF, which is to be expected.

**Table 3.** Properties of HF, CO<sub>2</sub> and N<sub>2</sub>O calculated at the MP2/TZ2P level (units as for Table 1)

HF	Energy	$r_e$	$\omega_1$			
	-100.324574	0.9181	4143			
CO <sub>2</sub>	Energy	$r_e$	$\omega_1$	$\omega_2$	$\omega_3$	
	-188.304230	1.1693	623	1325	2379	
	Expt <sup>a</sup>	1.160	673	1354	2398	
N <sub>2</sub> O	Energy	$r_{\text{NN}}$	$r_{\text{NO}}$	$\omega_1$	$\omega_2$	$\omega_3$
	-184.390870	1.156	1.182	544	1282	2194
	Expt <sup>b</sup>	1.128	1.184	589	1285	2223

<sup>a</sup> [19]

<sup>b</sup> [55], nb. fundamental frequencies



**Fig. 1.** Optimized MP2/TZ2P geometries for the monomers  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{HF}$  and for the complexes  $\text{OCO} \cdots \text{HF}$ ,  $\text{OCO} \cdots \text{FH}$ ,  $\text{N}_2\text{O} \cdots \text{HF}$  and  $\text{ONN} \cdots \text{HF}$ . Also included is the monomeric dipole direction. Bond lengths in  $\text{\AA}$ , angles in degrees

Our calculations on the T-shaped structure are also summarised in Table 4. For this quadrupole-dipole interaction, the value of  $D_0$  is  $264 \text{ cm}^{-1}$ , comprising a  $D_e$  of  $423 \text{ cm}^{-1}$ , a zpe of  $64 \text{ cm}^{-1}$  and a BSSE of  $95 \text{ cm}^{-1}$ . This T-shaped structure is a much weaker “complex” than the linear structure.

Table 4 also shows our values for the calculated harmonic frequencies of the complex, and the shifts when compared to the monomers. There are available values deduced experimentally from the properties of the linear complex in an argon matrix [37, 38] although of course these are not directly comparable with the calculations, being fundamental rather than harmonic properties, but the shifts should be comparable. The argon matrix will have an effect on the experimental frequencies that we cannot quantify, however, we do not expect the shifts to be dramatically affected by this. There is good agreement for the shifts of the HF vibration at  $-47 \text{ cm}^{-1}$ ; in a gas phase study Lovejoy et al. [36] has found a HF shift of  $-57 \text{ cm}^{-1}$ . The intermolecular frequencies show the very small bending frequency referred to above, indicating a very flat surface. The shear vibration at  $394 \text{ cm}^{-1}$  is quite large, and is in reasonable agreement with the value of  $313 \text{ cm}^{-1}$  deduced from the argon matrix studies of Andrews [37, 38].

**Table 4.** Properties of the CO<sub>2</sub>···HF complex calculated at the MP2/TZ2P level compared to experimental values (Units as for Table 1)

	OCO···HF (Linear) MP2	Expt <sup>a</sup>		OCO···FH (T-shaped) MP2
$r_{\text{OH}}$	1.942	1.91	$r_{\text{CF}}$	2.939
$r_{\text{HF}}$	0.921		$r_{\text{HF}}$	0.919
$\mu$	2.667	2.247	$\mu$	2.199
$D_e$	1125		$D_e$	406
$D_0$	392		$D_0$	264
$\omega_1(\text{CO}_2)$	618(-5) <sup>b</sup>	656(-7)	$\omega_1(\text{CO}_2)$	620, 625(-3, +2)
$\omega_2(\text{CO}_2)$	1338(+13)	1383, 1275(-1, -5)	$\omega_2(\text{CO}_2)$	1327(+2)
$\omega_3(\text{CO}_2)$	2397(+18)	2354(+10)	$\omega_3(\text{CO}_2)$	2382(+3)
$\omega_1(\text{HF})$	4096(-47)	3871(-47)	$\omega_1(\text{HF})$	4136(-7)
“bend”	10		“bend”	61, 69
“stretch”	125		imaginary	i137
“shear”	394		imaginary	i65

<sup>a</sup> Experimental values from [37, 38]

<sup>b</sup> Shifts in brackets

## 5. The N<sub>2</sub>O···HF complex

The first spectroscopic study by Joyner et al. [51] characterised N<sub>2</sub>O···HF as having a bent equilibrium geometry. This was supported by Andrews and Johnson [37]. Very recently Lovejoy and Nesbitt reported direct evidence for the existence of the complex ONN···HF, the geometrical isomer of NNO···HF, and found it to have a linear structure [52]. There have been many theoretical investigations on N<sub>2</sub>O···HF, all of which examined the bent structure [11, 12, 42–44, 46]. Again our purpose is to perform calculations at a higher level of theory than has been performed previously, and in particular we shall study both possible complexes.

