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Hydrogen Bonding in Long Chains of Hydrogen Fluoride and Long Chains and Large Clusters of Water Molecules

X. LCAO–MO Studies on Molecular Structure

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Energy band structures of one-dimensional $(HF)_n$- and $(H_2O)_n$-chains have been calculated (1) by extrapolation of CNDO/2–MO levels to infinite chain length and (2) by the CNDO/2 crystal orbital (CO) method. In the CO-calculations interactions up to fifth neighbours have been taken into account. Both types of calculations were performed using experimental geometries and CNDO/2 minimum geometries of the corresponding dimers $(HF)_2$ and $(H_2O)_2$. With the same geometries CO calculations on two-dimensional sheets of hydrogen bonded chains were performed too.

Due to end-effects the extrapolated MO bands are much broader than the bands obtained by the CO method. In the CO calculations further neighbour interactions play a non-negligible role and hence the nearest neighbour approximation is not sufficient for an accurate description of crystals containing hydrogen bonds.

MO calculations on one-dimensional chains of both systems show that the hydrogen bond energies increase with the number of monomers indicating the presence of cooperative effects. The hydrogen bond energies calculated with the CO method are usually somewhat larger than those extrapolated from the MO results. In three-dimensional networks of $(H_2O)_n$, however, the additional stabilization of clusters with respect to dimers is drastically diminished.

Key words: $(HF)_n$-chains – $(H_2O)_n$-chains – Hydrogen bond energies

1. Introduction

One of the most interesting properties of large structural units with hydrogen bonds is the lack of pairwise additivity of the intermolecular energy. MO-calculations on aggregates of some water [1, 2] or hydrogen fluoride [3, 4] molecules have shown that at certain intermolecular geometries the strength of the hydrogen bond increases with increasing number of molecules. The formation of clusters can be regarded therefore as a cooperative process. On small aggregates it was shown that *ab initio* and semi-empirical MO calculations give the same qualitative

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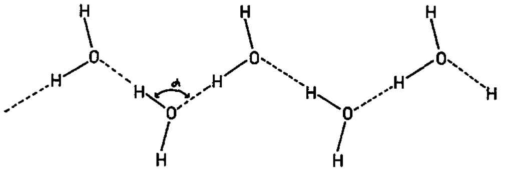

Fig. 1. One-dimensional $(H_2O)_n$-chain

Table 1. Molecular geometries applied for $(H_2O)_n$ and $(HF)_n$

Molecule	Geometry	Ref.	No.	Bond distances (Å)	Intermolecular angle α
H_2O	Experimental ice	[10]	1	$R_{OH_1} = 1.01$ $R_{OH_2} = 1.02^a$ $R_{OO} = 2.72^b$	109.47°
	CNDO/2-minimum $(H_2O)_2$	[11]	2	$R_{OH_1} = 1.03$ $R_{OH_2} = 1.05^a$ $R_{OO} = 2.54$	109.47°
HF	Experimental HF-crystal	[13]	1	$R_{HF} = 0.92$ $R_{FF} = 2.49$	180°
	CNDO/2-minimum $(HF)_2$	[12]	2	$R_{HF} = 1.01$ $R_{FF} = 2.44$	180°
	Experimental HF-crystal	[13]	3	$R_{HF} = 0.92$ $R_{FF} = 2.49$	120.1°
	CNDO/2-minimum $(HF)_2$	[12]	4	$R_{HF} = 1.01$ $R_{FF} = 2.44$	120.1°

[a] The hydrogen atom involved in the hydrogen bond of $(H_2O)_n$ is denoted by "H_2".
[b] Extrapolated to 0 °K.

results. Infinitely long chains of monomers forming hydrogen bonds have been calculated by Bacon and Santry [5, 6]. They have used a perturbation formalism to describe the long range interactions in the crystal.

In this paper the crystal-orbital method originally formulated by Del Re, Ladik and Biczó [7] was applied in a CNDO/2 version [8] to calculate the energy bands of one- and two-dimensional aggregates of water and hydrogen fluoride molecules. Direct CNDO/2–MO calculations on chains and clusters with increasing size were performed as well. Their results are compared with those of the crystal orbital calculations. To be able to do this in the crystal orbital calculations further neighbours interactions have been taken into account too.

2. Method of Calculations

All MO-calculations have been performed using the CNDO/2 approximation [9]. One-dimensional chains containing up to 8 H_2O molecules, tetrahedral clusters of $(H_2O)_n$ up to 5 tetrahedrons and HF chains up to 9 members have been calculated. The geometry used for the $(H_2O)_n$ chains is shown in Fig. 1. Bond lengths and bond angles were taken from experimental data [10] or from CNDO/2 calculations on the water dimer [11] (Table 1).

