

## ***Ab initio* calculation for properties of hydrogen bonded complexes $\text{H}_3\text{N}\cdots\text{HCN}$ , $\text{HCN}\cdots\text{HCN}$ , $\text{HCN}\cdots\text{HF}$ , $\text{H}_2\text{O}\cdots\text{HF}$**

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Self Consistent Field calculations, using TZ+2P basis sets, are reported on four hydrogen-bonded complexes. Vibrational frequencies, rotational constants, infrared and raman intensities are compared with available experimental data. The basis set superposition error is shown not to be important for the calculation of these properties with this basis set.

**Key words:** Hydrogen — Bonded complexes

### **1. Introduction**

Stimulated by many recent experimental studies, calculations on hydrogen bonded complexes are being reported in the literature. These complexes are a fertile ground for *ab initio* calculation, because Self Consistent Field (SCF) calculations appear reliable enough for some of the properties of interest, such as geometries and frequencies. Furthermore the size of system is such that good basis sets can be used. Most calculations report values for geometries and binding energies of these complexes. Here we extend to the calculation of vibrational properties. As we were completing this work, Frisch et al. [1] reported geometries and frequencies for the dimers  $(\text{AH}_n)_2$  of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$  and  $\text{HCl}$ , at the SCF level of accuracy. Our work nicely complements this, because three of our systems involve different monomers.

We stress the importance of using good basis sets; earlier studies [2, 3] on  $\text{H}_3\text{N}\cdots\text{HCl}$ ,  $\text{H}_2\text{O}\cdots\text{HF}$  showed that although small basis sets give quite reasonable

properties (such as frequency shifts), geometries are often poor unless polarisation functions are included. For example a calculation on  $\text{H}_3\text{N}\cdots\text{HCl}$  with a 4-31G basis gave an ionic structure, whereas the 6-31G\* basis gave the correct hydrogen bonded structure [2].

Most of the experimental information on hydrogen-bonded complexes has come from matrix isolation studies. The matrix environment causes a perturbation on the vibrational motion which is often as large as the effect of hydrogen bond [4, 5]. For example, for  $\text{HF}\cdots\text{HF}$ , matrix isolation studies [4] show frequency shifts which differ by  $25\text{--}35\text{ cm}^{-1}$  from the corresponding gas phase values.

Lack of inclusion of anharmonic effects as well as correlation effects in SCF derivative studies means that frequencies disagree with gas phase experimental values. However these discrepancies are present in both monomer and dimers and it appears that the calculated SCF frequency shifts [6] often agree well with experimental values. A detailed examination of the correlation effects may be found in the paper by Gaw et al. [7] on  $\text{HF}\cdots\text{HF}$ .

In this paper we present rotational constants, frequencies and frequency shifts, infrared and raman intensities, for the dimers  $\text{H}_3\text{N}\cdots\text{HCN}$ ,  $\text{HCN}\cdots\text{HCN}$ ,  $\text{HCN}\cdots\text{HF}$ , and  $\text{H}_2\text{O}\cdots\text{HF}$ . They will be compared to experimental work where available. In Sect. 2, the calculation details are discussed, in Sect. 3 the monomer properties are given and in Sect. 4 the dimer properties are analysed.

## 2. Method

The potential minima for the monomers and dimers were calculated at the SCF level of accuracy, using the standard analytic derivative method implemented in the Cambridge Analytic Derivative Package (CADPAC) [8]. Two basis sets were used (i) the Dunning double-zeta (4s, 2p/2s) [9] plus polarisation d function on C, N, O, F with exponents 0.8, 0.8, 0.8, 1.2, respectively, and p functions on H with exponent 1.0 (ii) the extended basis (5s, 3p/3s) [9] plus two sets of polarisation functions with exponents for C(1.2, 0.4), N(1.5, 0.5), O(1.5, 0.5), F(1.6, 0.5333) and H(1.5, 0.5). We call this extended basis set a TZ+2P basis. The frequencies were calculated from the analytic second derivatives; the infrared intensities are obtained by calculating the dipole moment derivatives as explained in [10]; the raman intensities are obtained by calculating the polarisability derivatives as explained in [11]. Formal expressions for the integrated absorption coefficient  $A_i$  and the raman scattering factor  $S_i$  are,

