

Effect of cooperativity on the O-H stretching force constant in associated water species

M C SHIVAGLAL, R BRAKASPATHY and SURJIT SINGH*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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Abstract. CNDO/force calculations have been employed to calculate the O-H stretching force constants for various structures of associated water species such as water-dimethylether, water-acetonitrile, water-lithium fluoride, linear and cyclic water polymers. The variation in the O-H stretching force constant in $A_m \dots O-H \dots D_n$ species where A_m and D_n represent, respectively, m number of electron-acceptor and n number of electron-donor molecules, is explained on the basis of the cooperativity effect. With increasing electron-acceptor power of A and electron-donor power of D, the hydrogen-bonded O-H stretching force constant is significantly reduced. The results obtained in these studies are in general agreement with experimental observations reported earlier.

Keywords. CNDO/force; force constant; associated water species; cooperativity effect.

1. Introduction

Frank and Wen (1957) proposed the cooperativity effect for the stability of the hydrogen-bonded structure of liquid water. Del Bene and Pople (1970, 1971, 1973) and Hankins *et al* (1970, 1973) on the basis of their *ab initio* MO studies concluded that linear water polymers exhibit a cooperative effect which results in the nonadditivity of hydrogen-bond energies. It was found that a linear trimer has a stabilization energy greater than the sum of the binding energies of the dimers and the energy of interaction of nonbonded water molecules. These observations indicate that the hydrogen-bond in $\dots O-H \dots$ species is stronger than that in $O-H \dots$ species. Several other studies (Newton and Ehrenson 1971; Lentz and Scheraga 1973, 1974; Johansson *et al* 1974; Karpfen *et al* 1974; Kistenmacher *et al* 1974; Schuster 1976; Hinton and Harpool 1977; Sheiden *et al* 1979; Clementie *et al* 1980; Scheiner 1983; Scheiner and Nagle 1983; Gaw *et al* 1984) have demonstrated that a string of several hydrogen-bonds can display a substantial amount of cooperativity with each member acting to enhance the stability of the total structure and affect the geometries of the others. Recent calculations by Brakaspathy and Singh (1986) on the effect of molecular interactions on the O-H stretching force constants for associated water species have augmented the existence of cooperativity. *Ab initio* calculations by Kurnig *et al* (1986) on $H_3N-HF-HF$ and $H_3P-HF-HF$ also show that the addition of the third sub unit to a pre-existing dimer leads to the

*For correspondence

contraction of the hydrogen-bond length and the stretching of the HF bonds and these stretchings are directly proportional to the reductions in the force constants. Some of the experimental investigations on the cooperativity effect include the work of Couzi *et al* (1970) on HF, Symons (1981) and Symons *et al* (1979, 1981) on alcohol and Luck and Schrems (1981, 1982) on alcohol and water in matrix isolated species. Recently Kleeberg *et al* (1986) have demonstrated the effect of cooperativity in aqueous solutions of electrolytes as well as solutions of simple alcohols and 1,4-butane diol in carbon tetrachloride. As an extension to our work on the effect of cooperativity on O–H stretching force constants for associated water species, we have now calculated the O–H stretching force constants for various hydrogen-bonded complexes using CNDO/force method. The details of the method may be found in our earlier publications (Kanakavel *et al* 1976; Annamalai and Singh 1982, 1983; Jothi *et al* 1982; Brakaspathy *et al* 1985; Brakaspathy and Singh 1985, 1986, 1987). An attempt is also made to quantify the cooperativity effect in terms of the O–H stretching force constants.

