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Hydrogen-bonded complexes involving HF and HCl: the effects of electron correlation and anharmonicity

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Calculations on the hydrogen-bonded complexes $HCN\cdots HF$, $H_2O\cdots HF$, $ClCN\cdots HCl$ and $(CH_3)_2O\cdots HCl$ are reported. SCF harmonic values for the HF and HCl frequency shifts are in considerable disagreement with experiment, by as much as $100\,cm^{-1}$. Calculations at the MP2 (harmonic) level yield improved agreement with experiment, reducing discrepancies to the order of $10\,cm^{-1}$. We have also calculated all the cubic and quartic force constants for $HCN\cdots HF$ at the SCF level, so that the anharmonic constants, x_{rs} can be evaluated. Although x_{11} ($\nu_1 =$ H–F stretch) is large and negative, it is more than compensated by a positive x_{16} ($\nu_6 = N\cdots H\text{–}F$ bend), so that the anharmonic correction to ν_1 is small and positive. The validity of these anharmonic studies is examined.

Key words: Hydrogen bonds — Frequency shifts — Anharmonicity

1. Introduction

Interest in hydrogen-bonded complexes continues unabated. This is partly due to the increasing amount of gas phase information becoming available from the spectroscopists as well as the increasingly sophisticated methodology employed by the *ab initio* quantum chemist. This paper is a contribution which falls in the latter category.

In the original analysis by Coulson [1], later extended by Morokuma [2], the hydrogen bond energy may be split into five effects: electrostatic, polarization, exchange, charge transfer, and dispersion. In principle, Self-Consistent-Field (SCF) calculations are capable of accurately accounting for the first four contributions. It is necessary, however, to introduce electron correlation to account for the dispersion effects. In practice, it is found that SCF calculations utilizing "good" basis sets (double-zeta plus polarisation, DZ+P, or better) adequately describe the geometry of hydrogen-bonded complexes, provided the geometry is completely optimised. At the same time, the *ab initio* quantum chemist can also calculate the harmonic frequencies, dissociation energies and infra-red intensities. It is the change in these properties as the complex is formed that are discussed in this paper. The experimentally observed trends are correctly predicted by theory e.g. frequency shift have the correct sign and order of magnitude, dissociation energies are calculated to be a few kcal/mol, and infra-red intensity enhancements are reproduced. This may be seen for example in an examination of the dimers $(AH_n)_2$, where $AH_n = NH_3$, H_2O, HF, PH_3, H_2S and HCl, recently presented by Frisch et al [3].

Here we study complexes involving HF and HCl, namely HCN···HF, H_2O···HF, ClCN···HCl and $(CH_3)_2O$···HCl. One of the principal reasons for this study is that the shift of the HX (X=F or Cl) fundamental, ν_1, on the hydrogen bond formation is very large. For HCN···HF it has recently been carefully measured by Wofford et al. [4], to be $-245\ \text{cm}^{-1}$. Recent calculations by us [5] at the SCF (harmonic) level predicted this shift to be $-171\ \text{cm}^{-1}$. It is clear, therefore, that there is still a considerable shift to be explained. For H_2O···HF, the ν_1 (the HF stretch) shift determined experimentally by Thomas [6] is $-353\ \text{cm}^{-1}$, whereas our calculations at the SCF (harmonic) level gave $-263\ \text{cm}^{-1}$. For $(CH_3)_2O$···HCl, the experimental situation is less clear; the infra-red spectrum [7] has a central peak at $2570\ \text{cm}^{-1}$, and has associated shoulders or satellites on each side, about $100\ \text{cm}^{-1}$ away. The spectroscopists believe that these shoulders are due to sum and difference combinations of ν_1 with ν_4 (the O···H stretch vibration). We have also studied ClCN···HCl.

To obtain a high degree of accuracy, the geometries of all the complexes were fully optimised using gradient techniques. This was first done at the SCF level. In attempt to account for dispersion effects we have employed second-order Møller-Plesset perturbation theory (MP2). Except for $(CH_3)_2O$···HCl, the geometries were again fully optimised and properties re-evaluated. The first complete calculation on the anharmonic effects of the HCN···HF system are also reported.

The overall conclusion from these calculations will be that proceeding beyond the SCF approximation brings *ab initio* calculations for frequency shifts into closer agreement with the best experimental numbers. It will also be seen that the accurate *ab initio* evaluation of anharmonic effects of such weakly bound hydrogen complexes is a much more difficult problem and very difficult to interpret. In this paper we shall discuss each system separately.

2. Quantum chemistry methodology

To carry out these investigations, it is necessary to use the most advanced quantum chemistry codes available. We use our own package, CADPAC [8], which routinely optimises geometries using analytic gradients and calculates both analytic second derivatives and infra-red intensities at the SCF level of accuracy. We have used two basis sets in these calculations: (i) the first denoted DZ+P, uses the Dunning double-zeta basis set ($4s\,2p/2s$) [9] plus polarisation d functions with exponents of 0.8 on C, N, O, F and p functions on H with exponents of 1.0; for Cl we use the Dunning double-zeta ($6s, 4p$) basis [10] plus a polarisation d function with exponent of 0.5. (ii) the second denoted TZ+2P, uses the Dunning ($5s, 3p/3s$) [9] basis with two sets of polarisation functions with exponents for C of (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). To go beyond the SCF approximation, we have recently developed an efficient second-order perturbation theory (MP2) energy and gradient program [11]. We are also able to calculate MP2 second derivatives analytically [11], and thus directly obtain harmonic frequencies.

