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A Theoretical Investigation of Electronic Reorganizations Accompanying Core and Valence Ionization in Simple Hydrogen Bonded Systems

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Non-empirical LCAO MO SCF calculations have been carried out on the ground state and core ionized states of some hydrogen bonded dimers, and in the particular case of H_2O the trimer has also been investigated. Comparison of absolute and relative binding energies and relaxation energies with respect to the corresponding monomers reveals that substantial changes occur in going to the associated species. The relaxation energies for a given core hole are shown to increase on going from monomer to dimer indicating that intermolecular contributions to relaxation energies are of the same sign irrespective of the sign for the shift in core binding energy. Creation of a core hole in the dimer species is shown to give rise to substantial changes in hydrogen bond energies compared with the neutral species. In the particular case of valence holes dominantly of 2*s* and 2*p* character it is shown that trends in shifts and relaxation energies parallel those for the core hole states.

Key words: Hydrogen bonded systems – Ionization, core and valence ~, of hydrogen bonded systems

1. Introduction

There has been considerable interest over the past few years in the theoretical examination of simple hydrogen bonded systems [1]. Extensive non-empirical studies of simple hydrogen bonded dimers has allowed a close examination of the relative importance of the contributing energy terms and as a result Allen has recently produced a simplified model which is capable of some predictive value for systems for which experimental data is as yet unavailable [2]. Whilst the most extensive studies reported to date, which have often included detailed geometry optimizations, refer to what might be termed "normal" hydrogen bonded systems there has also been considerable interest in strongly hydrogen bonded systems, the most comprehensively studied being the HF_2-system [1, 2]. In a recent publication we have investigated in some detail aspects of the potential energy surfaces of the bichloride ion and radical [3]. The ion constitutes a strongly hydrogen bonded system for which experimental data is available for both symmetric and unsymmetric systems. For the corresponding radical $HCl_2^{\cdot}$ the theoretical calculations have clarified the interpretation of experimental data and shown unambiguously that by contrast with the anion, the hydrogen bond strength is quite small.

Table 1. Geometries of monomers, dimer and trimer

Structure	R in Å [a]	θ, in deg. [b]	Ref.
NH_3	1.033	106.2	11
OH_2	0.957	104.54	12
FH	0.917	–	1
$H_3N\ldots H\text{-}OH$	2.91	4.0 [b]	11
$H_2O\ldots H\text{-}OH$	2.85	54.7	12
$HF\ldots H\text{-}OH$	3.11	69.8	1
$H_2O\ldots H\text{-}NH_2$	2.89	60.9	11
$H_2O\ldots H\text{-}F$	2.74	40.4	1
$(H_2O)_3$ [c]	2.85	54.7	12

[a] For monomers, R is the X–H distance, θ is the $H\widehat{X}H$ angle. For dimers, R is the heavy-atom separation, θ is defined in Fig. 1.

[b] This is the calculated angle between the N-acceptor axis and the centre-of-gravity axis of NH_3 (see Fig. 1).

[c] See Fig. 1b.

In a recent series of papers [4] we have systematically investigated electronic reorganizations accompanying core ionizations as a function of the local electronic environment in a series of molecules for the particular cases of C_{1s}, N_{1s}, O_{1s} and F_{1s} levels. Such studies have revealed significant variations in interatomic contributions to relaxation energies and in continuance of this we have considered prototype systems for assessing the importance and absolute magnitude of intermolecular contributions to relaxations accompanying core ionizations. Such an investigation is particularly apposite at this time since a considerable body of evidence is accumulating from studies of adsorbed molecules at surfaces that in the condensed phase there are significant intermolecular (extra molecular) contributions to relaxation energies [5]. As prototype systems which may be studied theoretically in some detail with a relatively modest computational expense, simple hydrogen bonded dimers and trimers have some considerable merit since they represent systems intermediate between isolated molecules for which only intramolecular relaxations are feasible and the condensed phase for which intermolecular contributions may well be of importance.

In this paper we describe a non-empirical LCAO MO SCF investigation of core and valence ionizations for a series of hydrogen bonded dimers involving H_2O, NH_3 and HF and for comparison the corresponding monomers and the H_2O trimer. The motivation for carrying out this work should already be apparent: namely, such systems form prototypes for investigating the importance of relaxation phenomena as a function of association, this forming a logical extension to our previous investigations. Secondly, the available data, both theory and experiment, for normal and strongly hydrogen bonded systems taken in conjunction with the equivalent cores concept suggests that there may well be interesting changes in hydrogen bond strengths in going from the neutral to core-ionized hydrogen bonded systems.

2. Computational Details

The calculations were performed using the ATMOL 2 system of programs [6], implemented on an IBM 370/195. It was of interest to compare basis sets; consequently, the calculations were performed using the following:

a) STO-4.31G [7] basis set, using Raimondi and Clementi's [8] best-atom exponents.
b) STO-4.31G basis set, using "optimized" exponents [4c] (i.e. for the hole-state, the core hole atom valence exponents are of the equivalent core)[1].
c) Double zeta basis set, using Clementi's [9] exponents.

Optimized geometries for both monomers and dimers were used. An extensive amount of data has been published, concerning these optimizations [10]. At the time at which these calculations were commenced, Pople's geometries for the water-ammonia systems, optimized at the STO-3G level [11], were used. For the water dimer and trimer, geometries given by Johnson, Herman and Kjellander [12] were used. These dimer geometries are in fact very similar to those optimized at the STO-4.31G level by Allen [13].

For the water-hydrogen fluoride system, Allen's STO-6.31G optimizations were available [1].

The details of the geometries used are given in Table 1, and Fig. 1.