$$A_i = (4\pi\epsilon_0)^{-1} \left( \frac{N_A\pi}{3c^2} \right) d_i \left( \frac{\partial\mu}{\partial Q_i} \right)^2$$

$$S_i = d_i \left( 45 \left( \frac{\partial\alpha}{\partial Q_i} \right)^2 + 7 \left( \frac{\partial\gamma}{\partial Q_i} \right)^2 \right)$$

where  $\alpha$  and  $\gamma$  are isotropic and anisotropic polarisabilities respectively.

### 3. Monomer properties

In Table 1, the geometric properties of the monomers  $\text{NH}_3$ ,  $\text{HCN}$ ,  $\text{HF}$  and  $\text{H}_2\text{O}$  are reported. They are compared with the recent near Hartree-Fock values for  $\text{NH}_3$  and  $\text{H}_2\text{O}$  of Amos [12], and experimental values [13-16]. This shows the present values are very close to the Hartree-Fock limit; bond lengths are within  $10^{-3}$  Å and bond angles are within  $0.5^\circ$  of the values of Amos.

In Table 2, the frequencies and infrared and raman intensities are reported, and again compared with experiment [16-23]. It is recalled that the *ab initio* calculates harmonic frequencies and experimental values for these are given. Except the umbrella frequency mode of  $\text{NH}_3$ , all the other modes are within  $15\text{ cm}^{-1}$  of those obtained with very large basis set calculations. This indicates the basis sets used in these calculations are large enough to calculate the properties at the SCF level. Note that  $\text{HCN}$  is particularly difficult molecule for the calculation of dipole moment derivatives; see for example the variety of results from correlated wavefunction calculation in [24].

The effect of basis set superposition error (BSSE) has been considered during the course of the calculations. Using the DZP basis, the geometry of  $\text{NH}_3$  was optimised in the presence of the  $\text{HCN}$  basis and the  $\text{HCN}$  geometry was optimised in the presence of the  $\text{NH}_3$  basis (the N-H was held fixed). The resulting monomer geometries showed a maximum bond length change of  $10^{-5}$  Å, and the frequencies changed by less than  $1\text{ cm}^{-1}$ . The total energies changed by  $50\text{ cm}^{-1}$  for  $\text{HCN}$  and  $180\text{ cm}^{-1}$  for  $\text{NH}_3$ . This strongly indicates that the BSSE is insignificant in the calculation of properties reported in this paper; any such effects will be even smaller for larger basis sets.

### 4. The properties of the four dimers

#### a. $\text{H}_3\text{N}\cdots\text{HCN}$

The only *ab initio* study known to us is by Kollman et al.<sup>25</sup> who performed a partial optimisation using a 4-31G basis set. We have carried out a complete

**Table 1.** Equilibrium geometries<sup>a</sup> of monomers, compared with near Hartree-Fock and experimental values

		DZ+P	TZ+2P	Hartree-Fock <sup>12</sup>	Expt <sup>b</sup>
$\text{NH}_3$	$R_{\text{N-H}}$	1.001	0.999	0.998	1.012
	HNH	108.2	107.5	108.1	106.7
$\text{H}_2\text{O}$	$R_{\text{O-H}}$	0.944	0.941	0.940	0.958
	HOH	106.6	106.0	106.3	104.5
$\text{HCN}$	$R_{\text{C-H}}$	1.062	1.057		1.066
	$R_{\text{C-N}}$	1.136	1.124		1.153
$\text{HF}$	$R_{\text{H-F}}$	0.901	0.899		0.917

<sup>a</sup> Bond lengths in Å and bond angles in degrees. <sup>b</sup>  $\text{NH}_3$  data from [13];  $\text{H}_2\text{O}$  data from [14];  $\text{HCN}$  data from [15];  $\text{HF}$  data from [16].