2. Results and discussion

2.1 Symmetrical and unsymmetrical hydrogen-bonded water complexes

In figures 1 and 2 are shown the stretching force constants for 9 associated species formed between water and dimethylether (W–DME) as well as between water and acetonitrile (W–AN). The O–H stretching force constants for the corresponding

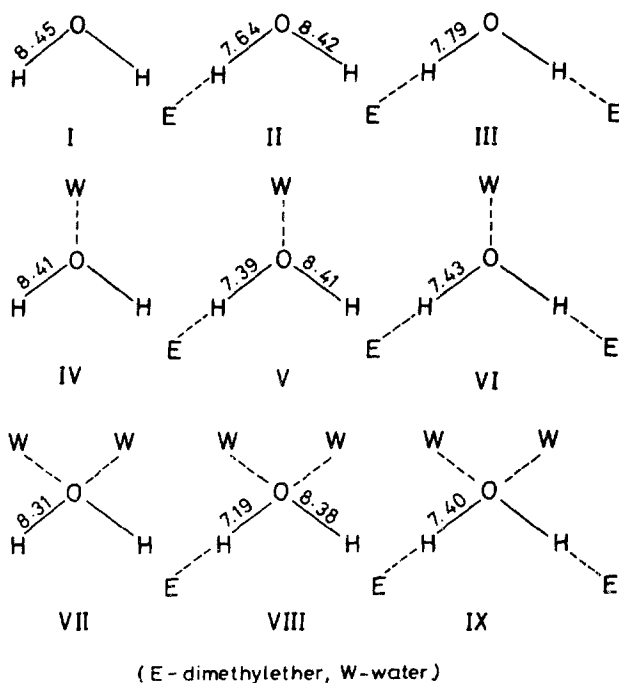


Figure 1. Variations in the O–H stretching force constants for water–dimethylether system.

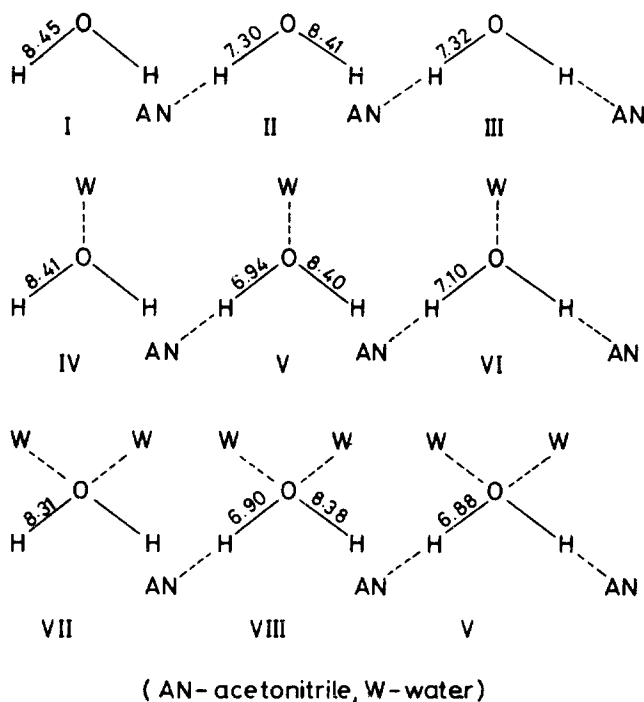


Figure 2. Variations in the O-H stretching force constants for water-acetonitrile system.

self-associated water species (W-W) are given in figure 3 for comparison (Brakaspathy and Singh 1986). Variations in the force constants for W-DME complexes are similar to that of the corresponding W-W species, whereas it is significantly higher for W-AN complexes. These results indicate that water and dimethylether have similar basicity whereas acetonitrile is more basic than water and dimethylether. When acetonitrile and dimethylether are involved in hydrogen-bonding through one of the two O-H bonds of the water molecule in unsymmetrically hydrogen-bonded species (structure II in figures 1 and 2), the force constant is found to decrease as per general expectation. The reduction in the force constant for the hydrogen-bonded O-H bond varies between 9 to 14% of the force constant of the free water molecule, whereas that for the nonhydrogen-bonded O-H bond is 1% only. When both O-H bonds are involved in hydrogen-bonding as in symmetrically hydrogen-bonded species (structure III in figures 1 and 2), the O-H force constant is found to be slightly higher than that for the unsymmetrically hydrogen-bonded water species (structure II in figures 1 and 2). When the lone pair of electrons on the oxygen atom of the centre water molecule is involved in hydrogen-bonding with a neighbouring water molecule, the force constant for the nonhydrogen-bonded O-H bond shows only a slight reduction, whereas that for the hydrogen-bonded O-H bond shows significant reduction. When one of the lone-pair electrons is involved in hydrogen-bonding (structure V in figures 1 and 2), the reduction is about 3-4% of the value of the hydrogen-bonded O-H stretching force constant of the species where the lone-pair electrons of the oxygen atom are not involved in hydrogen-bonding (structure II in figures 1 and 2), whereas when both the lone pairs of electrons are involved in