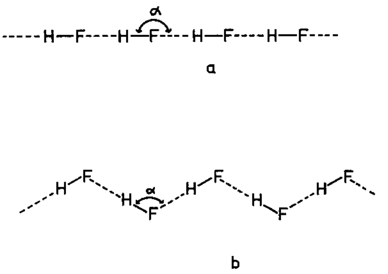

Fig. 2 a,b

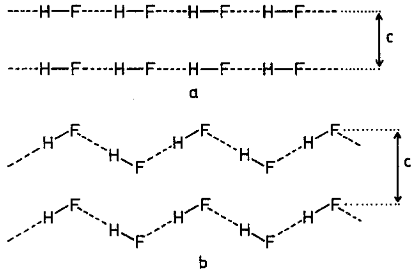

Fig. 3 a,b

Fig. 2. One-dimensional $(HF)_n$-chain (linear arrangement **a**, $\alpha = 180°$ and bent arrangement **b**, $\alpha = 120.1°$)

Fig. 3. The geometry of the calculated two-dimensional periodic HF clusters. **a** Cluster with linear $(HF)_n$-chains; **b** cluster with bent $(HF)_n$-chains. The geometries of the chain were the same as in the one-dimensional cases (CNDO/2-minimum and experimental), for the F–F distance between F-atoms belonging to two adjacent chains c a value of 3.10 Å (sum of van der Waals radii) was used

The two geometric arrangements applied for $(HF)_n$-chains are shown in Fig. 2. In the case of the linear $(HF)_n$-chains again two geometries were used, one with the distances at the CNDO/2 minimum of the HF dimer [12] and one with the experimental values taken from HF-crystals [13]. In the crystal, however, the HF molecules show a bent arrangement (Fig. 2). Therefore calculations were performed on both linear and bent $(HF)_n$ chains using the geometric input data summarized in Table 1.

Crystal orbital calculations on one-dimensional $(H_2O)_\infty$- and $(HF)_\infty$-chains have been performed with the geometries described above. Additionally two-dimensional periodic $(HF)_\infty$ clusters have been calculated using the geometric arrangements of chains shown in Fig. 3.

The formalism of the CNDO/2 CO method in the first neighbour approximation was presented already for one-dimensional [8] and two-dimensional periodic systems [14]. In the case of further neighbours interactions we can write the equations of the CNDO/2 CO method for a two-dimensional periodic system as

$$\boldsymbol{F}(k_1, k_2)\, \boldsymbol{c}_i(k_1, k_2) = \varepsilon_i(k_1, k_2)\, \boldsymbol{c}_i(k_1, k_2)\,, \tag{1}$$

$$\boldsymbol{F}(k_1, k_2) = \sum_{q_1=-N_1}^{N_1} \sum_{q_2=-N_2}^{N_2} e^{i(k_1 q_1 a_1 + k_2 q_2 a_2)} \cdot \boldsymbol{F}(q_1, q_2) \tag{2}$$

where k_1 and k_2 represent the two components of the quasi momentum $\vec{k}$. Hence, the two-dimensional lattice vectors are defined as $R_{\vec{q}} = q_1 a_1 \vec{i} + q_2 a_2 \vec{j} \cdot \vec{i}$ and $\vec{j}$ are unit vectors pointing in the two directions of periodicity with elementary translations a_1 and a_2, respectively. Finally N_1 and N_2 are the numbers of the neighbours taken into account in the two different directions. If we denote the part of the matrix $\boldsymbol{F}_1(k_1 k_2)$, which contains the first neighbours interactions [14] by $\boldsymbol{F}^{(1)}(k_1, k_2)$, we can write:

$$\boldsymbol{F}_1(k_1, k_2) = \boldsymbol{F}^{(1)}(k_1, k_2) + \tilde{\boldsymbol{F}}(k_1, k_2) \tag{3}$$

where $\tilde{\boldsymbol{F}}(k_1, k_2)$ can be defined:

$$\tilde{\boldsymbol{F}}(k_1, k_2) = \sum_{|q_1|+|q_2|=2}^{N_1+N_2}{}' \; e^{i(k_1 q_1 a_1 + k_2 q_2 a_2)} \cdot \boldsymbol{F}(q_1, q_2)\,. \tag{4}$$

Here q_1 and q_2 can have both signs. The prime after the summation symbol indicates that the summation has to be extended for all pairs of q_1 and q_2 which sum up to a given value of $(|q_1|+|q_2|)^1$. The elements of $\tilde{F}(q_1, q_2)$ with $|q_1|+|q_2| \geqq 2$ are calculated according to

$$\tilde{F}(q_1, q_2)_{\mu,\nu} = \beta^{(0)}_{A,B}\, S_{\mu,\nu}(q_1, q_2) - \tfrac{1}{2} P_{\mu,\nu}(q_1, q_2)\, \gamma_{A,B}(q_1, q_2) \tag{5}$$

where μ belongs to atom A ($\mu \in A$) and ν to atom B ($\nu \in B$). The overlap integrals $S_{\mu\nu}$, the generalized bond order $P_{\mu\nu}$ and the two electron coulomb integrals γ_{AB} are defined in Eq. (6).