To calculate anharmonic effects, we have available a program which calculates SCF energy third derivatives analytically [12], and fourth derivatives by finite differences of these. This means we are able to calculate the anharmonic constants, x_{rs}, using the standard second-order perturbation formulae. As a check on the validity of the second order perturbation theory we have also available the variational vibrational program [13] which when given a force field of any triatomic molecule expressed in internal coordinates, is able to directly obtain the vibrational eigenvalues. Using the L-tensor formalism of Hoy, Mills and Strey [14] we have produced internal coordinate force fields through fourth order for HF, HCN and HCN···HF. We have then used the variational vibrational program to study the pseudo-triatomic N···HF, with the relevant force constants taken from HCN···HF.

We shall see that is necessary to use all these quantum chemistry procedures in these studies.

3. HCN···HF

The authors have recently reported results from their SCF studies [5] with DZ+P and TZ+2P basis sets. These results have been incorporated into Tables 1–4 for completeness. Earlier calculations by Curtiss and Pople [15], Benzel and Dykstra [16] and Bouteiller et al. [17] either did not work with such large basis sets or completely optimise the geometry of the complex. There is a recent review by Legon and Millen [18] on the spectroscopic information of this complex.

In Tables 1 and 2, calculated properties of the monomers are reported. It is appropriate to note that the HF bond length is much improved over SCF values at the MP2 level; the same is true for the harmonic frequency. For HCN, the harmonic frequencies are again substantially improved by MP2, although the geometries are not so improved, especially the triple bond length. In Table 3, the anharmonic constants for HF and HCN are reported. Note the excellent agreement with the experimental values reported by Mills [19], and Strey and Mills [20]; this degree of agreement is typical of many of our calculations on simple molecules [21]. In H_2O, where the experimental numbers are most sound (i.e. including Darling-Dennison type effects), we find that x_{rs} values computed

Table 1. Equilibrium geometries[a] of monomers, calculated at various levels of accuracy

		SCF/DZ+P	SCF/TZ+2P	Hartree-Fock[b] limit	MP2/DZ+P	Expt[c]
HF	$R_{\mathrm{H-F}}$	0.901	0.899	0.897	0.925	0.917
HCl	$R_{\mathrm{H-Cl}}$	1.274		1.264	1.280	1.275
HCN	$R_{\mathrm{C-H}}$	1.062	1.057		1.069	1.066
	$R_{\mathrm{C\equiv N}}$	1.136	1.124		1.184	1.153
H_2O	$R_{\mathrm{O-H}}$	0.944	0.941	0.940	0.962	0.958
	$\measuredangle \mathrm{HOH}$	106.6	106.0	106.3	104.5	104.5
ClCN	$R_{\mathrm{C-Cl}}$	1.651			1.656	1.629
	$R_{\mathrm{C\equiv N}}$	1.136			1.191	1.163
$(CH_3)_2O$[d]	$R_{\mathrm{O-C}}$	1.394				1.410
	$R_{\mathrm{C-H_1}}$	1.083				1.091
	$R_{\mathrm{C-H_2}}$	1.090				1.100
	$\measuredangle \mathrm{COC}$	113.7				111.7
	$\measuredangle \mathrm{H_1CO}$	107.7				107.2
	$\measuredangle \mathrm{H_2CO}$	111.5				110.8
	$\measuredangle \mathrm{H_2CH_1}$	108.5				108.7

[a] Bond lengths in Å and bond angles in degrees

[b] NH_3 and H_2O data from [50]; HF and HCl data from [37]

[c] H_2O data from [51], HCN data from [52], HF and HCl data from [36] ClCN data from [38] and $(CH_3)_2O$ data from [53]

[d] See Fig. 1 for definition

[21] at the SCF level are in error by typically 10%. In cases where the experimentally derived constants do not include terms such as Darling-Dennison constants, the theoretical values of x_{rs} may be more reliable.

In Table 4, results from our calculations on the complex are reported. At the SCF level we note that the HF bond length is increased. The frequency shifts (harmonic) are all of the correct order of magnitude. It should be noted that the

Table 2. Harmonic frequencies (ω) and fundamentals (ν) in cm^{-1}; theory vs experiment for the monomers

		SCF (ω)			MP2 (ω)	Expt[b]	
	Mode	DZP	TZ+2P	Limit[a]	DZP	ω	ν
HF	ν_1	4511	4471	4469	4193	4138	3961
HCl	ν_1	3134		3181	3061	2991	2885
HCN	ν_1	3638	3600		3506	3442	3312
	ν_2	861	869		719	727	713
	ν_3	2406	2408		1998	2129	2097
H_2O	ν_1	4166	4128	4130	3913	3832	3657
	ν_2	1752	1760	1747	1665	1648	1595
	ν_3	4289	4228	4231	4059	3942	3756
ClCN[a]	ν_1	2578			2119		2216
	ν_2	790			738		744
	ν_3	443			367		378

[a] H_2O data from [14]; HF and HCl data from [38]

[b] H_2O data from [14], HCN data from [54], HF data from [37]

Table 3. Anharmonic constants x_{rs} for HF and HCN, calculated at the SCF level

Molecule		Calc (DZP)	Expt[a]
HF	x_{11}	−89.0	−88.7
HCN	x_{11}	−46.9	−52.7
	x_{22}	−7.9	−2.6
	x_{21}	−13.2	−18.9
	x_{31}	−16.7	−13.1
	x_{32}	−1.1	−3.4
	x_{33}	−3.2	−11.6

[a] HF data from [19] and HCN data from [20]

ν_1(HF), ν_1(CH), ν_3(CH), ν_2(HCN-bend) (monomer notation) are now all accurately known from the experimental work of Wofford et al. [4]. Of those, only the ν_1(HF) is in significant disagreement with our calculated values; at TZ+2P level the discrepancy is $-64\ \text{cm}^{-1}$. Agreement at the SCF level for the intermolecular frequencies is also reasonable.