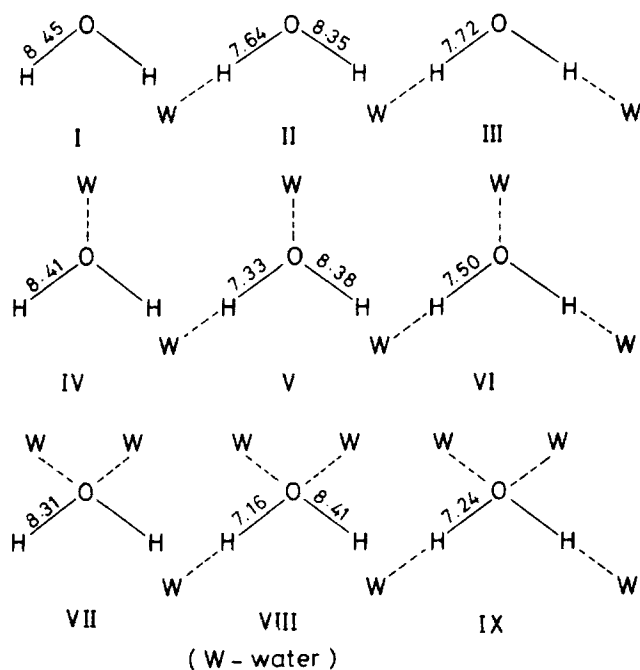


Figure 3. Variations in the O-H stretching force constants for water-water system.

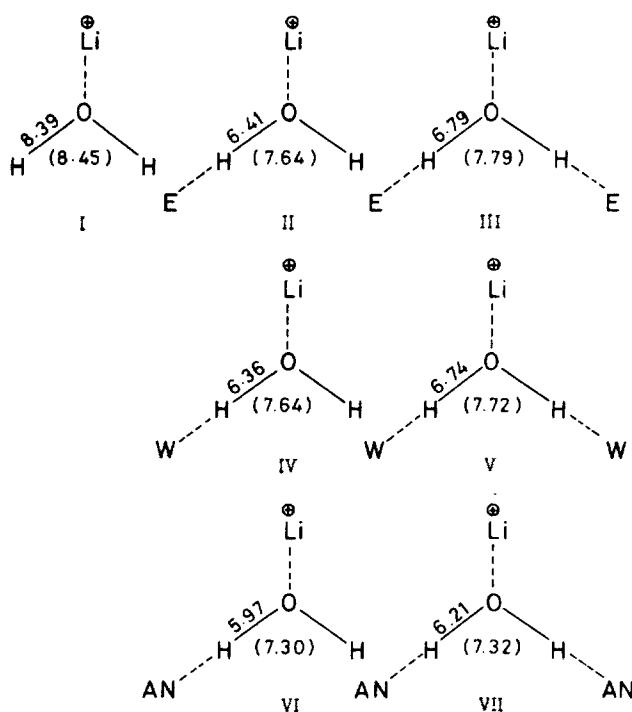
hydrogen-bonding (structure VII in figures 1 and 2), the reduction in the stretching force constants for the hydrogen-bonded O-H stretching mode is nearly 5–6%.