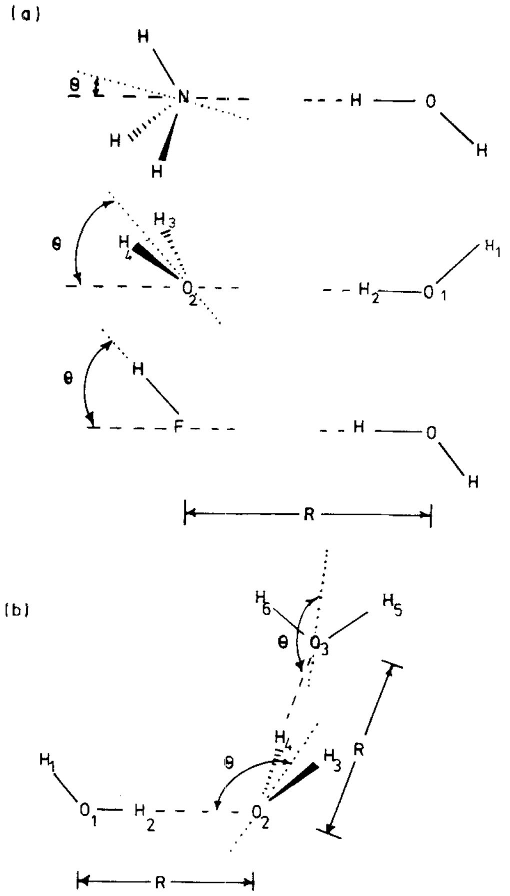

Fig. 1. Definitions of R and θ. Dimers were calculated in the conformations shown. Dotted line is centre of gravity axis of acceptor

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[1] The equivalent cores for core-ionized nitrogen, oxygen and fluorine are taken as oxygen, fluorine and neon, respectively.

It should be noted that for the dimer geometries:

a) All monomer units are held at the previously quoted values.
b) All hydrogen bonds are assumed to be linear.

Neither of these assumptions is likely to be in serious error since the published work shows relatively minor changes in terminal bond length and bond angles consequent upon formation of a given dimer from the relevant monomers [14].

3. Results and Discussions

3.1. Core and Valence Ionizations for Water; Water Dimer and Trimer

3.1.1. Binding Energies

The changes in absolute and relative binding energies for the O_{1s} level in going from water monomer to dimer to trimer as a function of basis set are shown in Table 2[2]. As expected on the basis of our previous work [4] whilst the double zeta and "optimized" 4.31G basis set calculations are in excellent agreement with the experimentally determined binding energy for H_2O (see Table 8) the straightforward STO-4.31G basis set calculation considerably overestimates the binding energy. This largely arises from an underestimate of the relaxation energy as is readily apparent from comparison with Koopmans' Theorem and this will be discussed in some detail in the next section.

Also displayed in Table 2 are the calculated shifts in binding energies for the O_{1s} levels in going from monomer to dimer to trimer. Although the hydrogen bond strengths (for the neutral systems) are quite small (see later) (<0.02 eV) the shifts in core binding energies are substantial. Thus in going from the monomer to dimer the O_{1s} level of the component providing the hydrogen for hydrogen bond formation O1 decreases in binding energy whilst the other component O2 increases such that the computed shift is in excess of 2 eV. Although as we have previously noted the small "unoptimized"

Table 2. Absolute and relative binding energies for the O_{1s} level in water, water dimer, and water trimer (in eV)

		Double Zeta		STO-4.31G		"Optimized" Exponent	
Molecule[a]		B.E.	ΔB.E.	B.E.	ΔB.E.	B.E.	ΔB.E.
Water Monomer	O 1s	539.75	(0)	545.49	(0)	539.12	(0)
Water Dimer	O1 1s	538.42	−1.33	544.11	−1.38	537.85	−1.27
	O2 1s	540.51	+0.76	546.39	+0.90	539.98	+0.86
Water Trimer	O1 1s	538.03	−1.72	543.72	−1.77	537.46	−1.66
	O2 1s	539.21	−0.55	545.04	−0.45	538.73	−0.39
	O3 1s	540.86	+1.10	546.74	+1.25	540.24	+1.21

[a] For details of numbering, see Fig. 1b.

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[2] Absolute binding energies are defined as energy-differences between neutral and ionized systems, with respect to the vacuum level.

4.31G basis overestimates absolute binding energies the computed differences are closely similar to those for the "optimized" and double zeta basis. A similar picture emerges for the trimer. Namely, O3 which acts as an electron donor is calculated to shift to higher binding energy, with respect to the monomer, whilst O1 shifts to lower binding energy. The central oxygen O2 of the water molecule which acts as both a donor and acceptor is calculated to decrease in binding energy and indeed comparison with the dimer suggests that a simple additive model is applicable. Thus considering the shifts in binding energy for the O_{1s} levels of a water molecule either providing the hydrogen or the lone pair for bonding to the hydrogen of the hydrogen bond suggests a shift with respect to the monomer for the central oxygen of the trimer that is in excellent agreement with that computed directly for the trimer (viz., the O1, O2 shift for the dimer vs. the shift with respect to the monomer for O2 in the trimer). The span in binding energies for the trimer is calculated to be substantially (about 0.7 eV) larger than for the dimer. With the development of molecular beam techniques for producing such species in the gas phase and with the advent of ESCA instrumentation requiring extremely small partial pressures for the production of high resolution spectra of adequate signal-to-noise ratio it will be of interest to see if these predictions are verified. As a corollary to this it seems likely that in going from the gas phase monomer to the condensed phase (physically adsorbed at a surface for example) at sub-monolayer coverage where association might produce a range of hydrogen bonded species (dimers, trimers etc.) there would be a considerable variation in line width as a function of degree of association at the surface. Unfortunately, the literature data refers either to mono or multilayer coverage [5, 15] so that there is no data currently available which is pertinent to this point.