At the MP2(DZ+P) level, it is seen that the correlation correction substantially improves the SCF discrepancy in the shift of ν_1(HF); a correlation (harmonic) contribution to the shift of $-49\ \text{cm}^{-1}$ is calculated, which in light of the anharmonic data presented below appears to be the prime reason for the ν_1(HF) discrepancy at the SCF level. Other significant changes due to correlation are for the intermolecular stretch frequency ($+19\ \text{cm}^{-1}$) and the shear frequency ($+52\ \text{cm}^{-1}$). If we add the MP2 correlation correction to the TZ+2P SCF results, then predicted values for the shifts of ν_1(HF), ν_1(CH), ν_2(HCN-bend), ν_3(CN) are −220, −2, +3, $+33\ \text{cm}^{-1}$ compared to the experimental values of −245, −1, +13, $+24\ \text{cm}^{-1}$. Likewise the intermolecular harmonic frequencies for stretch (ν_4), shear (ν_6) and bend (ν_7) are predicted to be 178, 633, 98 compared to the best experimental (anharmonic) values [22–24] of 162.9, 550, and $72 \pm 4\text{cm}^{-1}$.

For the fully deuterated complex, DCN···DF the MP2/DZ+P values for the shifts of ν_1(DF),ν_1(CD), ν_2(DCN-bend), ν_3(CN) are −172, +13, +11 and $+41\ \text{cm}^{-1}$ and the new intermolecular frequencies for stretch, shear and bend are 191, 502 and $112\ \text{cm}^{-1}$.

Of course, all these calculations are in the harmonic approximation, whereas the experimentally observed frequencies are fundamentals. There is often a considerable difference between the two as illustrated by the HF monomer where ω_1 is 4138 and ν_1 is $3961\ \text{cm}^{-1}$. By perturbation theory, these are related through

$$\nu_r = \omega_r + x_{rr}(1+g_r) + \tfrac{1}{2} \sum_{r \neq s} x_{rs} g_s, \tag{1}$$

where g_r is the degeneracy of the vibrational state r.

Although such perturbation theory works well for strongly bounded molecules, for weakly bonded complexes the validity of the perturbation theory is indeed

Table 4. The HCN···HF complex

(a) Geometry (bond lengths in Å and bond angles in degree)

	SCF/DZP	SCF/TZ+2P	MP2/DZP	Expt [18]
R_{HF}	0.912	0.906	0.936	
R_{FN}	2.840	2.884	2.737	2.805
R_{CN}	1.133	1.122	1.179	
R_{CH}	1.062	1.058	1.068	

(b) Dipole moment, μ (in debye)

	HF	HCN	Complex	$\Delta\mu$
SCF/TZ+2P	1.92	3.24	5.94	0.78
Expt [31]			5.61	0.80

(c) Binding energy, D_0 (kcal/mol)

SCF/DZP	SCF/TZ+2P	MP2/DZP	Expt [18]
4.0	3.9	4.1	4.5 ± 0.4

(d) Computed harmonic frequencies and frequency shifts[a] at various levels compared with experimental fundamental values

Mode	SCF/DZ+P	SCF/TZ+2P	MP2/DZ+P	Expt [4]
ν_1(HF)	4322 (−189)	4300 (−171)	3955 (−238)	3716.2 (−245.2)
ν_1(HCN)	3638 (0)	3593 (−7)	3511 (+5)	3310.3 (−1.14)
ν_3(HCN)	2437 (+31)	2427 (+19)	2050 (+45)	2120.9 (+24.1)
ν_2(HCN)	878 (+17)	881 (+12)	727 (+8)	726.5 (+13.1)
"bend"	108	84	122	72±4 [24]
"stretch"	176	159	195	162.9 [22]
"shear"	645	581	697	550.0 [23]

[a] Frequency shifts are given in parenthesis

(e) Anharmonic constants, in cm^{-1}

1—HF stretch, 2—CH stretch, 3—CN stretch, 4—weakbond "stretch", 5—HCN bend, 6—"shear" and 7—"bend"

x_{11}	−110.76	x_{21}	−0.29	x_{61}	+45.2	x_{73}	−1.99	g_{55}	5.68
x_{22}	−46.78	x_{31}	+3.16	x_{71}	+4.56	x_{54}	−0.39	g_{56}	22.3
x_{33}	−7.99	x_{32}	−14.08	x_{52}	−17.5	x_{64}	−15.12	g_{77}	1.06
x_{44}	−3.55	x_{41}	+5.03	x_{62}	−0.73	x_{74}	−3.50	g_{65}	0.06
x_{55}	−3.17	x_{42}	−0.11	x_{72}	−0.64	x_{56}	−2.48	g_{75}	1.41
x_{66}	−51.3	x_{43}	−1.14	x_{53}	−0.94	x_{75}	+1.41	g_{76}	0.71
x_{77}	−2.29	x_{51}	+1.32	x_{63}	−6.72	x_{76}	−13.38		

(f) Anharmonic corrections to harmonic frequencies, calculated from Eq. (1) (in cm^{-1})

$\Delta\nu_1$(HF) +12. $\Delta\nu_1$(HCN) −3, $\Delta\nu_3$(HCN) +8, $\Delta\nu_2$(HCN) −8, "bend" −21, "stretch" −26, "shear" −158 in question. Even so, it seemed worthwhile to calculate by *ab initio* means tne anharmonic constants x_{rs} for the HCN$\cdots$HF complex. This was done at the DZ+P level and the constants are reported in Table 4.