$$S_{\mu,\nu}(q_1, q_2) = \int \chi_\mu^{\vec{0}} \chi_\nu^{q_1,q_2}\, dV \tag{6a}$$

$$P_{\mu,\nu}(q_1, q_2) = \frac{2}{u} \int_u dk_1\, dk_2 \left\{ \sum_{j=1}^{n} c^*_{j,\mu}(k_1, k_2)\, c_{j,\nu}(k_1, k_2)\, e^{i(k_1 q_1 a_1 + k_2 q_2 a_2)} \right\} \tag{6b}$$

$$\gamma_{A,B}(q_1, q_2) = \int |\chi^{\vec{0}}_{ns_A}(1)|^2 \frac{1}{r_{12}} |\chi^{q_1,q_2}_{ns_B}(2)|^2 \cdot dV_1 \cdot dV_2 \tag{6c}$$

χ_μ^0 stands for the μ-th AO in the $\vec{0}$-th reference cell and $\chi_\nu^{q_1,q_2}$ for the ν-th AO of the cell characterized by q_1, q_2. u denotes the volume of the first Brillouin zone and finally n represents the number of filled bands. The corresponding expressions for further neighbours interactions in a one dimensional chain can be derived from Eq. (3)–(6c) in a straight-forward way.

For one-dimensional chains the CO calculations have been performed until 5th neighbours interactions. To give one example: from the 4th neighbours we obtain the following contribution to Eq. (6b):

$$P_{\mu,\nu}(4) = \frac{a_1}{2\pi} \int_{-\pi/a_1}^{\pi/a_1} dk_1\, c_{j,\mu}(k_1)\, c_{j,\nu}(k_1) \{\cos 4k_1 a_1 + i \sin 4k_1 a_1\}\,. \tag{7}$$

Previous calculations with first neighbours interactions have shown that it was sufficient to take only 5 different values of k_1 in the interval from 0 to π/a. In this case the dependence of the constants $c_{j,\mu}$ and of the functions $\cos k_1 a_1$ and $\sin k_1 a_1$, respectively, on k_1 is approximated well enough by 5 points. In the case of 4th neighbours interaction, however, we must take into account more than 5 k-values because of numerical reasons. For a reasonable description of the functions $\cos 4k_1 a_1$ and $\sin 4k_1 a_1$ evidently more individual points are necessary. Therefore we have performed the calculations up to 5th neighbours using 5, 9, 15 and 25 different k_1 values for the $(H_2O)_\infty$ chain at the CNDO/2 minimum geometry. As the detailed results in Table 2 show the energy bands calculated with 9 different k_1 values are practically indistinguishable from those obtained with 25 k_1 values. Hence, we have used always 9 different values of k_1 in all subsequent further neighbours calculations.

In the case of the two-dimensional periodic clusters the definitions according to the usual crystallographic notations of 1st, 2nd, 3rd, etc. neighbours interactions are shown in Fig. 4. 9 different values of k_1 and 9 different values of k_2 leading to 81 different values of pairs k_1, k_2 were calculated for these examples.

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[1] In the case of further neighbours interactions we have to modify properly also the diagonal elements $F(0,0)_{\mu,\mu}$ of $F^{(1)}(k_1, k_2)$ by adding the term

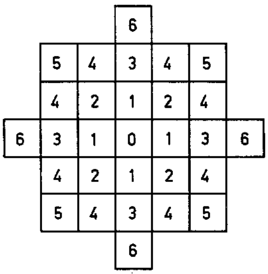
$$\sum_B (P_{BB} - Z_B) \left[\sum_{q_1+q_2}' \gamma_{A,B}(q_1, q_2) \right]$$

to the original expression.

Table 2. The dependence on the number of *k* values of the highest and lowest unfilled energy bands of the $(H_2O)_\infty$ one-dimensional chain (geometry 2) with 5th neighbours interactions

Number of *k* values	5	9	15	25
Highest[a]	−17.959	−16.953	−16.953	−16.953
filled	−13.439	−14.597	−14.597	−14.597
band	4.520	2.356	2.356	2.356
Lowest[a]	7.046	7.048	7.048	7.048
unfilled	8.284	8.281	8.281	8.281
band	1.238	1.233	1.233	1.233

[a] The first number gives the lower limit of the band, the second one the upper limit and the third one the band width. All values in eV.



			6			
	5	4	3	4	5	
	4	2	1	2	4	
6	3	1	0	1	3	6
	4	2	1	2	4	
	5	4	3	4	5	
			6			

Fig. 4. The definition of the further neighbours interactions in a two-dimensional periodic cluster. The numbers written into the cells denote which neighbours interactions with respect to the reference cell (cell with 0) they represent

Table 3. Energy bands of one dimensional $(H_2O)_n$-chains extrapolated from CNDO/2–MO calculations[a]

Number of band	Type of band	Geom. 1			Geom. 2		
		ε_{max} (in eV)	ε_{min}	$\Delta\varepsilon$	ε_{max} (in eV)	ε_{min}	$\Delta\varepsilon$
1	σ	10.07	—	3.09	10.56	—	4.85
2	σ	—	6.98		—	5.71	
3	π	—16.09	—	3.75	−14.29	—	5.98
4	σ	—	−19.86		—	−20.27	
5	σ	−20.71	−22.18	1.47	−20.41	−23.35	2.94
6	σ	−37.01	−42.09	5.08	−35.29	−43.45	8.16

[a] The largest $(H_2O)_n$-chain calculated contained 8 H_2O molecules.