For the monomer and dimer it is possible to identify unambiguously the O_{2s} levels which are somewhat core-like in character. This also proved to be the case for the trimer; however, with the double zeta basis set, there were convergence problems, in that it was difficult to converge on the O_{2s} levels *localized* on the individual oxygen atoms. For all three systems it proved possible to identify valence-ionized states dominantly of O_{2p} character; however, there were again convergence problems for the double zeta basis set. It is of interest to compare the shifts with those for the O_{1s} levels as shown in Table 2. As a starting point we may briefly consider the absolute binding energies computed for the O_{2s} and O_{2p} valence levels of water monomer (shown in Table 8). The extensive calculations of Meyer [16] indicate that correlation energy corrections are opposite in sign for the $2s$ and $2p$ levels and this is clear from the present data for which the ΔSCF calculations overestimate the binding energy for the former and underestimate for the latter. Since the orbitals are relatively localized however, we may reasonably expect that correlation energy terms would tend to cancel in comparing *shifts* in binding energies.

A perusal of the data in Table 3 clearly demonstrates that both in terms of magnitude and sign the shifts for the valence O_{2s} and O_{2p} levels are closely similar to those for the core levels, despite the fact that the absolute binding energies differ by a substantial amount. Although convergence problems prevent a detailed comparison of the computed shifts as a function of basis set it is worthwhile noting that the shifts computed for the trimer using Koopmans' Theorem are closely similar for the double zeta and

Table 3. Changes in valence binding energies on association

	STO-4.31G		Double Zeta	
	Δ (ΔSCF)	Δ Koopmans'	Δ (ΔSCF)	Δ Koopmans'
Oxygen $2s$[a]				
Monomer	(0)	(0)	(0)	(0)
Dimer O1	−1.16	−1.05	−1.16	−1.05
O2	+0.98	+1.25	+ 0.86	+1.14
Trimer O1	−1.55	−1.42		−1.42
O2	+0.21	+0.21		+0.11
O3	+1.32	+1.62		+1.51
Oxygen $2p$[a]				
Monomer	(0)	(0)	(0)	(0)
Dimer O1	−1.12	−1.05	−1.12	−1.04
O2	+0.96	+1.53	+0.53	+1.42
Trimer O1	−1.12	−1.40		−1.40
O2	−0.11	−0.23		+0.52
O3	+1.34	+1.30		

[a] Absolute B.E.s quoted in Table 8.

STO-4.31G bases. This is not unexpected on the basis of a comparison of the calculated (ΔSCF) shifts for the dimer shown in Table 2.

3.1.2. Relaxation Energies

The calculated relaxation energies and differences therein in going from monomer to dimer to trimer for the particular case of the O_{1s} levels are shown in Table 4. As we have previously noted, the particular features of interest in this investigation are the intermolecular contributions to relaxation energies as a function of association.

Whilst the absolute magnitudes of the relaxation energies are underestimated by the calculations at the 4.31G level, the differences are in excellent agreement with those obtained for the double zeta basis set. Comparison with the shifts in binding energies recorded in Table 2 reveals that irrespective of whether the binding energy of a given O_{1s} core level increases or decreases in going from monomer to dimer to trimer, the relaxation energies are always larger for the associated species. Furthermore the relaxation energy change is largest for O2 of the trimer which involves the central of the three units. This increase in relaxation in going to the associated systems is in agreement with experimental data on physisorbed species at surfaces [5, 15], where the difference in energy scales when due allowance has been made for work function has been attributed to this source. An interesting feature arising from these experimental data is that the so-called "relaxation shift" is observed to be virtually the same for both core and valence levels, which at first sight might seem a little surprising since the absolute magnitudes of the relaxation energies themselves are so different. By contrast, for chemisorbed species in which there is substantial perturbation of certain valence levels (and hence indirectly core levels) the contributions to shifts arising from changes in relaxation energies are difficult to unravel.

Table 4. Changes in O_{1s} relaxation energies on association of water

Molecule		Double Zeta	STO-4.31G	"Optimized" Exponent	
				a	b
Monomer	O 1s	(0)	(0)	(0)	(0)
Dimer	O1 1s^c	+0.11	+0.16	+0.06	+0.06
	O2 1s	+0.37	+0.38	+0.42	+0.66
Trimer	O1 1s^c	+0.13	+0.20	+0.08	+0.08
	O2 1s	+0.51	+0.57	+0.51	+0.75
	O3 1s	+0.37	+0.41	+0.45	+0.99

[a] The reference for the relaxation energy corresponds to Koopmans' Theorem for the unoptimized STO-4.31G basis.

[b] The reference for the relaxation energy corresponds to the average of the negative of the Fock eigenvalue for the g-state molecule in the "optimized" and unoptimized STO-4.31G basis sets.

[c] Absolute values of R.E. are quoted in Table 8.

It is clear that hydrogen bond formation involves a substantial perturbation of the valence electron distribution and hence although as we have seen the relaxation energies for the core levels increase on association, matters are not so clear-cut for the valence levels and this is indicated in Table 5. For the essentially core-like O_{2s} levels the relaxation energies for dimer and trimer hole states are larger than for the monomer and it is significant that the magnitude of these differences are comparable with those for the O_{1s} core levels themselves, despite the large difference in absolute magnitude for the relevant relaxation energies.

Table 5. Changes in O_{2s} and O_{2p} relaxation energies on association of water

		STO-4.31G	Double Zeta
Oxygen 2s^a			
Monomer		(0)	(0)
Dimer	O1	+0.11	+0.10
	O2	+0.27	+0.28
Trimer	O1	+0.13	
	O2	+0.38	
	O3	+0.30	
Oxygen 2p^a			
Monomer		(0)	(0)
Dimer	O1	+0.07	+0.07
	O2	+0.56	+0.50
Trimer	O1	+0.09	
	O2	−0.12	
	O3	−0.04	

[a] Absolute values of R.E. quoted in Table 8.