The values show that x_{11} has shifted from -89 in the monomer HF to -111 in the complex. If this was all that was important, this would show a significant anharmonic contribution to ν_1 ($-44\ \mathrm{cm}^{-1}$). There is very little change of the diagonal x_{rr} for HCN and the x_{1r}, where r are the modes of HCN, are relatively small. Thus if one only looked at the stretches of the complex, our anharmonic analysis and harmonic shifts would suggest $\Delta\nu_1 = -224\ \mathrm{cm}^{-1}$, which is close to experiment ($-245\ \mathrm{cm}^{-1}$). However it is immediately observed that the next most significant contribution to ν_1 is x_{16} which is large and positive (where ν_6 is the intermolecular shear vibration). It has been thought by others (see the discussion by Sandorfy [25] on $(CH_3)_2O\cdots HF$) that x_{14} should be large (where ν_4 is the N$\cdots$H stretch in our system), but from our analysis it is much smaller. Using the full list of anharmonic constants, the anharmonic contribution to the shift to the ν_1(HF), ν_1(CH), ν_3(CN) and ν_2(HCN-bend) intramolecular vibrations (monomer notation) is calculated to be +12, −3, +8 and $-8\ \mathrm{cm}^{-1}$. The anharmonic contribution to the intermolecular frequencies ν_4, ν_6, ν_7 are −26, −158 and $-21\ \mathrm{cm}^{-1}$. If one adds these to the best correlated values given above one gets no significant improvement in the agreement between calculated and experimental values, indeed most are inferior.

To test the validity of this anharmonic analysis, we considered the model triatomic system N$\cdots$H–F, using the relevant internal force constants from HCN$\cdots$HF. This model triatomic can now be examined by the standard variational vibrational energy procedure [13] as well as the second-order treatment used previously. This we have done and the calculated fundamentals are compared below. Using Eq. (1) the fundamentals are: 186 (ν_4), 488 (ν_6) and 4138 (ν_1) cm^{-1} while those from the variational program are; 241 (ν_4), 487 (ν_6) and 4208 (ν_1) cm^{-1}. The harmonic values are 208 (ω_4), 573 (ω_6) and 4321 (ω_1) cm^{-1}. This great discrepancy between the variationally calculated fundamentals and those derived from perturbation theory certainly brings into question the value of a perturbation-theory-based anharmonic analysis of hydrogen bonds. We observe, however, that the ν_1 discrepancy is something we have met before: in the Whitehead-Handy [26] variational calculations for the fundamentals of H_2O using the Hoy-Mills-Strey [14] potential which was derived from perturbation theory, there was a similar $60\ \mathrm{cm}^{-1}$ discrepancy between variational and perturbation theory values for both the symmetric and asymmetric stretch vibrations. It was then shown by Carney et al. [27] that if the potential was transformed to an expansion in Simons-Parr-Finlan [28] coordinates $(\Delta r/r)^p$, the variational calculations then agreed with the experimental values! We have also performed calculations with a transformed potential [29], this time in terms of $(1-e^{-\alpha\Delta r})^p$, and on doing this the variational fundamentals are 215 (ν_4), 450 (ν_6) and 4142 (ν_1). Now there is agreement with perturbation theory for ν_1! However the story is not so good for N$\cdots$D–F, on which we carried out a similar analysis. The results for ν_1 were: variational (Dunham) $3063\ \mathrm{cm}^{-1}$, variational (transformed) $3038\ \mathrm{cm}^{-1}$, perturbation theory

3088 cm^{-1}. So here the perturbation theory analysis does not pick up a sufficient shift.

The conclusion of this discussion on anharmonic effects is that as far as ν_1(HF) is concerned (i) the lightness of the H atom and the weakness of the hydrogen bond makes a Dunham expansion inappropriate (ii) there is significant disagreement between variational and perturbation theory values for ν_1 for a quartic Dunham potential, in common with calculations on other hydrogen containing triatomics. This means that terms higher than quartic in cartesian displacement coordinates cannot be ignored in a theoretical investigation of anharmonic effects on hydrogen-bonded systems.

As far as the intermolecular vibrations are concerned, it is difficult to make valuable comments because of the weakness of the N···H bond. Both variational and perturbation calculations agree that there should be a large ($\approx -100\ cm^{-1}$) anharmonic contribution to ν_6 (the shear). For the stretch, the variational calculations suggest an increase in ν_4 whereas perturbation theory suggests a decrease. Clearly little of value can be taken from such evidence.

Returning to the parent HCN···HF molecule, using the model triatomic as a guide, the anharmonic studies suggest a small positive shift for ν_1, due to the competing effects of x_{11} and x_{16}. There is also a large negative anharmonic contribution to ν_6. For the remaining fundamentals, it appears that anharmonic effects are small. In particular we note that our calculated value for x_{14} is small.

We have calculated the hydrogen bond strength. At the SCF and MP2 levels (DZ+P basis), D_e was found to be 7.2 and 9.1 kcal/mol, calculated from the difference in energy of the optimised complex and monomer geometries. The effect of Basis Set Superposition Error (BSSE) must also be considered [30], by recalculating the monomers with the additional basis functions from the other monomer being present (the geometry was not reoptimised). This gave new D_e values of 6.2 and 6.5 kcal/mol. To compare with experiment (so as to obtain D_0), zero-point vibrational energy must be added. This finally gave values of 4.0 and 4.1 kcal/mol at the SCF and MP2 levels. The calculations of Frisch et al. [3] indicate that higher orders of correlation correction (MP3, MP4) do not appear to affect the well depth. The experimental value [18] for D_0 is 4.5 ± 0.4 kcal/mol. We also note that the SCF value for the change 0.78 D in the dipole moment on the formation of the complex is in good agreement with the experimental value of 0.80 D [31].