The properties of the N<sub>2</sub>O monomer are reported in Table 3. The  $r_{\text{NN}}$  distance is calculated to be 0.028 Å too long. The reason for this is that N<sub>2</sub>O is not well described by a single reference based method—from the MP2 calculation, the dominant coefficient in any CI expansion will be of the order of 0.89 [53]. An MP2-6-31G\* optimisation by Yamashita and Morokuma [54] gave a  $r_{\text{NN}}$  which was 0.04 Å too long. Since the wavefunction deficiency will be almost the same in the monomer and the complex, it is believed that it should not have a serious effect on these calculations. There does not appear to be any experimental deduction of harmonic frequencies in the literature, so fundamentals are given in Table 3. We note that our calculated harmonic frequencies are all below the fundamentals, therefore we would not expect the MP2 harmonic frequencies to be in agreement with experimental harmonic frequencies if they existed. This is undoubtedly a reflection of the poor geometry. However SCF and CI calculations by Rice et al. [56] give harmonic frequencies substantially above the fundamentals.



The data from our calculations are given in Table 5. Two stationary points were found on the surface corresponding to the bent  $\text{NNO} \cdots \text{HF}$  structure and the linear  $\text{ONN} \cdots \text{HF}$  structure, as seen in Fig. 1. On calculation of the harmonic frequencies both these stationary points are characterised as minima. We believe this is the first theoretical observation of the second minimum on the surface. The linear structures for  $\text{CO}_2 \cdots \text{HF}$  and  $\text{ONN} \cdots \text{HF}$  could be considered unusual as it may be thought that the oxygen (or nitrogen for  $\text{ONN} \cdots \text{HF}$ ) lone pair-hydrogen interaction would give rise to bent structures as for  $\text{N}_2\text{O} \cdots \text{HF}$ . This interaction is obviously not the dominant contribution to the total intermolecular potential for the linear systems.

The bent structure was calculated to have a  $D_0$  of  $235 \text{ cm}^{-1}$  comprising a  $D_e$  of  $927 \text{ cm}^{-1}$ , a zpe of  $442 \text{ cm}^{-1}$  and a BSSE of  $250 \text{ cm}^{-1}$ . The linear structure was calculated to have a  $D_0$  of  $555 \text{ cm}^{-1}$  ( $D_e = 1282 \text{ cm}^{-1}$ , zpe =  $492 \text{ cm}^{-1}$ , BSSE =  $235 \text{ cm}^{-1}$ ), and thus we predict the linear structure to be more stable than the bent structure by  $320 \text{ cm}^{-1}$ . We must beware of the large BSSE which makes this prediction uncertain. It is perhaps surprising when one realises that the monomer dipoles are opposed in the linear structure. Using the pseudodiatomic approximation [1], Lovejoy and Nesbitt [52] suggested an experimental binding energy for the linear structure of  $260 \text{ cm}^{-1}$ , rather smaller than our value.

Previous theoretical calculations have been performed on the bent  $\text{NNO} \cdots \text{HF}$  structure, at the 6-31G\* SCF level [46], which predict an equilibrium bond length,  $r_{\text{OH}}$ , of  $1.95 \text{ \AA}$  and an NOH angle of  $116.3^\circ$ , these results being fortuitously close to experiment. The experimental  $r_{\text{OH}}$  of  $1.94 \text{ \AA}$  and NOH angle of  $116^\circ$  [51] are probably in considerable error as they are predicted by defining an equilibrium structure which is planar but keeping the  $r_{\text{cm}}$  (distance between monomeric centre of masses) fixed at the distance found for the vibrationally averaged structure

**Table 5.** Properties of  $\text{N}_2\text{O} \cdots \text{HF}$  calculated at the MP2/TZ2P level, and comparison with experiment

	Calculated		Experimental <sup>a</sup>		Calculated	
	NNO $\cdots$ HF	Shifts	NNO $\cdots$ HF	Shifts	ONN $\cdots$ HF	Shifts
$r_{\text{H-bond}}^b$	1.945				1.992	
$r_{\text{HF}}$	0.922				0.922	
$\mu$	2.906				2.274	
$D_e$	927				1282	
$D_0$	235				555	
$\omega_1(\text{N}_2\text{O})$	542, 560	-12, +6	583	-5	546	-8
$\omega_2(\text{N}_2\text{O})$	1282	0	1307	+24	1304	+49
$\omega_3(\text{N}_2\text{O})$	2175	-19	2250	+29	2240	+46
$\omega_1(\text{HF})$	4058	-85	3851	-68	4056	-87
“bend”	33				26	
“stretch”	140				126	
“shear”	391, 430		325, 328		420	

<sup>a</sup> Experimental frequencies of  $\text{NNO} \cdots \text{HF}$  in an Ar matrix from [37]

<sup>b</sup> This is the O-H distance in  $\text{N}_2\text{O} \cdots \text{HF}$  and the N-H distance in  $\text{ONN} \cdots \text{HF}$

(which is non planar). Our calculated  $r_{\text{OH}}$  of 1.945 Å is in good agreement with experiment but our NOH angle of 121.3° is considerably different. As can be seen in Fig. 1, the intermolecular bond lengths are changed a little upon complexation, the HF bond in both complexes being increased by 0.004 Å.