3.1.3. Population Analysis

Although a Mulliken population analysis provides only a crude indication of electron distributions in molecules it is none the less useful in outlining broad features of charge migrations. Considering firstly the ground state species, we may investigate the change in total population for a given water molecule as a function of association. In going from the monomer to dimer, for example, electron density is transferred from the water molecule containing O2 to that containing O1, and the calculated changes in populations for the two units are 0.039 and 0.108 electrons respectively for the double zeta and 4.31G basis sets. In going from the dimer to trimer, considering firstly hydrogen bonding the monomer unit containing O3 to that containing O2, the change in population on the former is 0.042 (0.116) electrons for the two basis sets, i.e. almost the same charge transfer as computed for the dimer. The concomitant modification of charge transfer involving the other hydrogen bond is extremely small (0.006 electrons for both basis sets). We may alternatively view the trimer as being formed from hydrogen bonding involving the monomer unit containing O1 and the dimer (monomer providing hydrogen of hydrogen bond). The charge migration from dimer to monomer then amounts to 0.045 and 0.114 electrons for the two bases, comparable to those discussed above. The change in population for the monomer unit containing O3 is again very small (0.008, 0.004 electrons).

For the particular case of the STO-4.31G basis set we have computed the bond overlap population of the dimer and it is interesting to note that this is quite close in magnitude to the calculated change in population for the monomer units on forming the dimer. This implies not unreasonably that charge transfer is dominantly into the hydrogen bonding region and we will return to this theme in a later section.

The changes in valence electron populations on going from the ground state to core-ionized species are shown in Table 6 and from these certain trends are clearly discernible. For water monomer, creation of a core hole on oxygen results in a substantial increase in valence electron population on oxygen at the expense of the two hydrogens, and it is interesting to note that whilst the absolute magnitudes of electron populations depend very markedly on the basis set, the differences reported in Table 6 are remarkably similar. For the dimer and trimer there is again a substantial increase in valence electron population on the atom on which the core hole is located largely at the expense of the directly bonded hydrogens. If the directly bonded hydrogen is involved in hydrogen bonding, the charge flow is highly asymmetric, a much greater proportion of the overall increase in electron population on oxygen coming at the expense of electron migration from the other directly bonded hydrogen.

For the core-ionized species it is of interest to compare the overall changes in valence electron population of a given monomer as a function of association and compare these with the corresponding figures for the ground states. For the dimer we have previously indicated that formation from the monomers is accompanied by electron transfer to the molecule providing the hydrogen for hydrogen bond formation. Creation of a core hole on O1 in the dimer considerably enhances this electron drift from one unit to the other and the computed increase in population for the monomer unit containing O1 compared with the neutral system is 0.065e and 0.083e for the double zeta and STO-4.31G bases respectively. By contrast, creation of a core hole on O2 drastic-

Table 6. Changes in valence population on core-ionization of water species

		Double Zeta	STO-4.31G			Double Zeta	STO-4.31G
Monomer[a]	O*[b]	−0.528	−0.556	Trimer[a]	O1*	−0.500	−0.522
	H1	+0.264	0.278		H1	+0.279	+0.292
	H2	+0.264	0.278		H2	+0.149	+0.139
					O2	−0.019	−0.009
					H3	+0.049	+0.054
					H4	+0.030	+0.028
Dimer[a]	O1*	−0.503	−0.524		O3	−0.018	−0.017
	H1	+0.277	+0.289		H5	+0.024	+0.027
	H2	+0.161	+0.152		H6	+0.005	+0.008
	O2	−0.027	−0.019				
	H3	+0.046	+0.051		O1	+0.072	+0.079
	H4	+0.046	+0.051		H1	+0.038	+0.041
					H2	−0.058	−0.049
	O1	+0.075	+0.082		O2*	−0.526	−0.559
	H1	+0.039	+0.041		H3	+0.261	+0.270
	H2	−0.067	+0.058		H4	+0.148	+0.135
	O2*	−0.547	−0.587		O3	−0.023	−0.015
	H3	+0.250	+0.261		H5	+0.044	+0.049
	H4	+0.250	+0.261		H6	+0.044	+0.049
					O1	+0.022	+0.025
					H1	+0.006	+0.007
					H2	−0.015	−0.014
					O2	+0.069	+0.072
					H3	+0.034	+0.035
					H4	−0.065	−0.056
					O3*	−0.546	−0.587
					H5	+0.247	+0.259
					H6	+0.248	+0.259

[a] For details of numbering, see Fig. 1.
[b] *Indicates core-ionized atom.

ally reduces the capabilities of the monomer unit for electron transfer for hydrogen bond formation and the computed reductions in electron transfer compared with the ground state are 0.047e and 0.066e for the two basis sets. The population analysis with the double zeta basis set even suggests that the overall electron transfer is very small and in the opposite sense to that for the ground state. A similar picture emerges for the trimer. Creation of a core hole on O1 is accompanied by an increase in electron transfer from the dimer of 0.07e (0.092e) and it is significant that there is a concomitant increase of 0.013e (0.019e) in electron donation from the monomer containing O3, and it will become clear that this is related to the computed change in hydrogen bond strength for the core-ionized species. By contrast, creation of a core hole on O3 causes a significant reduction in electron transfer to the dimer of 0.050e (0.069e) and indeed for the double zeta basis set the monomer unit in the core-ionized species becomes very weakly electron accepting.

The core ionization of the central monomer unit (O2) is accompanied by a considerable increase in valence electron population of 0.1183 (0.15e) the donation from the monomer units containing O1 and O3 being somewhat similar: 0.052e (0.070e) and 0.066e (0.083e).

3.1.4. Changes in Hydrogen Bond Strength Accompanying Core Ionizations

The substantial reorganization of valence electron distribution concomitant with core ionization inferred from the population analyses would suggest significant changes in the energetics of hydrogen bond formation.