3. Results

In Table 3 the energy bands of one-dimensional $(H_2O)_n$-chains extrapolated from the energy levels of the series H_2O, $(H_2O)_2$, $(H_2O)_3$ up to $(H_2O)_8$ are presented. Table 4 contains the extrapolated energy bands of linear $(HF)_n$-chains. In Table 5 the energies for hydrogen bonds in the one-dimensional $(H_2O)_n$- and $(HF)_n$-chains are shown as functions of the number of monomers. Two geometries were applied for $(HF)_n$ and one for $(H_2O)_n$. Table 6 shows the extrapolated hydro-

Table 4. Energy bands of one dimensional $(HF)_n$-chains extrapolated from CNDO/2–MO calculations[a]

Number of band	Type of band	Geom. 1			Geom. 2			Geom. 3			Geom. 4		
		ε_{max} (in eV)	ε_{min}	$\Delta\varepsilon$	ε_{max} (in eV)	ε_{min}	$\Delta\varepsilon$	ε_{max} (in eV)	ε_{min}	$\Delta\varepsilon$	ε_{max} (in eV)	ε_{min}	$\Delta\varepsilon$
1	σ	11.102	6.408	5.694	10.530	3.809	6.721	10.381	6.775	3.606	9.758	4.272	4.486
2	π	−19.809	−22.884	3.075	−16.870	−23.395	6.525	−19.153	−21.727	2.574	−17.197	−21.373	4.176
3	π	−19.809	−22.884	3.075	−18.530	−23.395	4.865	−19.667	−23.039	3.372	−18.446	−23.714	5.268
4	σ	−19.047	−27.101	8.054	−18.530	−27.400	8.870	−22.401	−26.230	3.829	−21.988	−26.660	4.672
5	σ	−42.638	−48.706	6.068	−40.815	−48.788	7.973	−42.665	−49.185	6.520	−40.831	−49.177	8.346

[a] The largest $(HF)_n$ chain contained 9 HF molecules.

Table 5. Hydrogen bond energies of $(HF)_n$- and $(H_2O)_n$-chains

	Geometry	Number of Monomers: n	$\overline{\Delta E}$[a] (kcal/mole)	$\Delta E_{n-1\to n}$[b] (kcal/mole)
$(HF)_n$	CNDO/2-minimum linear (3)	2	9.50	9.50
		3	10.88	12.25
		4	11.62	13.12
		5	12.08	13.45
		6	12.38	13.60
		7	12.60	13.68
		8	12.76	13.72
		9	12.89	13.75
$(HF)_n$	CNDO/2-minimum bent (4)	2	9.59	9.59
		3	11.06	12.53
		4	11.86	13.46
		5	12.35	13.82
		6	12.68	13.99
		7	12.91	14.08
		8	13.09	14.13
		9	13.22	14.16
$(H_2O)_n$	CNDO/2-minimum (2)	2	8.68	8.68
		3	9.63	10.59
		4	10.12	11.11
		5	10.43	11.34
		6	10.61	11.44
		7	10.78	11.50
		8	10.89	11.54

[a] The definition of $\overline{\Delta E}$ is given in Eq. (8). [b] The definition of $\Delta E_{n-1\to n}$ is given in Eq. (9).

gen bond energies for all the geometries of one-dimensional chains and for tetrahedral clusters together with the results of CNDO/2 crystal orbital calculations. In Table 7 the energy bands calculated by the CNDO/2 CO method are given for one-dimensional $(H_2O)_\infty$-chains CNDO/2-minimum geometry and experimental geometry. Table 8 contains the energy bands structures for one-dimensional $(HF)_\infty$-chains with the four geometries previously described.

Table 6. The hydrogen bond energies for one-dimensional $(HF)_n$- and $(H_2O)_n$-chains and for tetrahedral water clusters calculated by MO- and CO-methods

Aggregates	Geom. No.	ΔE (kcal/mole)	$\Delta E_{n-1\to n}$	$\varepsilon_{H.B.}$ 1.n.i.[d] (kcal/mole)	$\varepsilon_{H.B.}$ 5.n.i.
$(HF)_n$ chains	1	− 8.29(9)[a]	− 8.41(9)	− 7.47[c]	− 8.32
	2	−12.89(9)	−13.75(9)	−12.72	−13.66
	3	− 7.93(9)	− 8.41(9)	− 8.79	− 9.35
	4	−13.22(9)	−14.16(9)	−15.06	−15.95
$(H_2O)_n$-chains	1	− 6.57(8)	− 6.71(8)	− 7.37	− 7.58
	2	−10.89(8)	−11.54(8)	−14.77	−15.27
$(H_2O)_n$		− 9.15(2)[b]			
Tetrahedral clusters		− 9.30(4)			
CNDO/2 min. geom.		− 9.30(5)			

[a] In parentheses the number of monomers used for the determination of the hydrogen bond energies is shown.

[b] The number of tetrahedrons is given in parentheses. An oxygen-oxygen distance of 2.51 Å gave the energy minimum.

[c] Calculated by the crystal orbital method as the difference of the total energy per unit cell and that of the single molecule.

[d] "z.n.i." means, that interactions up to the z^{th} neighbours have been taken into account.