In figure 4 is shown the cooperativity effect of the interaction of Li^+ ions for W-DME, W-W and W-AN complexes. The O-H stretching force constant varies from 8.45 $\text{mdyn}/\text{\AA}$ for the monomer water to 7.64 $\text{mdyn}/\text{\AA}$ for hydrogen-bonded O-H in a water dimer and to 7.30 $\text{mdyn}/\text{\AA}$ for W-AN complexes. When the lone-pair electrons of the oxygen atom of the water molecule are involved in interaction with a Li^+ ion, the hydrogen-bonded O-H stretching force constant reduces to 6.41, 6.36, and 5.97 $\text{mdyn}/\text{\AA}$ respectively for W-DME, W-W and W-AN complexes. The effect of cooperativity on the hydrogen-bonded O-H force constant on association with Li^+ ion, is found to be more for W-D complexes where D is a stronger electron donor like acetonitrile. Further, the change in force constant is found to be more when the lone-pair electrons on the oxygen atom interact with Li^+ ion (figure 4) rather than with water molecules (figures 1 to 3). One can thus surmise that in the complex $\text{A} \cdots \text{H}_2\text{O} \cdots \text{D}$, the stronger the electron-donor (D) and electron-acceptor (A) molecules, the higher is the effect of cooperativity on the hydrogen-bonded O-H stretching force constant. If the electron accepting powers are assumed to increase in the order $\text{H}_2\text{O} < \text{Li}^+ < \text{Be}^{2+} < \text{Al}^{3+}$ and the donor powers are assumed to increase in the order $\text{DME} < \text{W} < \text{AN} < \text{DMSO} < \text{pyridine}$, the effect of cooperativity may be highest for the $\text{A} \cdots \text{H}_2\text{O} \cdots \text{D}$ complex where A is Al^{3+} and D is DMSO or pyridine.

2.2 Linear and cyclic water polymers

The structures of linear water polymers involving upto six molecules are shown in figure 5 along with their O-H stretching force constants. Calculations have been

performed on planar, nonplanar and alternate *cis* and *trans* structures. However, since the energies are found to be not too different, only planar structures are considered here for the sake of brevity. To simplify the comparison of the hydrogen-bonded O-H stretching force constants, the O-H bonds are denoted by $A_m \dots O-H \dots D_n$, where A_m are the m number of water molecules linearly hydrogen-bonded preceding the O-H bond under consideration and D_n are the n number of water molecules succeeding the O-H bond. The symbols A and D typically denote electron-acceptor and electron-donor water molecules respectively. The stretching force constant values for the hydrogen-bonded O-H bonds for the six linear polymers are given in table 1. The value of $8.45 \text{ mdyn}/\text{\AA}$ for the O-H stretching force constant of water monomer is reduced to $7.72 \text{ mdyn}/\text{\AA}$ when one donor molecule is attached to the water molecule; the value decreases when n increases from 1 to 5 in O-H... D_n structures. On the other hand, though the O-H stretching force constant shows a steady decrease in its value when m increases from 0 to 5 in $A_m \dots O-H$ structures, the reduction is not very significant. The reduction of the hydrogen-bonded O-H stretching force constants shows a systematic trend when m and n values increase from 1 to 5 in $A_m \dots O-H \dots D_n$ structures indicating an interesting demonstration of the cooperativity effect. The hydrogen-bonded O-H stretching force constant is found to be similar for



(AN-acetonitrile, E-dimethylether, W-water)

Figure 4. Effect of Li^+ on the hydrogen-bonded O-H stretching force constants for water-dimethylether, water-water and water-acetonitrile complexes. The values in parentheses are the corresponding O-H force constant values taken from figures 1 to 3 where Li^+ is not involved in the interaction.

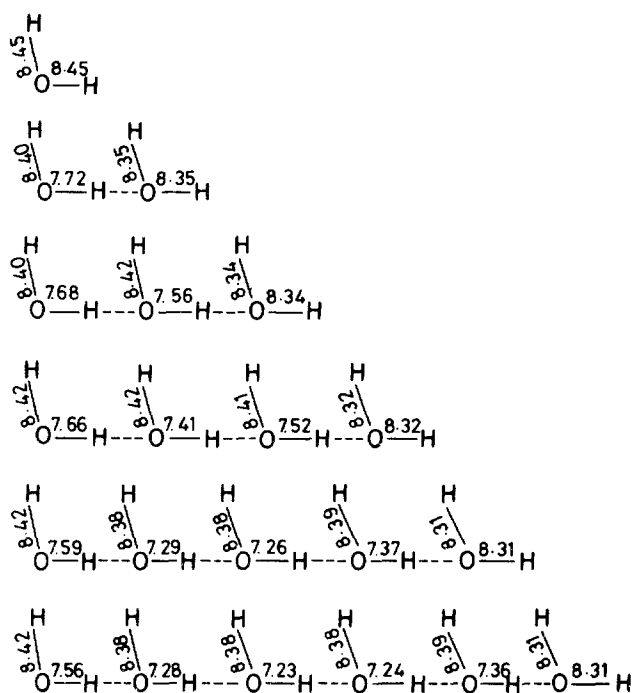


Figure 5. O-H stretching force constants for linear water polymers.