Table 5 shows the calculated harmonic frequencies of the  $\text{NNO} \cdots \text{HF}$  complex and the experimental fundamental frequencies in an Ar matrix [37]. These are not directly comparable though we can again look at the frequency shifts upon complexation. We see that the shifts are in reasonable agreement although there is a scatter but this could partly be due to the effect of the matrix rather than the interaction between the two molecules. The HF stretch in the complex is calculated to be  $4058 \text{ cm}^{-1}$ , red shifted  $85 \text{ cm}^{-1}$  from the calculated HF monomer frequency as compared to an experimental red shift of  $68 \text{ cm}^{-1}$ . The other intramolecular frequency shifts upon complexation are all small, less than  $20 \text{ cm}^{-1}$  which once again emphasises the weakly bound nature of the system. The intermolecular shear splits in the complex, experimentally by  $3.4 \text{ cm}^{-1}$  and theoretically by  $39 \text{ cm}^{-1}$  and it was this splitting that led experimentalists to believe the structure was bent.

In the case of the linear  $\text{ONN} \cdots \text{HF}$  isomer we calculate a hydrogen bond length of 1.992 Å and a centre of mass separation of 4.076 Å. From an analysis of their experimental near infra-red spectrum Lovejoy and Nesbitt predict an  $r_{\text{cm}}$  of 4.143 Å using the pseudodiatomic approximation.

Very recently Kukolich et al. [57] have reported microwave studies on the linear structure, and compared it to the bent structure. Kukolich et al. predict an  $r_{\text{cm}}$  of 4.457 Å. More interesting is the fact they they predict a well depth of  $1031 \text{ cm}^{-1}$  for the linear structure (using the pseudodiatomic approximation), and only a depth of  $101 \text{ cm}^{-1}$  for the bent structure. It is encouraging that these studies agree with our prediction that the linear structure is more stable. However, there is great disparity between the two experimentally deduced values for the well depth of  $\text{ONN} \cdots \text{HF}$ .

The harmonic frequencies for the linear complex are given in Table 5. The HF stretching frequency is red shifted by  $87 \text{ cm}^{-1}$  upon complexation and thus can be compared with the red shift of  $61 \text{ cm}^{-1}$  observed by Lovejoy and Nesbitt [52]. The intermolecular frequencies have a maximum value of  $420 \text{ cm}^{-1}$  for the shear and a smallest value of  $26 \text{ cm}^{-1}$  for the degenerate intermolecular NNO bend. We predict a value of  $126 \text{ cm}^{-1}$  for the intermolecular stretch as compared to the value of  $96 \text{ cm}^{-1}$  predicted by Kukolich et al. [57].

## 6. Conclusion

In this paper we have examined several complexes formed with HF, by the *ab initio* MP2 method using a TZ2P quality basis set. It may be of interest to gather in a table the calculated values for some significant properties of the complexes, and therefore in Table 6 we report (i) changes in the HF bond length on formation of the complex (ii) changes in the HF frequency (iii)  $D_e$  (iv) the basis set

**Table 6.** Some properties of hydrogen-bonded complexes formed with HF, calculated at the MP2/TZ2P level

Monomer	$\Delta r_{\text{HF}}/\text{\AA}$	$\Delta\omega_{\text{HF}}/\text{cm}^{-1}$	$D_e/\text{cm}^{-1}$	BSSE/ $\text{cm}^{-1}$	$D_0/\text{cm}^{-1}$
H <sub>2</sub> O <sup>a</sup>	+0.018	-363	3455	557	1916
CO	+0.001	-20	560	162	10
OC	+0.006	-154	1426	168	642
CO <sub>2</sub> (linear)	+0.003	-47	1125	278	392
N <sub>2</sub> O (bent)	+0.004	-85	927	250	235
ON <sub>2</sub> (linear)	+0.004	-87	1282	235	555

<sup>a</sup> H<sub>2</sub>O ··· HF values from [6]

superposition error (v)  $D_0$ , calculated from (iii), (iv) and the calculated zero point vibrational energy. Note that  $D_e$  in this discussion refers to the uncorrected dissociation energy.