Table 7. Energy bands of $(H_2O)_\infty$ chains calculated by CO-method at 9 different values of k[a]

Number of band	Energy bands (eV) Geometry No. 1 1.n.i.[b]	3.n.i.[b]	5.n.i.[b]	Geometry No. 2 1.n.i.[b]	3.n.i.[b]	5.n.i.[b]
1	9.287(π)	9.289(π)	9.294(π)	9.105(0)	9.131(3π/8)	9.132(3π/8)
	9.243(0)	9.256(0)	9.257(0)	9.066(π)	9.032(π)	9.042(π)
	0.044	0.033	0.037	0.039	0.099	0.090
2	8.496(π)	8.477(π)	8.476(π)	8.330(π)	8.284(π)	8.281(π)
	7.555(0)	7.546(0)	7.550(0)	7.055(0)	7.048(0)	7.048(0)
	0.941	0.931	0.926	1.275	1.236	1.233
3	−16.149(0)	−16.128(0)	−16.130(0)	−14.622(0)	−14.602(0)	−14.597(0)
	−17.422(π)	−17.422(π)	−17.424(π)	−16.926(π)	−16.946(π)	−16.953(π)
	1.273	1.294	1.294	2.304	2.344	2.356
4	−18.406(0)	−18.400(0)	−18.401(0)	−18.256(0)	−18.261(0)	−18.265(0)
	−19.554(π)	−19.556(π)	−19.558(π)	−19.188(π)	−19.210(π)	−19.215(π)
	1.148	1.156	1.157	0.932	0.949	0.950
5	−21.267(0)	−21.251(0)	−21.251(0)	−21.167(0)	−21.157(0)	−21.159(0)
	−21.800(π)	−21.743(π)	−21.740(π)	−22.767(π)	−22.654(π)	−22.648(π)
	0.533	0.492	0.490	1.600	1.496	1.489
6	−37.055(π)	−37.089(π)	−37.089(π)	−35.492(π)	−35.568(π)	−35.571(π)
	−41.843(0)	−41.888(0)	−41.887(0)	−42.927(0)	−43.051(0)	−43.048(0)
	4.788	4.799	4.798	7.435	7.483	7.477

[a] The first number gives the upper limit, the second one the lower limit of the energy band. The third number represents the band width. The numbers in parantheses are the k-values of the band limits.

[b] "z.n.i." means that interactions up to the z^{th} neighbours have been taken into account.

Table 8. Energy bands of $(HF)_\infty$ chains calculated by CO-method at 9 different values of k[a]

Number of band	Energy bands (eV)					
	Geometry No. 1			Geometry No. 3		
	1.n.i.[a]	3.n.i.	5.n.i.	1.n.i.	3.n.i.	5.n.i.
1	10.686(π)	10.689(π)	10.694(π)	9.540(π)	9.496(π)	9.498(π)
	6.914(0)	6.965(0)	6.957(0)	7.737(0)	7.727(0)	7.729(0)
	3.772	3.724	3.737	1.803	1.770	1.769
2	−19.284(0)	−19.334(0)	−19.327(0)	−19.565(0)	−19.588(0)	−19.600(0)
	−21.252(3π/8)	−21.266(3π/8)	−21.276(3π/8)	−21.077(π)	−21.119(π)	−21.130(π)
	1.986	1.932	1.949	1.513	1.531	1.530
3	−21.150(π)	−21.164(π)	−21.174(π)	−21.322(π)	−21.357(π)	−21.368(π)
	−21.297(0)	−21.312(0)	−21.322(0)	−21.469(0)	−21.504(0)	−21.514(0)
	0.148	0.148	0.148	0.147	0.147	0.147
4	−21.276(π/4)	−21.290(π/4)	−21.300(π/4)	−22.894(0)	−22.917(0)	−22.925(0)
	−26.918(π)	−26.921(π)	−26.923(π)	−25.842(π)	−25.826(π)	−25.832(π)
	5.642	5.630	5.623	2.948	2.909	2.907
5	−42.947(π)	−42.974(π)	−42.970(π)	−43.039(π)	−43.097(π)	−43.107(π)
	−48.311(0)	−48.334(0)	−48.331(0)	−48.771(0)	−48.841(0)	−48.849(0)
	5.363	5.361	5.361	5.732	5.744	5.742
Number of band	Geometry No. 2			Geometry No. 4		
	1.n.i.	3.n.i.	5.n.i.	1.n.i.	3.n.i.	5.n.i.
1	9.857(π)	9.859(π)	9.863(π)	8.358(π)	8.293(π)	8.298(π)
	4.777(0)	4.843(0)	4.853(0)	6.023(0)	6.036(0)	6.035(0)
	5.080	5.015	5.011	2.334	2.257	2.263
2	−17.239(0)	−17.294(0)	−17.306(0)	−18.161(0)	−18.202(0)	−18.210(0)
	−20.849(π/2)	−20.867(π/2)	−20.878(π/2)	−20.348(π)	−20.400(π)	−20.419(π)
	3.609	3.573	3.572	2.187	2.199	2.209
3	−20.759(π)	−20.777(π)	−20.795(π)	−20.967(π)	−21.009(π)	−21.022(π)
	−20.938(0)	−20.956(0)	−20.975(0)	−21.147(0)	−21.188(0)	−21.202(0)
	0.180	0.180	0.180	0.180	0.180	0.180
4	−20.883(3π/8)	−20.901(3π/8)	−20.912(3π/8)	−22.457(0)	−22.489(0)	−22.501(0)
	−27.073(π)	−27.068(π)	−27.073(π)	−25.958(π)	−25.972(π)	−25.932(π)
	6.190	6.167	6.160	3.501	3.439	3.431
5	−41.483(π)	−41.499(π)	−41.519(π)	−41.679(π)	−41.742(π)	−41.756(π)
	−47.807(0)	−47.828(0)	−47.843(0)	−48.340(0)	−48.431(0)	−48.441(0)
	6.324	6.329	6.323	6.661	6.689	6.685