For the dimer, the calculated hydrogen bond energy of 4.8 kcal/mole for the double zeta basis set is in good agreement with experiment (5.1 kcal/mole) [17], whilst the smaller basis set tends to overestimate the bond strength (11.9 kcal/mole). Comparison of dimer and trimer provides a hydrogen bond energy of 6.5 kcal/mole (14.1 kcal/mole), whilst for dissociation of trimer into monomers an average bond energy of 5.7 kcal/mole (12.9 kcal/mole) is obtained, where the figures in brackets refer to the STO-4.31G basis. Both of these are significantly higher than for the dimer itself. The effect of creating a core hole in the dimer and trimer is dramatic in terms of the computed changes in hydrogen bond strength and this is indicated in Table 7.

Considering firstly the dimer, creation of a core hole on O1 for which the population analysis indicates an increase in electron donation from the monomer containing O2, is accompanied by a large increase in hydrogen bond strength such that it is now comparable with typical hydrogen bond strengths for such species as HF_2^- and HCl_2^- [18]. By contrast, the hydrogen bond strength for the species with the core hole located on O2 is very substantially less than for the neutral system and it is significant that the changes in hydrogen bond energy are closely similar for the two bases sets[3].

Table 7. Changes in hydrogen bond strengths on core ionizations

Molecule	Core Hole	Hydrogen Bond between	Double Zeta in kcal/mole	STO-4.31G in kcal/mole
Dimer[a]	O1*	O1...O2	+30.66	31.77
	O2*	O1...O2	−17.42	−20.74
Trimer[b]	O1*	O1...O2	+40.57	+41.98
		O2...O3	+9.95	+10.17
	O2*	O1...O2	−17.16	−20.27
		O2...O3	+30.90	+32.25
	O3*	O1...O2	−7.19	−7.03
		O2...O3	−24.63	−27.74

[a] Relative to ground-state hydrogen bond strength.
[b] Relative to average ground-state hydrogen bond strength.
(A positive sign indicates an *increase* in hydrogen bond energy.)

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[3] It should be evident from the data in Table 7 and Fig. 4 (to be discussed later) that the "vertical" binding energies referred to here are associated with a repulsive part of the potential energy surface for the core-ionized species (as opposed to the attractive part for the O1 core-ionized system, in this case), and represent lower bounds to the hydrogen bond strength. This does not necessarily imply that the surface for this core-ionized state does not have a minimum which is lower in energy than the dissociation limit.

For the trimer, creation of a core hole on O1 is again accompanied by a very large increase in hydrogen bond energy and this effect is relayed to the other hydrogen bond. These changes are again qualitatively in line with those expected on the basis of the population analyses. Creation of a core hole an O2 increases the hydrogen bond strength with respect to the monomer unit containing O3 and causes a decrease with respect to O1. Finally for core hole O3 in the trimer both hydrogen bond energies decrease with respect to the neutral system.

It should be emphasized that these energies refer to vertical processes and represent lower bounds to the adiabatic processes. Thus it seems likely that the large increase in hydrogen bond strength in certain cases will be accompanied by a decrease in hydrogen bond length, whereas for those systems in which there is a decrease in hydrogen bond strength the equilibrium geometries may well involve an increase in hydrogen bond length. The lifetimes of the core hole states, however, are determined by de-excitation predominantly by the Auger process and are likely to be in the range of $\sim 10^{-13}$ sec. This is several orders of magnitude too short to be of any chemical significance and since the transitions from the ground state are vertical a discussion of hydrogen bond energies in terms of vertical processes seems eminently reasonable. The large calculated changes in hydrogen bond energies and the implication of substantial changes in equilibrium geometries for the core-ionized species does however have important ramifications with respect to vibrational fine structure accompanying core ionization, a field of considerable current interest from both an experimental and theoretical standpoint [4d].

3.2. Core and Valence Ionization for Hydrogen Bonded Dimers Involving H_2O and H_2O, NH_3 and HF

3.2.1. Binding Energies

The calculated absolute binding energies for the monomers are shown in Table 8, for the core levels and for valence orbitals largely of lone pair character. For the N_{1s}, O_{1s} and F_{1s} levels, the calculations are in excellent agreement with experiment for the double zeta and "optimized" STO-4.31G bases [19-22]. For the STO-4.31G basis set however, the relaxation energies are underestimated and consequently the calculated absolute binding energies are too large. For the valence levels the calculated binding energies are overestimated (2*s*) or underestimated (2*p*) compared with experiment and this is attributable not only to deficiencies in the basis sets but more importantly to the neglect of correlation energy changes which are opposite in sign for the two levels. The changes in core binding energies with respect to the appropriate monomer are shown for all of the dimer species studied in Fig. 2.

Since the shifts in binding energies and changes in relaxation energies (to be discussed in the next section) are virtually the same for all three basis sets employed (namely double zeta, STO-4.31G and "optimized" STO-4.31G) only the results for the double zeta basis are presented in Fig. 2.

Considering firstly the O_{1s} core-ionized species, the shifts with respect to the water monomer are in the opposite sense depending on whether the hydrogen is provided by

Table 8. Absolute binding energies and relaxation energies of monomer units

Molecule	Level	Double Zeta		STO-4.31G		"Optimized" Exponent		Experimental
		B.E.	R.E.	B.E.	R.E.	B.E.	R.E.[a]	B.E.
Ammonia	N 1*s*	405.76	16.82	409.91	13.68	405.73	17.83 16.56	405.58 [19]
	2*s*	29.20	1.63	29.15	1.82			~27 [20]
	2*p* (lone pair)	9.09	2.10	8.46	2.14			10.85 [21]
Hydrogen fluoride	F 1*s*	693.94	20.91	701.27	16.22	692.25	25.24 22.15	694.22 [19]
	2*s*	41.18	2.06	40.26	2.36			39.56 [22]
	2*p* (lone pair)	14.81	2.44	12.01	2.67			16.12 [22]
Water	O 1*s*	539.75	19.16	545.49	15.35	539.12	21.71 19.55	539.7 [21], 539.88 [19]
	2*s*	34.82	1.87	34.45	2.16			~32 [20], 32.2 [21],
	2*p* (lone pair)	11.19	2.43	9.55	2.58			12.61 [21]

[a] Upper R.E. value obtained from (g.st. Koopmans' – ΔSCF B.E.), lower R.E. value obtained from (av. Koopmans' – ΔSCF B.E.).