**Table 2.** Harmonic frequencies, i.r. and raman intensities; theory vs experiment for the monomers

	Mode	DZP	Frequencies (cm <sup>-1</sup> )		Expt <sup>a</sup>
			TZ+2P	Hartree-Fock <sup>12</sup>	
NH <sub>3</sub>	$\nu_2$	1114	1135	1099	1022
	$\nu_4$	1803	1800	1787	1691
	$\nu_1$	3725	3689	3690	3506
	$\nu_3$	3872	3811	3815	3577
H <sub>2</sub> O	$\nu_1$	4166	4128	4130	3832
	$\nu_2$	1752	1760	1747	1648
	$\nu_3$	4289	4228	4231	3942
HCN	$\nu_2$	861	869		727
	$\nu_3$	2406	2408		2129
	$\nu_1$	3638	3600		3442
HF	$\nu_1$	4511	4471		4138

<sup>a</sup> NH<sub>3</sub> data from [17]; H<sub>2</sub>O data from [18]; HCN data from [19]; HF data from [16]

Intensities <sup>a</sup>					
Mode	Infrared		Raman		
	TZ+2P	Expt <sup>b</sup>	TZ+2P	Expt <sup>c</sup>	
NH <sub>3</sub>	$\nu_2$	195.4	145.2±7.3	5.4	
	$\nu_4$	38.8	15.6	14.8	
	$\nu_1$	0.01	4.9	108.6	
	$\nu_3$	5.8	3.2	82.0	
H <sub>2</sub> O	$\nu_1$	14.4	2.2	70.2	108±14
	$\nu_2$	92.1	53.6	4.1	0.9±0.2
	$\nu_3$	69.7	44.6	28.5	19.2±2.1
HCN	$\nu_2$	66.2	50.2	1.8	
	$\nu_3$	9.7	0.2	48.3	
	$\nu_1$	76.0	59.3	14.1	
HF	$\nu_1$	147.3		25.6	

<sup>a</sup> i.r. intensities in km/mole, raman intensities in A<sup>4</sup>/amu

<sup>b</sup> NH<sub>3</sub> datas from [20]; H<sub>2</sub>O datas from [21]; HCN datas from [22]

<sup>c</sup> [23]

optimisation using our basis sets (TZ+2P has 114 basis functions). The structure is shown in the figure.

The rotational constants ( $h/8\pi^2Ic$ ) for this symmetric top structure are calculated to be (0.1003, 6.39) and (0.098, 6.45) cm<sup>-1</sup>, at the DZP and TZ+2P levels. The experimental microwave value from the work of Klemperer's group [26] is 0.101 cm<sup>-1</sup>. It is better to compare the calculated rotational constant directly with the latter value, rather than geometries as the experimental structure is deduced from the rotational constants assuming the monomer geometries do not change. For a strongly bound dimer there is a significant change in the monomer geometries, especially in the proton donor bond length (cf. H-C for dimer 1.068 Å, for

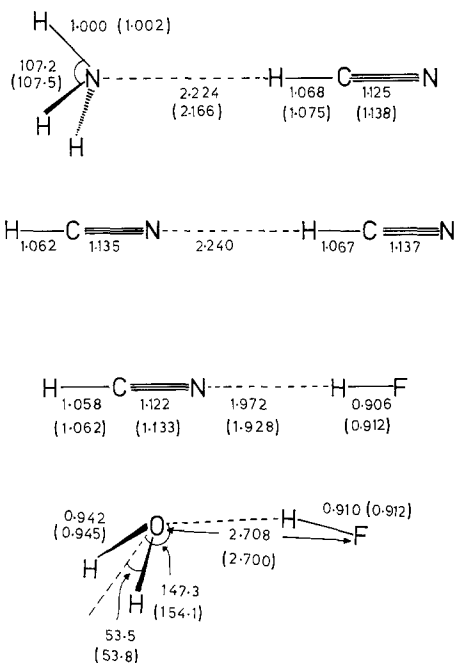


Fig. 1. The structure of the dimers, calculated with TZ+2P basis (DZP values in brackets)

monomer 1.057 Å). However Klemperer [26] reports an N...H distance of 2.156 Å, in comparison to our calculated value of 2.224 Å.