[a] see Table 7.

In Table 9 the band structures obtained for the two-dimensional HF clusters with the mentioned four geometries are presented and finally Table 10 contains a comparison of the forbidden band widths.

4. Discussion

Hydrogen Bond Energies

The nonadditivity of hydrogen bond energies in clusters is demonstrated clearly in Table 5. We see that the energy of interaction increases considerably with the number of monomers. The same result was obtained by very accurate

Table 9. Energy bands of two-dimensional $(HF)_\infty$-aggregates calculated by CO method at 9 different values for k_1 and k_2[a]

Number	Geometry No. 1			Geometry No. 3		
of band	1.n.i.	3.n.i.	6.n.i.	1.n.i.	3.n.i.	6.n.i.
1	$10.835(\pi/\pi)$ $6.683(0/0)$ 4.152	$10.764(\pi/2;\pi/2)$ $6.687(0/0)$ 4.086	$10.744(\pi/2;\pi/2)$ $6.649(0/0)$ 4.095	$9.849(\pi/\pi)$ $7.429(0/0)$ 2.420	$9.704(\pi/\pi)$ $7.442(0/0)$ 2.262	$9.869(\pi/\pi)$ $7.591(0/0)$ 2.278
2	$-19.152(0/\pi)$ $-21.211(3\pi/8;3\pi/8)$ 2.059	$-17.499(0/0)$ $-29.111(\pi/4;\pi/4)$ 11.612	$-19.215(0/0)$ $-27.104(\pi/4;\pi/4)$ 7.889	$-19.477(0/0)$ $-21.191(\pi/\pi)$ 1.714	$-17.788(0/0)$ $-27.108(\pi/2;\pi/2)$ 9.310	$-17.666(0/0)$ $-26.953(\pi/2;\pi/2)$ 9.287
3	$-21.111(\pi;\pi/2)$ $-21.288(3\pi;4/\pi)$ 0.177	$-19.405(\pi/2;0)$ $-29.116(\pi/4;\pi/4)$ 9.711	$-21.137(\pi/2;0)$ $-27.108(\pi/4;\pi/4)$ 5.971	$-21.309(\pi/\pi)$ $-21.469(0/0)$ 0.160	$-19.525(\pi/\pi)$ $-27.786(\pi/2;\pi/2)$ 8.260	$-18.386(\pi/\pi)$ $-27.646(\pi/2;\pi/2)$ 9.287
4	$-21.240(\pi/4;3\pi/8)$ $-26.980(\pi/0)$ 5.740	$-19.553(0/0)$ $-30.873(\pi/4;\pi/4)$ 11.320	$-21.270(0/0)$ $-29.870(\pi/4;\pi/4)$ 8.600	$-22.632(0/0)$ $-25.922(\pi/\pi)$ 3.291	$-20.586(0/0)$ $-30.668(5\pi/8;\pi/2)$ 10.082	$-20.444(0/0)$ $-30.547(5\pi/8;\pi/2)$ 10.103
5	$-42.740(\pi/\pi)$ $-48.554(0/0)$ 5.814	$-41.127(\pi/2;\pi/2)$ $-53.826(\pi/4;\pi/4)$ 12.699	$-42.853(\pi/2;\pi/2)$ $-51.831(\pi/4;\pi/4)$ 8.978	$-42.790(\pi/\pi)$ $-49.154(0/0)$ 6.364	$-41.442(3\pi/8;\pi/2)$ $-52.753(\pi/\pi)$ 11.311	$-41.299(3\pi/8;\pi/2)$ $-52.618(\pi/\pi)$ 11.319
Number	Geometry No. 2			Geometry No. 4		
of band	1.n.i.	3.n.i.	6.n.i.	1.n.i.	3.n.i.	6.n.i.
1	$10.015(\pi/\pi)$ $4.407(0/0)$ 5.608	$9.898(\pi/\pi)$ $4.496(0/0)$ 5.402	$9.913(\pi/\pi)$ $4.519(0/0)$ 5.394	$8.719(\pi/\pi)$ $5.628(0/0)$ 3.091	$8.597(\pi/\pi)$ $5.752(0/0)$ 2.845	$8.647(\pi/\pi)$ $5.792(0/0)$ 2.855
2	$-16.991(0/\pi)$ $-20.813(\pi/2;5\pi/8)$ 3.822	$-17.170(0/0)$ $-26.767(\pi/2;\pi/2)$ 9.597	$-17.186(0/0)$ $-26.761(\pi/2;\pi/2)$ 9.574	$-17.948(0/0)$ $-20.465(\pi/\pi)$ 2.517	$-16.339(0/0)$ $-26.227(\pi/2;\pi/2)$ 9.888	$-16.336(0/0)$ $-26.172(\pi/2;\pi/2)$ 9.836
3	$-20.726(\pi;\pi/2)$ $-20.905(0;\pi/2)$ 0.179	$-20.764(\pi;\pi/2)$ $-26.772(\pi/2;\ /2)$ 6.008	$-20.757(\pi;\pi/2)$ $-26.766(\pi/2;\pi/2)$ 6.008	$-20.950(\pi/\pi)$ $-21.143(0/0)$ 0.193	$-19.168(\pi/\pi)$ $-27.475(\pi/2;\pi/2)$ 8.307	$-19.146(\pi/\pi)$ $-27.452(\pi/2;\pi/2)$ 8.307
4	$-20.853(3\pi/8;3\pi/8)$ $-27.170(\pi/0)$ 6.317	$-20.895(3\pi/8;0)$ $-29.612(3\pi/4;\pi/2)$ 8.717	$-20.888(3\pi/8;0)$ $-29.687(3\pi/4;\pi/2)$ 8.798	$-22.215(\pi/\pi)$ $-26.029(0/0)$ 3.814	$-20.201(0/0)$ $-30.402(5\pi/8;\pi/2)$ 10.201	$-20.175(0/0)$ $-30.430(5\pi/8;\pi/2)$ 10.255
5	$-41.329(\pi/\pi)$ $-48.047(0/0)$ 6.718	$-41.445(\pi/\pi)$ $-51.650(3\pi/8;\pi/2)$ 10.205	$-41.427(\pi/\pi)$ $-51.664(3\pi/8;\pi/2)$ 10.237	$-41.481(\pi/\pi)$ $-48.735(0/0)$ 7.254	$-40.049(\pi/\pi)$ $-52.160(3\pi/8;\pi/2)$ 12.111	$-40.020(\pi/\pi)$ $-52.155(3\pi/8;\pi/2)$ 12.135