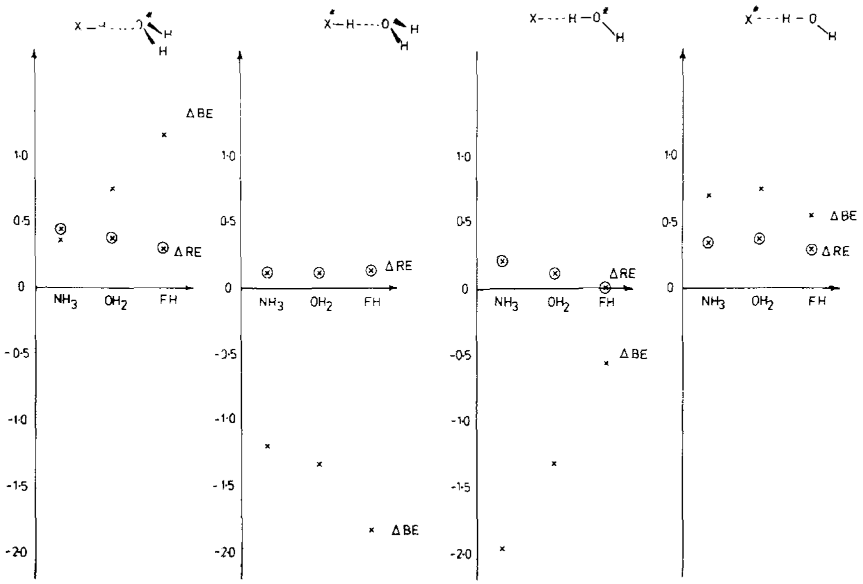

Fig. 2. Changes in core (1*s*) binding energies and relaxation energies on association (in eV). * Indicates location of core hole

X or by the water monomer under consideration. For either situation the magnitude and direction of the shifts are qualitatively in agreement with simple electronegativity considerations. Thus with water providing the hydrogen for the hydrogen bond, the effect of this hydrogen bonding on the O_{1s} level is a shift to lower binding energy, the effect being largest for the best donor: viz. the shifts are in the order $NH_3 > H_2O > HF$. Conversely, if a core hole is created on the oxygen of a water monomer hydrogen for the hydrogen bond, the reduced efficiency as a donor is manifest in a shift to higher binding energy which increases in the order $NH_3 > H_2O > HF$.

The picture which emerges for the systems in which water is hydrogen bonded to X and a core hole is created on X is slightly more complicated. Thus when X provides the hydrogen for hydrogen bond formation the increased electron donation from water lowers the core binding energies, the shifts being in the order $NH_3 < H_2O < HF$. When the hydrogen for hydrogen bond formation is provided by water monomer and the core hole is created on X, the shifts are small and to higher binding energy and are comparable for $X = NH_3$, H_2O and HF. Although superficially this may seem surprising, the previous discussion on the water dimer and changes in population accompanying core ionization therein provides a straightforward rationalization. Thus in comparing the populations for the core-ionized dimers with those for the monomers from which they may be constructed, the calculated changes are extremely small and indeed for the double zeta basis set the overall electron transfer is to the core-ionized monomer.

In the particular case of a neutral water monomer X, the electronic environment is not too dissimilar to the isolated core-ionized species. It is interesting to note that for the dimers involving core holes located on the water monomer the shifts in binding energy for the two distinct hydrogen bonding situations show a smooth decrease in the series $NH_3 > H_2O > HF$ (shifts 2.35, 2.08, 1.73 respectively), the centroid of these shifts[4] being at a lower binding energy for $X = NH_3$ and H_2O, and higher binding energy for X = HF, the energy reference being the isolated monomer.

For these dimers, hole states corresponding approximately to removal of valence 2*s* and 2*p* electrons may be identified from the manifold of valence-ionized states and behave in an analogous manner to the core hole states. This is shown in Fig. 3 and the comparison with Fig. 2 is quite striking both in respect of the signs and magnitudes of the calculated shifts.

3.2.2. Relaxation Energies

As we indicated at the outset, one of the prime motivations for this study was to investigate changes in relaxation energies as a function of association. The absolute