4. H_2O···HF

The situation for H_2O···HF is similar to that of HCN···HF in many respects. The complex was fully optimized both at the SCF and MP2, levels with both DZ+P and TZ+2P basis (79 basis functions). Harmonic frequencies and properties were also calculated. Monomer properties are again shown in Tables 1 and 2. The bond lengths and angle of H_2O improve significantly at the MP2/TZ+2P level over the SCF/TZ+2P level (error 0.001 Å, 0.5^0). A similar improvement occurs in the harmonic frequencies.

Again there are few calculations in the literature, none of which completely optimise the geometry of the complex at a correlated level. The papers of Bouteiller et al. [32], Szczesniak et al. [33] and Lister and Palmieri [34] have been reviewed by us in our earlier paper. Szczesniak et al. performed MP2 and MP3 calculations on the complex, but without adjusting the H_2O geometry. They observed that correlation increases both the bond length and the inversion potential barrier for H_2O in $H_2O\cdots HF$, and concentrated their discussion on absolute frequencies, rather than frequency shifts.

Table 5. $H_2O\cdots HF$ complex; comparison of theory and experiment

(a) Geometry (bond lengths in Å and bond angles in degree)

	SCF/DZP	SCF/TZ+2P	MP2/DZP	MP2/TZ+2P	Expt [35]
R_{HF}	0.912	0.910	0.934	0.935	
R_{OF}	2.700	2.708	2.652	2.642	2.662
R_{OH}	0.945	0.942	0.963	0.960	
∡HOH	107.6	107.0	105.5	105.0	
∡OFH	1.6	1.7	2.8	2.2	
ϕ^a	25.9	32.7	43.1	52.1	46

[a] ϕ is the angle between the C_2 axis of H_2O and $O\cdots F$

(b) Dipole moment, μ (in debye)

	HF	H_2O	Complex
SCF/TZ+2P	1.92	2.02	4.38
Expt [35]			4.05

(c) Binding energy, D_0 (kcal/mol)

SCF/DZP	SCF/TZ+2P	MP2/DZP	MP2/TZ+2P	Expt [6]
5.8	4.8	6.0	5.5	5.5±1.6

(d) Frequencies and frequency shifts[b] at various levels

	SCF		MP2		
Mode	DZ+P	TZ+2P	DZP	TZ+2P	Exptl shift
ν_1 (acceptor)	4159 (−7)	4119 (−9)	3915 (+2)	3848 (−10)	
ν_2 (acceptor)	1757 (+5)	1760 (0)	1668 (−3)	1654 (−3)	
ν_3 (acceptor)	4279 (−10)	4218 (−10)	4041 (−18)	3960 (−20)	
ν_1 (donor)	4252 (−259)	4207 (−264)	3881 (−340)	3791 (−363)	3608 (−353) [6]
ν_a (bend)	150	182	231	232	
"stretch"	224	220	263	270	176±15 [35]
ν_b (bend)	226	234	244	252	
ν_c (shear)	654	644	720	742	
ν_d (shear)	794	786	859	862	

[b] Frequency shifts are given in parenthesis

Our calculations at the SCF/TZ+2P level for this complex show that the best calculated HF harmonic frequency shift is in error by -89 cm^{-1} when compared to the experimental value. There is little change in the H_2O frequencies from the monomer. For the intermolecular stretch there is reasonable agreement between experiment [35] (176±15 cm^{-1}) and calculated harmonic (220 cm^{-1}) values. The most significant change is the correlation correction to the ν_1 shift of -99 cm^{-1}, which brings the total shift to -363 cm^{-1}, within 10 cm^{-1} of the experimental value. The effect of electron correlation increases the intermolecular stretch frequency to 270 cm^{-1}, an error of +80 cm^{-1} when compared with the experimental (anharmonic) value of 176±15 cm^{-1}, determined by Kisiel et al. [35] from microwave rotational spectrum.

For $D_2O\cdots DF$ the $\nu_1(DF)$ frequency shift at the MP2/TZ+2P level is calculated to be -263 cm^{-1}.

Our computer resources precluded an anharmonic study on $H_2O\cdots HF$ similar to that on $HCN\cdots HF$. We can only suggest that the anharmonic correction to the intramolecular modes may be small, and that most of the remaining discrepancies will be due to basis function deficiency and electron correlation effects.

The binding energy, D_0, at the MP2(TZ+2P) level (including BSSE) is calculated to be 5.5 kcal/mol. Again this is in good agreement with the experimental value of 5.5±1.6 kcal/mol [6]. The dipole moment change at the SCF level is calculated to be 0.4 D.

5. ClCN···HCl

There is no reported data, either experimental or theoretical, on this complex. We have performed DZ+P calculations on ClCN, HCl and ClCN···HCl. For HCl, our SCF bond length of 1.274 Å is fortuitously in agreement with the experimental value [36] (the Hartree-Fock limit value [37] is 1.26 Å); it is more realistic to note that the MP2(DZ+P) value is much closer to experiment than the Hartree-Fock limit value [37]. The same is true for the harmonic frequency. The monomer ClCN geometry does not agree well with experiment [38] at the SCF level of theory. The MP2 geometry appears not much better, although the CN bond is too long by 0.03 Å, the same that it is for HCN at this level. Some of these errors may be attributed to basis set deficiency. There appears to be no published experimental data on the harmonic frequencies of ClCN, but the CN stretch at the MP2 level is ≈100 cm^{-1} less than the observed fundamental. A similar difference is seen between our calculated CN stretch of HCN and the observed fundamental. Agreement between the MP2 ω_2, ω_3 and experimental ν_2 and ν_3 for ClCN is good.