[a] see Table 7.

Table 10. Widths of the forbidden band between the valence and conduction bands

	Geom. No.	CNDO/2 MO (eV)	CNDO/2 CO (eV)	
			1.n.i.[a]	5.n.i.
$(HF)_\infty$	1	26.217	26.166	26.284
	2	20.679	22.016	22.159
	3	25.928	27.302	27.329
	4	21.469	24.184	24.245
$(H_2O)_\infty$	1	23.070	23.704	23.680
	2	20.000	21.677	21.645

[a] "z.n.i." means, that interactions up to the z^{th} neighbours have been taken into account.

ab initio calculations [2], which of course were restricted to the first few members of the series. Hence we can conclude that there are cooperative effects in the formation of long $(HF)_n$ or $(H_2O)_n$ chains. The increased hydrogen bond energy is brought about by charge transfer along the chain, which leads to an increase of both the basicity of the lone pair and the acidity of the proton involved in the hydrogen bond.

The next interesting question was to find out the number of neighbours, which gave a significant contribution to the increase in bond energy mentioned above. The average hydrogen bond energy $\overline{\Delta E}$ Eq. (8) is not an appropriate quantity for that

$$\overline{\Delta E}(n)=\frac{E[(\mathrm{HX})_n]-\mathrm{n}\cdot E(\mathrm{HX})}{\mathrm{m}}; \qquad (8)$$

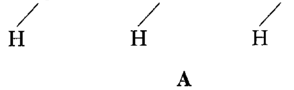
m: number of hydrogen bonds, n: number of monomers; for one dimensional chains: $m = n - 1$

purpose, because the relative weight for the chain ends is different in chains of different length. This is also the reason for the slow convergence of this quantity with increasing length of the chain (Table 5). More suitable for our purpose however, is the energy of the "last" hydrogen bond, which describes the insertion of a monomer in an already existing chain ($\Delta E_{n-1\to n}$)

$$\Delta E_{n-1\to n}=E[(\mathrm{HX})_n]-\{E[(\mathrm{HX})_{n-1}]+E(\mathrm{HX})\} \qquad (9)$$

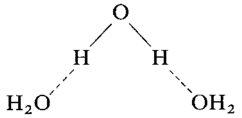
Table 5 shows that in both cases $(HF)_n$ and $(H_2O)_n$ chains this quantity converges much faster than $\overline{\Delta E}$. The last pronounced increase in hydrogen bond energy is found for the fifth neighbour. In the case of infinite chains, of course, $\overline{\Delta E}$ and $\Delta E_{n-1\to n}$ have to become identical.

In Table 6 the hydrogen bond energies for chains of water molecules are compared with the values obtained for three-dimensional tetrahedral arrangements. The additional stabilization of the clusters is reduced drastically. Only a small amount of extra hydrogen bond energy of the oligomers compared with the dimer remains. This result can be explained easiliy. In tetrahedral arrangements of water molecules (Fig. 5) we do not find exclusively the favourable sequential arrangement of water molecules in a chain (**A**),

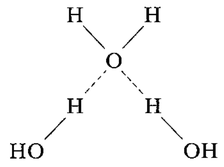


A

but also structural units, where one water molecule uses both hydrogens or both lone pairs from hydrogen bonds (**B**, **C**).