Whilst we cannot rely on the absolute values for  $D_0$  because of the deficiencies of both the basis set and the MP2 method, we can expect the trends in the table to be indicative of the relative properties of the complexes. We are not surprised to observe the greater the change in  $r_{\text{HF}}$ , the greater the frequency shift and the greater the bond strength. The H<sub>2</sub>O interaction is probably dominated by the dipole-dipole interaction, but for the other complexes the quadrupole-dipole interaction becomes of greater importance.

Dykstra and co-workers [13-15, 25, 26, 30] have performed valuable studies on hydrogen bonded complexes in recent years. In particular they have studied many HF complexes e.g. HF ··· HF, NN ··· HF, OC ··· HF, HCCH ··· HF and HCN ··· HF. Their earlier studies, using very accurate *ab initio* methods (SCEP or ACCD) analysed the different factors contributing to the strength of the hydrogen bond. For example, for OC ··· HF they showed that electrostatic plus exchange, induction and correlation effects each contribute about 300  $\text{cm}^{-1}$ . For the much stronger HCN ··· HF the three effects were 1602, 620 and 175  $\text{cm}^{-1}$ . These studies underline the importance of including all effects in calculations on these complexes. Dykstra et al. appear to be at a disadvantage because they do not have available automatic geometry optimisation and frequency determination with their advanced correlated wavefunction methods. On the other hand they have carefully studied the effects of basis set superposition error, and conclude, as we must, that it has to be included, and that if it is large, then the calculations must be viewed with caution [13]. This is also supported by the careful study of BSSE effects on the HF dimer by Schwenke and Truhlar [61]. Following on from their earlier work Liu and Dykstra [15] have recently presented a combined experimental-theoretical treatment of vibrational transition frequency shifts, and applied it to HF complexes. They assume the interaction potential is linear, choosing the slope to be such that the resulting potential for HF gives the correct change in the fundamental HF frequency, using an accurate HF monomer potential. With this interaction, they are then able to predict the change in the

HF bond length on complexation. For  $\text{OC} \cdots \text{HF}$ , this predicts a change of  $0.008 \text{ \AA}$ , to be compared with our *ab initio* value of  $0.006 \text{ \AA}$ .

Our contribution to these general studies is that we are able, at not a great cost, to use a reasonable correlated method (MP2), albeit not quite of the standard of coupled cluster methods (CC), to optimise the geometries and determine the frequencies of these complexes. Dykstra et al. show that in the complex the proton donor molecule has to change geometry significantly, and therefore, if one can, we believe it is important to report studies which automatically include this.

It is very expensive for the quantum chemist to predict the quantities in Table 6 with greater accuracy at this time, as this would involve complete geometry optimisation and calculation of vibrational frequencies at a higher than MP2 level of theory, with larger basis sets. On application of the MP2 method to the more weakly bound complexes, significant errors are possible in  $D_e$  and  $D_0$ , although this is no worse than the experimental situation for the linear structure  $\text{ONN} \cdots \text{HF}$ . In some cases, the MP2 method may not be completely reliable; a recent study with the more accurate CPF method [58] on  $\text{H}_2\text{CO} \cdots \text{HCl}$  [59] suggests that MP2 values, for a given basis set, may be predicting shifts in the hydrogen donor molecule bond lengths which are too large, resulting in too large shifts for the frequencies. The well depths may be too deep as a consequence. For the cases where the errors are significant, the more accurate CPF, ACCD or CCSD methods can be used, however these are computationally more expensive than the MP2 method. The problem of the basis set size must also be addressed; this can be measured by the basis set superposition error, which we have seen has a significant effect on binding energies. The BSSE may be reduced by employing a larger basis set, with diffuse functions being important. Such calculations will be substantial. We must finally add that the experimentalist is interested in fundamental, not harmonic, frequencies and also note that there will be an anharmonic contribution to  $D_0 - D_e$ , which may be significant for large amplitude, low frequency modes. This means that the *ab initio* quantum chemist must also tackle the problem of anharmonic effects, because they must be significant for some of the vibrational modes [60]. In a previous paper [6] we examined the anharmonic effects in  $\text{HCN} \cdots \text{HF}$ , but our conclusions were that it was far from clear how best to treat them.

However, after taking into account this discussion, we believe that there are interesting conclusions to be drawn from the comparison of our MP2/TZ2P results with available experimental and theoretical data for all three complexes. Firstly, it can be argued that the predicted structures are valid, and that the numbers presented in Table 6 are of the correct order of magnitude for binding energies and better for the other quantities. We also observe that all the predicted HF harmonic frequency shifts are accurate to within  $40 \text{ cm}^{-1}$  of observed shifts in fundamental frequencies. As is well known, this quantity can vary significantly depending on the acceptor molecule, and therefore such a prediction is valuable. Thus, although the MP2 method is of course not the most reliable of the correlated methods for the calculation of binding energies, its efficiency and the availability

of analytic gradients and second derivatives makes the prediction of structures and all vibrational frequencies feasible, even for complexes with many degrees of freedom.

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