The frequencies and frequency shifts of the intramolecular modes, and the new intermolecular modes are given in Table 3, with the experimental data where available. In Table 3(b) similar results are presented for D<sub>3</sub>N...DCN.

In Table 4 the infrared and raman intensities are reported, calculated at the TZ+2P level of accuracy. The changes in the intensities when compared with the monomer are also reported.

The perpendicular bands for the NH<sub>3</sub> part of the dimer are not detected experimentally, because it is seen that these modes are not affected by the hydrogen bonding, and will overlap the monomer bands.

It is to be noted that the experimental frequency shifts refer to fundamentals, whereas the calculations are for harmonics. The calculated values are likely therefore to be too large by 10%. The frequency shifts are in reasonable agreement with experiment. In particular the red shifted CH agrees very well with the experimental value (obtained from an infrared spectrum) of Jones et al. [27]. The CN shift is a problem; although the experimentalists (gasphase [27]) appear to notice the presence of a new feature on the formation of the monomer, it is difficult for us to resolve the 10 cm<sup>-1</sup> discrepancy between the calculation and experiment. It seems unlikely that a larger basis set will have a significant effect. On the other hand the umbrella frequency  $\nu_2$  of NH<sub>3</sub> is always very difficult to calculate accurately: the shift is very sensitive to geometry. There is one reported

**Table 3.** Frequencies and frequency shifts<sup>a</sup> for the intramolecular modes, and the new intermolecular modes

(a) H <sub>3</sub> N...HCN			
Mode	DZP	TZ+2P	Exptl shift
$\nu_2$ (HCN)	1014 (+153)	1000 (+131)	
$\nu_3$ (HCN)	2377 (-29)	2382 (-26)	-11 [27]
$\nu_1$ (HCN)	3449 (-189)	3439 (-162)	-162 [27], -201 <sup>b</sup>
$\nu_2$ (NH <sub>3</sub> )	1207 (+93)	1203 (+68)	+90 [27]
$\nu_4$ (NH <sub>3</sub> )	1803 (0)	1799 (1)	
$\nu_1$ (NH <sub>3</sub> )	3716 (-9)	3682 (-7)	
$\nu_3$ (NH <sub>3</sub> )	3855 (-18)	3799 (-12)	
"Bend"	120	113	
"Stretch"	160	146	141 ± 3 [26]
"Shear"	323	302	

(b) D<sub>3</sub>N...DCN

Mode	DZ+P	TZ+2P	Expt [27]
$\nu_2$ (DCN)	782 (+95)	776 (+82)	
$\nu_3$ (DCN)	2083 (-78)	2083 (-68)	-35
$\nu_1$ (DCN)	2837 (-82)	2834 (-69)	-69
$\nu_2$ (ND <sub>3</sub> )	917 (+70)	914 (+51)	
$\nu_4$ (ND <sub>3</sub> )	1309 (0)	1305 (-2)	
$\nu_1$ (ND <sub>3</sub> )	2655 (-4)	2631 (-3)	
$\nu_3$ (ND <sub>3</sub> )	2838 (-14)	2796 (-9)	
"Bend"	101	95	
"Stretch"	151	138	
"Shear"	257	239	

<sup>a</sup> Shift from monomer values are given in parenthesis<sup>b</sup> G. Yarwood and I. W. M. Smith inform us that they observe the dimer C-H frequency at  $\approx 3110 \text{ cm}^{-1}$  (FTIR)**Table 4.** The infrared and raman intensities for H<sub>3</sub>N...HCN and D<sub>3</sub>N...DCN<sup>a</sup>