The geometry of the complex was first estimated using the Buckingham and Fowler [39] electrostatic model. For this, a Distributed Multipole Analysis (DMA) for the monomers was required [40]. The DMA analysis gave the following charge distribution on the monomers:

$$\mathrm{Cl}^{-0.02}\text{-}\mathrm{C}^{0.65}\equiv\mathrm{N}^{-0.62} \qquad \mathrm{H}^{0.11}\text{-}\mathrm{Cl}^{-0.11}.$$

The arrangement predicted by such a model was a linear N···H–Cl hydrogen bond. Attempts to locate other possible structures such as Cl–H···Cl–CN with a non-linear H···Cl–CN hydrogen bond using DMA were unsuccessful.

The geometry of the linear ClCN···HCl complex was optimised with a DZ+P basis at the SCF and MP2 levels of theory; the results are given in Table 6. It is seen that the N···H bond decreases by 0.2 Å and the HCl bond increased by 0.01 Å, on comparing the MP2 and SCF geometries. The binding energy (D_0) at the MP2 level (4.2 kcal/mol) is 1.6 kcal/mol greater than the SCF value.

The harmonic frequencies of the complex are also given in Table 6. It is seen again that correlation has a significant contribution to the ν_1 HCl shift (-58 cm^{-1}). The shifts of the ClCN vibrations are changed by ≈ 10 cm^{-1} on the introduction

Table 6. The ClCN···HCl complex

(a) Geometry

	SCF/DZP	MP2/DZP
R_{CCl}	1.6475	1.6509
R_{CN}	1.1349	1.1875
$R_{N\cdots H}$	2.2246	2.0408
R_{HCl}	1.2787	1.2889

(b) Dipole moment, μ (in debye) (SCF/DZP)

HCl	ClCN	Complex	$\Delta\mu$
1.40	3.03	5.56	1.12

(c) Binding energy D_0 (kcal/mol)

SCF/DZP	MP2/DZP
2.0	4.2

(d) Frequencies (in cm^{-1}) and infra-red intensities (in km/mol)

	Frequencies[a]		Intensities[b]
Mode	SCF/DZ+P	MP2/DZ+P	SCF/DZ+P
$\omega_{H\text{-}Cl}$	3069 (−65)	2938 (−123)	383 (10.4)
ω_{CN}	2592 (+13)	2147 (+28)	94 (1.4)
$\omega_{C\text{-}Cl}$	798 (+8)	756 (+18)	1.3 (0.3)
$\omega_{CN\text{-}bend}$	458 (+15)	369 (+2)	27 (2.6)
"bend"	33	41	2
"stretch"	84	104	2
"shear"	348	443	180

[a] The frequency shifts are given in parenthesis

[b] The intensity ratios relative to the monomer are given in parenthesis

of correlation effects. We would predict on the basis of these calculations that the ν_1 band for the complex should be near 2762 cm^{-1}, although it is possible that increased correlation and anharmonic effects would reduce it further. For the intermolecular vibrations, there is a large (+100 cm^{-1}) correlation contribution to the shear vibration (in HCN···HF correlation increased this frequency by 52 cm^{-1}). We also report the infra-red intensities of the complex, with the enhancements over the monomer intensities in parenthesis. Note the HCl intensity increases 10-fold.

The dipole moment of the complex (5.56 D, SCF) is increased by 1.13 D over the vector sum of the monomers.

6. $(CH_3)_2O\cdots HCl$

For $(CH_3)_2O\cdots HCl$, there is a considerable amount of experimental information on the HCl ν_1 stretching mode. The band structure attributed to this mode, for the gas-phase complex was published in 1965 by Bertie and Millen [41]. It has a broad structure consisting of four peaks with a central peak having its maximum at 2570 cm^{-1}. The frequencies of the four peaks are 2660, 2570, 2480 and 2360 cm^{-1}. After dismissing the possibility of the side bands being due to intramolecular ether vibrations, Bertie and Millen argued that they must be due to combinations of ν_1 with either ν_π (the intermolecular bend) or ν_σ (the intermolecular stretch). They favoured the latter and thus assigned the peaks $(0, \nu_\sigma) \rightarrow (1, \nu'_\sigma)$

2660 $(0,0) \rightarrow (1,1)$
2570 $(0,0) \rightarrow (1,0)$
2480 $(0,1) \rightarrow (1,0)$
2369 $(0,2) \rightarrow (1,0)$.

Since this investigation, there have been detailed studies of the temperature dependence of the band intensities. In the early 1970's, these assignments were modified by Lassegues et al. [42] and Bertie and Falk [43]. As the intensity of the 2480 cm^{-1} band did not change during the temperature variation, this band was reassigned as the $(0,0) \rightarrow (1,0)$ band. But more recently Millen and Schrems [7] investigated a series of twelve related isomers and their deuterated derivatives and came to a conclusion which favoured the original assignment. It should also be noted there are in the literature papers [44] which attempt a simple anharmonic analysis of these vibrations, which support one or other of the assignments. The ν_σ weak stretch has been measured by Berties and Falk [43] to be 119 cm^{-1}. There is a review which discusses all of this in great detail by Sandorfy [25].

These combinations bands have been analysed [25] in terms of perturbation theory; such an analysis on $(CH_3)_2O\cdots HF$ predicts that $x_{1,\sigma} = +70$ cm^{-1}, and this constant is said [25] to be "the key to all H-bond theories base on the coupling of these motions."

Our *ab initio* calculations on the monomers are reported in Tables 1 and 2. For ether our SCF optimised geometries all have bond lengths too short by ≈ 0.01 Å.

The best previous SCF calculation appears to be by Tsuboyama et al [45] using a MIDI-4 type basis set. In view of the number of vibrational frequencies for $(CH_3)_2O$, we do not publish them in Table 2. Experimental values for the fundamentals may be found in Shimanouchi [46].