B



C

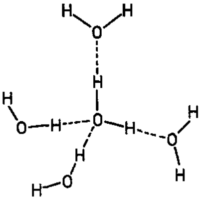


Fig. 5. Tetrahedral arrangement of water molecules

These structures, however, show even lower stabilization energies than twice the hydrogen bond energy of the dimer. The same result has been obtained by an *ab initio* calculation too [2] and can be interpreted in terms of decrease **B** of acidity of the protons or basicity of the lone pairs **C** by charge transfer to the central water molecule. In the three-dimensional network of tetrahedrons all three types of structural units occur. Hence, increase and decrease of hydrogen bond energy compensate each other and finally only a small residual effect remains.

One purpose of this paper is to compare MO and CO methods in their application to large hydrogen bonded clusters. There are two main approximations in the CO treatment which might cause some errors in the results. The Born-v. Karman periodic boundary condition can be interpreted most easily as the assumption of an infinite and cyclic crystal neglecting any kind of surface effects. In the one-dimensional case we represent our crystal by an infinite closed (cyclic) chain, in the two-dimensional case by the surface of an infinite sphere. The second approximation concerns the fact, that in an actual CO-calculation only a small number of neighbours can be taken into account explicitly. The MO-calculations on the other hand are limited to oligomers or clusters with a fairly small number of molecules. In this case it remains uncertain if the results are effected by the end-effects of fairly small chains or not.

In general there is good agreement between hydrogen bond energies extrapolated from MO results and calculated by the CO method (Table 6). In the most cases the CO results indicate somewhat stronger hydrogen bonds with the only exceptions of the two linear $(HF)_\infty$ chains (geometries 1 and 2). It is suggested that the difference between MO and CO results seems to depend on the geometries of the monomeric units and the intermolecular arrangement chosen. The geometries calculated in this paper do not provide enough material to give an explanation of this dependence.

Band structures

Table 3 shows that the bands of the $(H_2O)_n$-chains extrapolated from MO calculations are rather broad. The valence band resulting from a π-level overlaps with the σ-band below it. We find also an overlapping of the two unfilled σ-bands, 1 and 2 in Table 3. Furthermore, we can recognize that the band structure depends rather strongly on the geometry of the periodic unit.

In the case of the $(HF)_n$-chains we find broad bands too (Table 4). Again the three highest filled bands – two π- and one σ-band, lying in the same energy region – overlap strongly. In contrary to the $(H_2O)_n$-chains, however, it was possible here to determine the limits of the individual bands by symmetry arguments applied to the eigenvectors. As we have noticed already in the case of

$(H_2O)_n$ the detailed band structures and sometimes also the degeneracy of the bands is strongly depending on the geometries applied.

The CO-calculations on $(H_2O)_\infty$ and $(HF)_\infty$ show, that the numerical results for the bands depend less strongly on the number of neighbours taken into account than the hydrogen bond energies. Again we find, that in most cases there is a bigger change between 1st and up to 3rd neighbours calculations, than between the calculations including 3rd and 5th neighbours. In almost all cases the positions and widths of the bands differ strongly for all four geometries used.

It is further interesting to point out that, though we have only interactions through hydrogen bonds in our chains, the widths of the bands are rather large. For $(H_2O)_\infty$ we obtain 0.9 eV for the conduction band and 1.2 eV for the valence band in the case of the experimental geometry 1. In the $(HF)_\infty$ chain we find even broader bands: 1.8 eV for the conduction and 1.5 eV for the valence band in the experimental geometry 3.

All these results confirm the well known fact that the CNDO/2 method is only reliable for a qualitative discussion of relative energies and band structures, since the CNDO/2 geometries calculated by energy minimization differ appreciably from the experimental values. Especially the XH-bonds ($X = F$, O) are obtained much too long in CNDO/2 calculations.

Comparing the band structures of the chains $(H_2O)_\infty$ and $(HF)_\infty$ calculated by the CNDO/2–CO method with the extrapolated MO results on oligomers, we find that the energy centers of the bands do not differ very much. The extrapolated MO-band widths, however, are much larger than the corresponding CO-results. This difference most probably is caused by the fact, that the periodicity of the lattice is disturbed too much by effects resulting from the ends. The one electron states seem to be very sensitive to the lack of infinite chain length. Surface states are combined with the states inside the chain leading to broader bands.

The results obtained from two-dimensional periodic HF-aggregates (Table 9) show that the band structures are again quite sensitive to the geometries used. They depend more strongly on the number of neighbours taken into account than the band structures of the one-dimensional chains. This effect is most pronounced if we proceed from first neighbour interactions to interactions up to 3rd neighbours.

The forbidden ranges between conduction and valence bands are very large – 20 to 30 eV, cf. Table 10 – for all kinds of chains independently of the method applied. This result agrees with the well known insulator properties of these systems.

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