Mode	H <sub>3</sub> N...HCN		D <sub>3</sub> N...DCN	
	i.r.	Raman	i.r.	Raman
$\nu_2$ (donor)	82 (1.2)	4 (1.76)	24	4
$\nu_3$ (donor)	71 (7.3)	81 (8.3)	139	81
$\nu_1$ (donor)	358 (4.7)	55 (0.7)	80	1
$\nu_2$ (acceptor)	195 (1)	1 (0.2)	118	1
$\nu_4$ (acceptor)	44 (1.1)	14 (0.9)	26	6
$\nu_1$ (acceptor)	1 (-)	103 (0.9)	3	53
$\nu_3$ (acceptor)	20 (3.4)	86 (1.0)	16	46
"Bend"	4	10	2	8
"Stretch"	2	0	2	0
"Shear"	158	0	100	0

<sup>a</sup> The ratio for the complex to the monomer are given in parenthesis

**Table 5.** Frequencies and frequency shifts<sup>a</sup> for the intramolecular modes, and the new intermolecular modes for HCN...HCN and DCN...DCN

Mode	HCN...HCN		DCN...DCN	
	DZ+P	Exptl shift [34]	DZ+P	Exptl shift [34]
$\nu_2$ (donor)	937 (+76)		735 (+47)	
$\nu_3$ (donor)	2395 (-11)	-2.1	2132 (-29)	-24.9
$\nu_1$ (donor)	3569 (-69)	-65	2887 (-32)	-29.5
$\nu_2$ (acceptor)	874 (+13)		699 (+11)	
$\nu_3$ (acceptor)	2422 (+16)	+7.8	2169 (+8)	-1.2
$\nu_1$ (acceptor)	3636 (-2)	+10.8 <sup>b</sup>	2925 (+6)	+21.2 <sup>b</sup>
"Bend"	60		55	
"Stretch"	122	119	119	
"Shear"	159		146	

<sup>a</sup> Shift from monomer values are given in parenthesis

<sup>b</sup> Not observed, deduced from other experimental values

value of the intermolecular stretching frequency, which is in good agreement with the calculated value. This may be fortuitous, because it may well be that the intermolecular vibrations are very anharmonic; if this is the case analytic second derivative calculations may be very unreliable.

Although the basis set used here is not large enough for dipole derivative calculations, in comparison to other errors such as the use of SCF wavefunctions and the double harmonic approximation, the basis set limitation may not be a severe problem. We have in mind the fact that some of the intermolecular modes may be influenced by anharmonicity; that there are molecules for which SCF calculations give poor dipole moment derivatives whatever the basis set size. However we do believe that the basis sets used here are sufficient to indicate trends and orders of magnitude. As can be seen from Table 4, the i.r. intensity enhancement is in the proton donor stretching modes. The ratio of the intensity of the CH stretching vibration in the complex to the monomer is 4.7, and for the CN stretching vibration, it is 7.3, although this large enhancement may be an artefact of the calculation, because it is well known that at the SCF level the dipole moment derivatives of HCN have the wrong sign [28]. We also note the considerable i.r. intensity of the shear intermolecular vibration.

### (b) HCN...HCN

The optimised geometry of this linear structure is shown in the figure. Earlier studies on this molecule optimised only the hydrogen bond length with a small basis set [25, 29]. The experiments [30-33] also support the linear structure for this dimer. Our value for the rotational constant  $0.0584 \text{ cm}^{-1}$  agrees with the experimental value of  $0.0582 \text{ cm}^{-1}$  of Brown et al [30].

Although the binding energies calculated with this basis at the SCF level are likely to be unreliable, it is to be noted that the binding energy of HCN...HCN is calculated to be 5 kcal/mol compared to 7 kcal/mol for  $\text{H}_3\text{N}\cdots\text{HCN}$ , at the DZP level. When it is also noticed that the hydrogen bond length is greater for

HCN...HCN, it is reasonable to conclude that the hydrogen bond is stronger for  $\text{H}_3\text{N}\cdots\text{HCN}$  than it is for HCN...HCN, i.e.  $\text{NH}_3$  is a better electron donor than HCN.