Only two *ab initio* calculations have been reported on the complex, each assuming a planar type structure with HCl lying along the C_2 axis of ether; these are by Carnovale et al [47] and by Hinchliffe [48]. Hinchliffe used three small basis sets STO-3G, 4-31G and a Dunning basis set and found the hydrogen bond length O···H to be 1.46, 1.68 and 1.97 Å respectively. In all these calculations the monomer geometry was fixed at the experimental geometry, and only the hydrogen bond length optimised. In our SCF calculation initially all the parameters were varied within C_{2v} symmetry, to give the geometry of Fig. 1(b). There were seven very small frequencies ($|\omega| < 8\ \mathrm{cm}^{-1}$) including the translations and rotations; on examination the extra vibration was the O···H–Cl bend. All the parameters were also optimised in C_1 symmetry, this gave a C_5 symmetry structure Fig. 1(c), and again there were seven very small frequencies. The only difference between Fig. 1(b) and Fig. 1(c) is that in the latter the O···H–F is about 10° off the C_2 axis. The surface is therefore very flat to such distortions and it is not possible to give the O···H–F angle with any certainty. The properties of Fig. 1(c) are reported in Table 7. It was not possible for us to perform MP2 calculations on this system.

The binding energy (D_e) is calculated to be 5.2 kcal/mol; i.e. this complex is as stable as the other complexes reported in this paper.

The intra- and intermolecular vibrational harmonic frequencies, and shifts, are reported in Table 7. We have used Shimanouchi's [46] description of the modes. The infra-red intensities (with intensities relative to the monomer in parenthesis) are also reported. As far as the intramolecular frequencies of ether are concerned, the CO symmetric stretch shift of $-15\ \mathrm{cm}^{-1}$ agrees well with the experimental value [46] of $-16\ \mathrm{cm}^{-1}$. We also note that there appear to be significant shifts in the CH_3 stretching vibrational modes, of $\approx +20\ \mathrm{cm}^{-1}$.

The H–Cl shift is calculated at this level to be $-170\ \mathrm{cm}^{-1}$. There will be a significant correlation correction, which we estimate to be $-60\ \mathrm{cm}^{-1}$ from our ClCN···HCl calculations, to give a predicted shift of $-230\ \mathrm{cm}^{-1}$. If we argue, as from our HCN···HF studies above, that the anharmonic correction to the shift is small, then using the H–Cl fundamental [36] at $2885\ \mathrm{cm}^{-1}$, this would predict the HCl line in the complex to lie at $2655\ \mathrm{cm}^{-1}$. Evidence from HCN···HF and H_2O···HF suggests that our shifts calculated by this approach are still too small by $\approx 40\ \mathrm{cm}^{-1}$, and so on this basis one would suggest that the HCl line lies at $2615\ \mathrm{cm}^{-1}$. This is midway between the observed peaks at $2660\ \mathrm{cm}^{-1}$ and $2570\ \mathrm{cm}^{-1}$ in the infra-red spectrum! But these calculations so appear to rule out the possibility that the peak at $2480\ \mathrm{cm}^{-1}$ is the HCl line.

Our calculations on HCN···HF, Table 4, reported a value (x_{14}) for the anharmonic constant relating the HF stretch with the N···H stretch of $5\ \mathrm{cm}^{-1}$. This is much at variance with the experimental value for $(CH_3)_2O$···HF of $+70\ \mathrm{cm}^{-1}$. This points to, (but no more) the possibility that the side peaks may have been

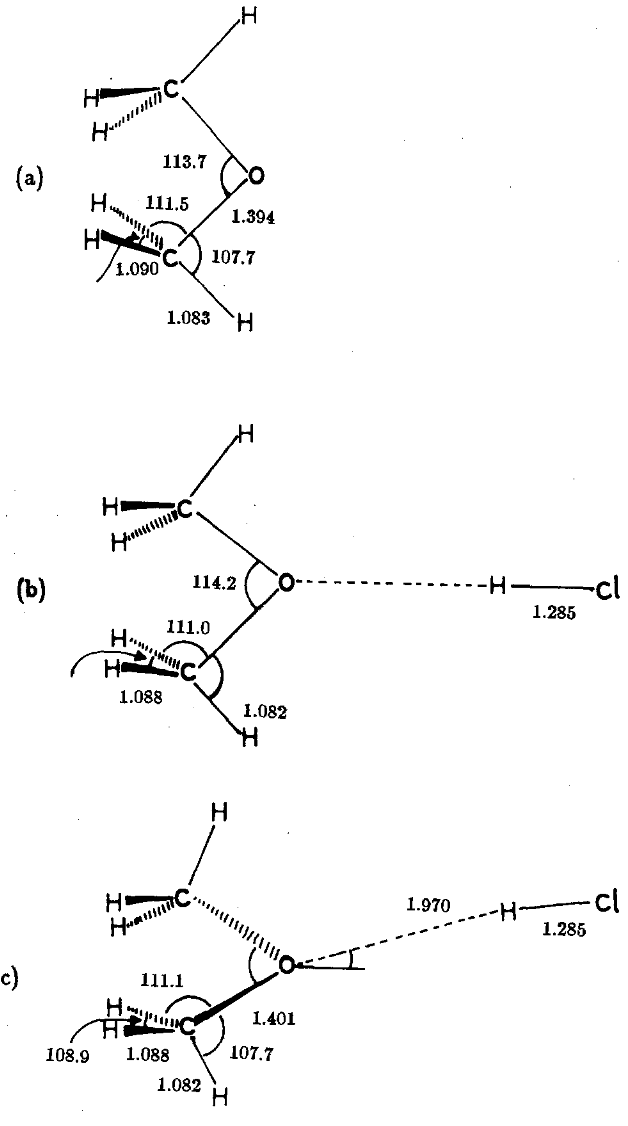

Fig. 1. Geometries (SCF/DZP) of ether and ether-HCl

misassigned. An analysis of our variational calculations also support a small value for this constant.