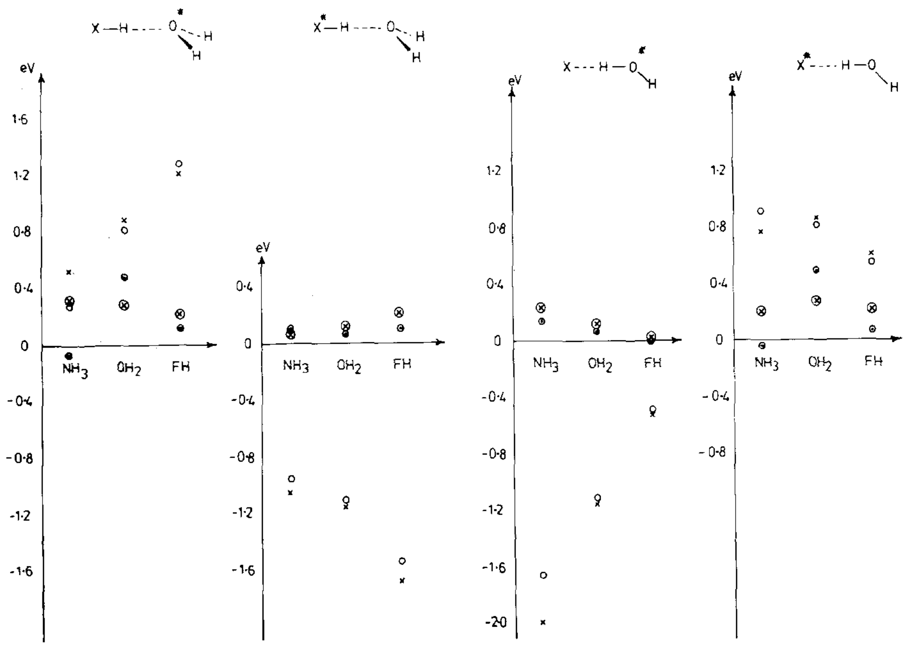

Fig. 3. Changes in valence (2*s* and 2*p*) binding energies and relaxation energies on association (in eV). x Indicates changing in 2*s* binding energy, ⊗ indicates change in 2*s* relaxation energy, ○ indicates change in 2*p* binding energy, ⊙ indicates change in 2*p* relaxation energy

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[4] The centroids are defined by taking the average of the O_{1s} shifts, with respect to the water monomer, for the two, distinct hydrogen bonding situations, viz: $X \ldots H\text{-}\overset{*}{O}H$ and $X\text{-}H \ldots \overset{*}{O}H_2$.

magnitudes of the computed relaxation energies for the monomers for both the core and valence 2*s* and 2*p* levels are given in Table 8. In defining relaxation energies computed from the "optimized" STO-4.31G basis two possibilities present themselves. Firstly, the reference for the unrelaxed system can be taken as the negative of the Fock eigenvalue for the neutral molecule using the "unoptimized" STO-4.31G basis set, or alternatively we may average this with the corresponding Fock eigenvalue for the neutral molecule using the "optimized" basis. Comparison with the relaxation energies computed with the double zeta basis set shows that the relaxation energies based on the "optimized" STO-4.31G calculations for the hole state species are in much better agreement than those computed directly for the standard 4.31G basis. The absolute magnitudes of the relaxation energies computed from the "optimized" STO-4.31G basis are closer to those for the double zeta basis when the reference for the "unrelaxed" system is taken as the average over the Fock eigenvalues. In this connection it is worth noting that similar treatments have been carried out for all of the dimers and relevant hole states and the trends and differences for the relaxation energies are in good agreement with those calculated with the double zeta basis sets. However, the differences are rather closer to those calculated using the double zeta basis set when the reference for the relaxation energies (computed from the hole state calculations using the "optimized" equivalent core exponents) correspond to Koopmans' Theorem for the "unoptimized" STO-4.31G basis set calculations for the neutral molecule as may be seen, for example, in Table 4. The changes in relaxation energy on going from monomer to dimer for a given core hole are shown in Fig. 2. Considering firstly hydrogen bonded dimers involving a core hole on oxygen it is clear that although there are substantial shifts to lower binding energies when water provides the hydrogen for the hydrogen bond, and substantial increases in binding energy when the hydrogen bond is provided by X, the relaxation energy change with respect to the monomer is always positive. That is, in going to the associated system the relaxation energy increases irrespective of whether the binding energy for the core level increases or decreases. A similar situation obtains for dimers involving a core hole located on X. In all cases the increase in relaxation energy in going from monomer to dimer is relatively small, being in the range 0 to 0.42 eV. For the valence hole states the changes in relaxation energy are also shown in Fig. 3. For the 2*s* levels the absolute magnitudes of the changes in relaxation energy are closely similar to those for the core levels. This is interesting since the absolute magnitudes of the relaxation energies differ by an order of magnitude. The changes in relaxation energy on association are therefore proportionately larger for the valence 2*s* levels.

3.2.3. Population Analysis

As a starting point we may briefly consider the neutral dimers. Formation of a given hydrogen bonded dimer is accompanied by electron transfer to the monomer providing the hydrogen for hydrogen bond formation. The relative magnitudes of the electron transfer are consistent with a qualitative picture based on electronegativity considerations. Thus for H_2O acting as the acceptor, the increase in electron population compared with the monomer is in the order $NH_3 > H_2O > HF$. For the water monomer acting as a donor the dependence on the acceptor providing the hydrogen for hydrogen bond formation is somewhat less marked.

Considering now the hole state species, the calculated changes in electron population in terms of electron density transferred from one monomer unit to another are shown in Fig. 4 for the double zeta basis set. The corresponding figures for the STO-4.31G basis are in excellent overall agreement with these, as might have been anticipated from the results previously discussed for water, water dimer and trimer. Creation of a core hole on X, when X provides the hydrogen for hydrogen bond formation to water, is accompanied by increased electron donation from the water molecule in the order X = HF > $H_2O > NH_3$. These increases exactly parallel the change in bond overlap population between oxygen and the hydrogen involved in hydrogen bonding. We might therefore anticipate an increased hydrogen bond energy for such core-ionized species. With X acting as a donor to a core-ionized water molecule (which provides the hydrogen for hydrogen bond formation), there is again an increase in valence electron population on the core-ionized monomer compared with the ground state and this is in the order