The intra and intermolecular frequencies and frequency shifts are reported in Table 5, and they are compared with the recent gas phase experiments of Maroncelli et al. [34]. The frequency shifts are in good agreement, especially for the large CH shift. The smaller shifts, differ by  $\approx 10\text{ cm}^{-1}$ ; this could be due either to basis set inadequacy or experimental uncertainty because the dimer bands will lie close to the monomer bands.

For this dimer only the i.r. intensities are calculated and these are shown in Table 6 together with the intensity ratios reported by Maroncelli et al. The latter will not be accurate because they were calculated on the assumption that the C-H and C-N bond derivatives in the dimer were unchanged from the monomer values. Our calculations show that this enhancement is almost all due to the change in the derivatives, the normal modes being nearly unaltered. The same effect was noticed in earlier calculations on  $(\text{H}_2\text{O})_2$  [6]. The calculated intensities show that the intensity of the proton donor molecule modes are enhanced compared to the electron donor molecule modes. This is expected because the dipole moment changes more in the proton donor than in the electron donor.

### c. HCN...HF

This is a much studied dimer both theoretically [35–38] as well as experimentally [39–42]. In the previous study by Curtiss and Pople [36], an *ab initio* calculation on properties such as equilibrium geometry, frequency shifts and infrared intensities is reported, but using a small basis set (4-31G). Although some other theoretical studies have been reported with a larger basis set, for example, Benzel and Dykstra [35] used a TZP basis set, and Bouteiller et al. [37] used 6-31G and (10s, 6p) basis sets, they only did a partial optimization by fixing the monomer geometry at the experimental geometry and calculated only one or two frequencies. Here we will report our fully optimized structure with the DZP and TZ+2P

**Table 6.** The infrared intensities for HCN...HCN and DCN...DCN<sup>a</sup>

Mode	HCN...HCN		DCN...DCN	
	DZ+P	Expt [34]	DZ+P	Expt [34]
$\nu_2$ (donor)	84 (1.3)		24 (1.4)	
$\nu_3$ (donor)	47 (4.8)	(2)	97 (4.2)	(0.8)
$\nu_1$ (donor)	311 (4.1)	(1.02)	72 (3.3)	(1.04)
$\nu_2$ (acceptor)	76 (1.1)		22 (1.3)	
$\nu_3$ (acceptor)	39 (4.0)	(3)	60 (2.6)	(1.6)
$\nu_1$ (acceptor)	65 (0.8)	(0.98)	10 (0.4)	(0.94)
"Bend"	10		6	
"Stretch"	2		2	
"Shear"	122		104	

<sup>a</sup> The ratio for the complex to the monomer are given in parenthesis



**Table 7.** Frequencies and frequency shifts<sup>a</sup> for the intramolecular modes and the new intermolecular modes

(a) HCN...HF				
Mode	DZ+P	TZ+2P	Expt [41]	Calculated [36]
$\nu_2$ (HCN)	878 (+17)	881 (+12)		(+26)
$\nu_3$ (HCN)	2437 (+31)	2427 (+19)	+24 [40]	(+12)
$\nu_1$ (HCN)	3638 (0)	3593 (-7)		(-13)
$\nu_1$ (HF)	4322 (-189)	4300 (-171)	-251	(-127)
"Bend"	108	84	70 ± 24	86
"Stretch"	176	159	197 ± 15 [39], 155 ± 10	193
"Shear"	645	581	555 ± 3	561
(b) DCN...DF				
Mode	DZ+P	TZ+2P	Expt [41]	Calculated [36]
$\nu_2$ (DCN)	703 (+15)	704 (+10)		(+25)
$\nu_3$ (DCN)	2178 (+17)	2159 (+8)		(+4)
$\nu_1$ (DCN)	2933 (+14)	2910 (+7)		(+2)
$\nu_1$ (DF)	3134 (-162)	3118 (-123)	-187	(-93)
"Bend"	99	77	67	79
"Stretch"	172	155		189
"Shear"	465	419	416	405