The calculated intermolecular stretch harmonic frequency (106 cm^{-1}) agrees well with the experimental [43] value, (119 cm^{-1}). The intermolecular harmonic "bend" and "shear" are also in reasonable agreement with experiment. We also note the 15-fold enhancement of the H-Cl infra-red intensity on the formation of the complex.

Table 7. The $(CH_3)_2O\cdots HCl$ complex

(a) Geometry—see Figs. 1(b) and 1(c)

(b) Dipole moment (in debye) (SCF/DZP)

HCl	$(CH_3)_2O$	Complex
1.40	1.57	3.91

(c) Binding energy (D_e)

SCF/DZP	5.2 kcal/mol

(d) Frequencies, frequency shifts (in cm^{-1}) and intensities (in km/mol) (SCF/DZP)

Mode		Frequencies[a] calculated		Frequencies[a] expt [43]	Intensities[b] (km/mole)	
Torsion	a_2	200	(−9)		0	0
	b_2	254	(−8)		3.7	(0.4)
C-O-C deform	a_1	445	(+4)	(−3)	8.1	(2.3)
CO-*s*-stretch	a_1	1026	(−15)	(−16)	82.0	(1.8)
CO-*a*-stretch	b_1	1221	(−4)		49.6	(1.54)
CH_3 rock	a_2	1266	(0)		0	(0)
	b_2	1302	(0)		9.3	(0.9)
	b_1	1332	(−13)		166.8	(0.9)
	a_1	1395	(+5)		14.6	(1.4)
CH_3-*s*-deform	b_1	1592	(+1)	(+5)	8.1	(0.7)
	b_1	1623	(0)		12.9	(1.0)
	a_1	1627	(+2)		4.4	(1.2)
CH_3-*d*-deform	a_2	1612	(0)		0	(0)
	b_2	1625	(0)		14.4	(1.2)
	a_1	1641	(−3)		0	(0)
HCl stretch		2962	(−170)	(−316)	551.8	(15.0)
CH_3-*s*-stretch	b_1	3174	(+20)		63.3	(0.9)
	a_1	3187	(+18)		55.8	(0.7)
CH_3-*d*-stretch	a_2	3243	(+27)		0	(0)
	b_2	3245	(+27)		144.4	(0.8)
	b_1	3306	(+11)		39.5	(0.7)
	a_1	3308	(+11)		42.5	(1.1)
"bend"		≈10	(10)	50	4.1	
		35	(35)		0	
"stretch"		107	(107)	117±3	3	
"shear"		399	(399)	470	51.0	
		507	(507)		36.8	

[a] The frequency shifts are given in parenthesis

[b] The intensity ratios relative the monomer are given in parenthesis

In a recent paper, Bernadet and Fillaux [49] have presented a theoretical band shape analysis for gas phase $(CH_3)_2O\cdots HCl$ and $(CH_3)_2O\cdots DCl$. For this analysis they assumed, in common with other authors, that the shape for $(CH_3)_2O\cdots HCl$ arises from the coupling between the $\nu_1(HCl)$ and $O\cdots HCl$ (ν_σ) weak intermolecular stretch. In addition they assumed that for $(CH_3)_2O\cdots DCl$ it is important to include the effects of the coupling between $\nu_1(DCl)$ and the bend $O\cdots DCl$ (ν_π). For such a discussion, they assumed some force constants which can be approximately translated as ν_σ $(O\cdots HCl) = 119\ cm^{-1}$, $\nu_\pi(O\cdots HCl) = 100\ cm^{-1}$, $\nu_\sigma(O\cdots DCl) = 30\ cm^{-1}$, $\nu_\pi(O\cdots DCl) = 60\ cm^{-1}$. Our SCF calculations on the two complexes predict $\nu_\sigma(O\cdots HCl) = 107\ cm^{-1}$, $\nu_\pi(O\cdots HCl) = 35, \approx 10\ cm^{-1}$, $\nu_\sigma(O\cdots DCl) = 106\ cm^{-1}$, $\nu_\pi(O\cdots DCl) = 35, \approx 10\ cm^{-1}$. It is seen that our calculations predict only a small ($10\ cm^{-1}$) change in ν_σ between the proton and deuterium complexes (this is indeed true for all the complexes we have studied). Furthermore our investigations on $HCN\cdots HF$ do not show a significant combined correlation plus anharmonicity effect. Therefore we conclude that the assumed significant change in $\nu_\sigma(H \rightarrow D)$ is not supported by our calculations. We furthermore note that ν_π does not change ($H \rightarrow D$), and is smaller than the assumed values. Our view is therefore that there is much work to be done before the band shapes are understood completely.

7. Conclusion

The principal conclusion from this work is that calculations which include electron correlation at the simplest level (MP2) substantially improve the agreement between theory and experiment for the frequency shift of the proton donor.

From the studies of anharmonic effects on $HCN\cdots HF$, it is clear that individual contributions are significant, and that there appears to be substantial anharmonic coupling between the H-F vibration and the intermolecular shear mode. However, our calculations suggest that there may be some cancellation of these effects. There is considerable disagreement between perturbation and variational treatments of the pseudo-triatomic $N\cdots HF$; this must bring into question perturbation theory based analyses of anharmonic effects on hydrogen-bonded complexes.

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Please write to the authors (JFG) if further anharmonic data on $HCN\cdots HF$ are required.

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