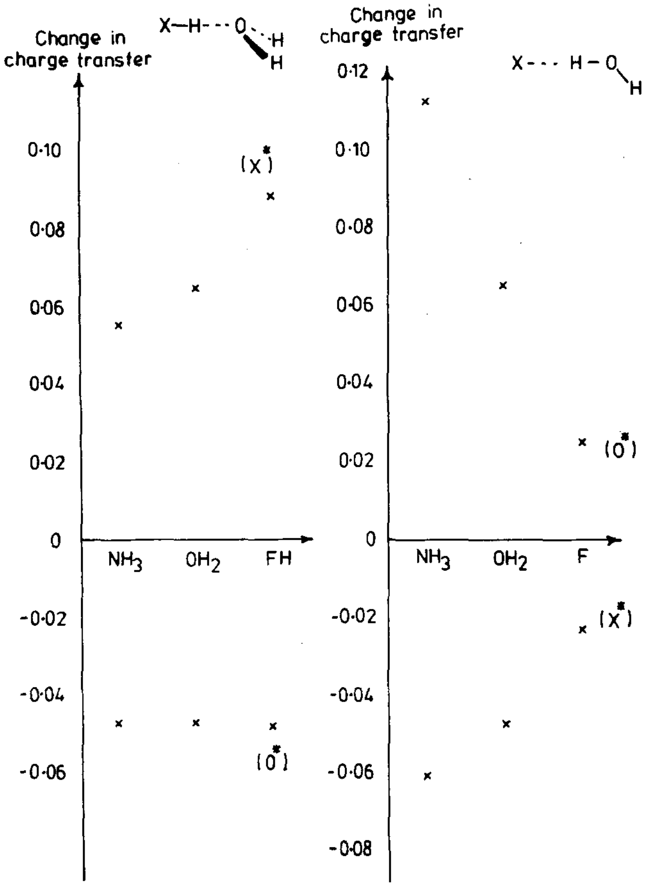

Fig. 4. Changes in electron population for a given monomer (relative to the ground-state dimer) on core ionization. + Sign indicates an *increase* in population transferred, – sign indicates a *decrease* in population transferred

$NH_3 > H_2O > HF$. The changes in populations are again largely accounted for by an increase in overlap population in the hydrogen bond region.

Creation of a core hole on the monomer unit not providing the hydrogen for hydrogen bond formation results in all cases in a reduction of valence electron population transfer with respect to the neutral dimers. For H_2O providing the hydrogen for hydrogen bond formation the changes in electron population are least for X = HF and largest for X = NH_3, whilst if X provides the hydrogen for hydrogen bond formation the reduction in population is closely similar for X = NH_3, H_2O and HF. The changes in bond overlap populations for the hydrogen bonds again follow these trends.

3.2.4. Changes in Hydrogen Bond Strengths Accompanying Core Ionizations

The population analyses, showing as they do substantial electronic reorganizations on creation of core holes in the dimer species, suggest that the hydrogen bond strengths in these species may be considerably different than for the neutral molecules.

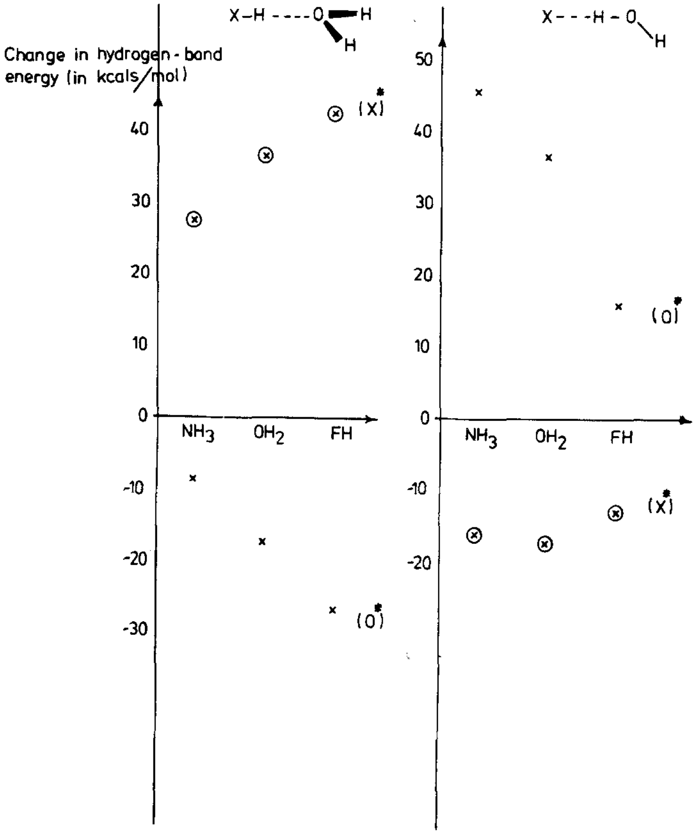

Fig. 5. Change in hydrogen bond strength (in kcal/mole) on core ionization of dimers. ⊗ Indicates core (1*s*) ionization on X (X = NH_3, H_2O, HF), x indicates core (1*s*) ionization on O in the other H_2O monomer unit

The calculated changes in hydrogen bond energies with respect to the neutral dimers are shown in Fig. 5 for the double zeta basis set and those for the STO-4.31G basis are closely similar. The computed changes are substantial and in a direction that might have been anticipated from the population analysis. Thus creation of a core hole on a monomer which provides the hydrogen for hydrogen bond formation substantially increases the hydrogen bond energy such that the species may be classified as strongly hydrogen bonded systems. By contrast, creation of a core hole on the other monomer unit leads to a substantial decrease in hydrogen bond strength (see footnote to 3.1.4).

As we have previously noted the lifetimes for such core-ionized species before undergoing de-excitation by the Auger process are such that the interesting chemistry which such species might be expected to exhibit is not available for direct investigation. However, the drastic changes in potential surfaces compared with the neutral dimers implied by these results suggest that the core ionizations should be accompanied by considerable vibrational fine structure. With the advent of high resolution instrumentation the direct study of such species in molecular beams at relatively modest partial pressures becomes a feasibility and it will then be of some interest to compare the theoretical predictions reported here with the experiment data.

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