<sup>a</sup> Shift from monomer values are given in parenthesis

basis sets. However we have not considered the two possible structures HCN...HF and HF...HCN; only the most stable structure found by Curtiss and Pople [36] is considered. The linear geometry obtained is in agreement with microwave spectrum results of Legon et al. [39]. The geometry is shown in the figure. In comparison to HCN...HCN the hydrogen bond length is shorter and the binding energy is 7 kcal/mol compared to 5 kcal/mol for HCN...HCN. This shows that HCN...HF is stronger than HCN...HCN; that is HF is a better proton donor than HCN.

Frequencies and frequency shifts are tabulated in Table 7, together with the previous theoretical results of Curtiss and Pople [36], the microwave spectrum results of Legon et al. [39] and the infrared spectrum results of Thomas [41]. The frequency shift  $\nu_{HF}$ , predicted by us to be  $-171 \text{ cm}^{-1}$ , does not agree with the infrared spectrum experimental value of  $-251 \text{ cm}^{-1}$ [41]. For the weak intermolecular bond stretching frequency, two experimental values are available [39, 41]. Our best value,  $159 \text{ cm}^{-1}$  is close to Thomas's value of  $155 \pm 10 \text{ cm}^{-1}$ . For this dimer the other two weak bond modes (bend and shear) are also observed experimentally [41] at value of  $70 \pm 24$ ,  $555 \pm 3$  and agree well with our calculated values of 84 and  $581 \text{ cm}^{-1}$ .

Similar results are given in Table 7(b) for the deuterated species DCN...DF, and similar comments apply to those made above for HCN...HF.

**Table 8.** The infrared and raman intensities for HCN...HF and DCN...DF<sup>a</sup>

Mode	HCN...HF			DCN...DF	
	i.r.	i.r. [36]	Raman	i.r.	Raman
$\nu_2$ (acceptor)	60 (0.9)	115	2	12	4
$\nu_3$ (acceptor)	25 (2.6)	19	55	43	48
$\nu_1$ (acceptor)	87 (1.1)	107	15	21	1
$\nu_1$ (donor)	707 (4.8)	710	63	361	34
"bend"	30	12	6	20	6
"Stretch"	3	4	0	2	0
"Shear"	346	496	4	196	2

<sup>a</sup> The ratio for the complex to the monomer are given in parenthesis

The infrared and raman intensities are given in Table 8 together with the previous calculated infrared intensity values of Curtiss and Pople [36]. Since the previous values were calculated with a small basis set, they differ considerably from the present results. However, they are in qualitative agreement; i.e., the HF stretching mode is the most intense of all. We note the five fold increase in the intensity of HF vibration compared to the monomer, and also the large intensity for the shearing intermolecular mode.

#### d. $H_2O...HF$

Several theoretical papers [3, 43–46] have been published on this dimer. Of these, only two of the calculations used a reasonable basis set. Bouteiller, Allavena and Leclercq used a 6-31G\* basis set in the SCF, and they also did CI calculations to examine the effect of correlation on the geometry and force constants [43]. However they only did a partial optimization and calculated only two of the frequencies. Szczesniak et al. [44] used a 6-3111G\*\* and DZ+2P basis sets in their SCF and MP2 calculations. In the optimization, the internal geometry of  $H_2O$  was held fixed at its experimentally determined structure and they calculated only two of the frequencies. In order to compare with other dimers and to have

**Table 9.** Frequencies and frequency shifts<sup>a</sup> for the intramolecular and the new intermolecular modes for  $H_2O...HF$  and  $D_2O...DF$ 

Mode	DZ+P	$H_2O...HF$		$D_2O...DF$
		TZ+2P	Exptl. shift	
$\nu_1$ (acceptor)	4159 (-7)	4119 (-9)		2969 (-7)
$\nu_2$ (acceptor)	1757 (+5)	1760 (0)		1289 (+0.6)
$\nu_3$ (acceptor)	4279 (-10)	4218 (-10)		3094 (-6)
$\nu_1$ (donor)	4252 (-259)	4207 (-264)	-353 [48]	3052 (-189)
$\nu_a$ (bend)	150	182		138
"Stretch"	224	220	198 [47]	210
$\nu_b$ (bend)	226	234		170
$\nu_c$ (shear)	654	644		478
$\nu_d$ (shear)	794	786		565

**Table 10.** The infrared and raman intensities for H<sub>2</sub>O...HF and D<sub>2</sub>O...DF<sup>a</sup>

Mode	H <sub>2</sub> O...HF		D <sub>2</sub> O...DF	
	i.r.	Raman	i.r.	Raman
$\nu_2$ (acceptor)	94 (1.0)	3 (0.7)	52	2
$\nu_1$ (acceptor)	79 (5.5)	72 (1.0)	42	37
$\nu_3$ (acceptor)	115 (1.6)	27 (1.0)	66	14
$\nu_1$ (donor)	678 (4.6)	41 (1.6)	353	22
$\nu_a$ (bend)	155	0.8	100	0.5
"Stretch"	87	0.4	28	0.1
$\nu_b$ (bend)	3	2	0.7	1
$\nu_c$ (shear)	226	1	126	0.5
$\nu_d$ (shear)	194	0.2	101	0.1

<sup>a</sup> The ratio for the complex to the monomer are given in parenthesis

a full set of properties we have carried out a full geometry optimization using DZP and TZ+2P basis sets. Although Lister and Palmieri [3] calculated all the frequencies, they used a small basis set in their calculation, the geometry was predicted incorrectly, they obtained a C<sub>2v</sub> structure rather than C<sub>s</sub>. However, we have not considered all possible structures because of Szczesniak et al [44] clearly show the most stable structure to be C<sub>s</sub>. Our calculated structure is shown in figure. Compared to HCN...HF, H<sub>2</sub>O...HF is more strongly bound (8 kcal/mol cf 6 kcal/mol). Compared to all the other dimers considered here, the optimized structure is of C<sub>s</sub> symmetry, with a pyramidal oxygen atom and the hydrogen bond is not linear, being bent by 1.7°. This agrees with *ab initio* results of Szczesniak et al. [44], and the most recent rotational spectrum results of Cazzoli et al. [47].

The frequencies and frequency shifts are reported for H<sub>2</sub>O...HF and D<sub>2</sub>O...DF in Table 9. Only two of the frequencies are reported from gas phase work; for the HF stretch our value (−263 cm<sup>−1</sup>) is in poor agreement with the experimental value (−353 cm<sup>−1</sup>). The latter value must obviously be questioned. On the other hand the intermolecular stretch vibrational values (220 cf 198 cm<sup>−1</sup>) are in good agreement. In Table 10, the i.r. and raman intensities are reported. Kollman and Allen have also reported some values, our intensity ratio for the HF stretch is 4.6 compared to their value of 5. We note the large intensity values for four of the intermolecular vibrations.

## 5. Conclusion

Taking our results in conjunction with previous results of Kollman and Allen [49] on H<sub>3</sub>N...H<sub>2</sub>O and H<sub>2</sub>O...HCN, we can confirm that the electron donor ability of the monomers obeys NH<sub>3</sub> > H<sub>2</sub>O > HCN > HF.

In general our values for the intramolecular frequency shifts agree with the limited experimental data within 15 cm<sup>−1</sup> (with exceptions). We have shown that at this level basis set superposition errors do not affect our predictions. What is remarkable is the excellent agreement in general between the very limited experimental

data on the intermolecular frequencies (especially the hydrogen bond stretch frequencies) and our theoretical values. We suggest that analytic second derivative calculations for these may be quite valuable indicators to experimentalists, in spite of obvious anharmonic effects. Our values for the i.r. and raman intensities are probably reasonable within an order of magnitude, but there is as yet no experimental values for these quantities.

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