Table 1. O-H stretching force constants (mdyn/Å) for linear water polymers $A_m \cdots O-H \cdots D_n$.

		<i>n</i>					
<i>m</i>	0	1	2	3	4	5	
0	8.45	7.72	7.68	7.66	7.59	7.56	
1	8.35	7.56	7.41	7.29	7.28		
2	8.34	7.52	7.26	7.23			
3	8.32	7.37	7.24				
4	8.31	7.36					
5	8.31						

$A_3 \cdots O-H \cdots D_2$ and $A_2 \cdots O-H \cdots D_3$ and have the least value so far determined for the systems considered (7.24 and 7.23 mdyn/Å respectively).

In figure 6 and table 2 are given the nonhydrogen-bonded and hydrogen-bonded stretching force constants for cyclic water polymers, $(H_2O)_n$ $n = 2$ to 6. Only the force constants for planar structures are shown in the figure. The calculations were also made on other distorted configurations but the O-H stretching force constants were found to be similar to the values obtained for the planar configuration and therefore are not considered for discussion. The hydrogen-bonded O-H stretching force constant is found to decrease for $(H_2O)_n$ complexes when n increases from 2 to 6. The value is found to be 6.92 mdyn/Å for $(H_2O)_6$ which is much lower than

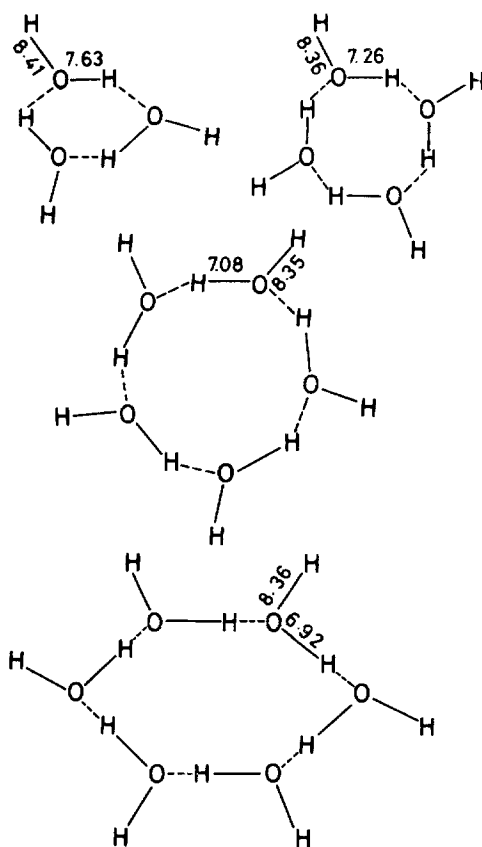


Figure 6. O-H stretching force constants for cyclic water polymers.

Table 2. O-H stretching force constant (mdyn/Å) for $(\text{H}_2\text{O})_n$ cyclic polymers.

$n =$	1	2	3	4	5	6
Terminal	8.45	8.40	8.41	8.36	8.35	8.36
Bonded	—	7.79	7.63	7.26	7.08	6.92

the lowest value obtained in the linear polymers for $\text{A}_3 \dots \text{O}-\text{H} \dots \text{D}_2$ or $\text{A}_2 \dots \text{O}-\text{H} \dots \text{D}_3$ structures.

2.3 Complexes of water with F^- ions

The O-H stretching force constants for complexes of water with F^- ions are given in figure 7. The interaction of the F^- ion with water decreases the hydrogen-bonded O-H stretching force constant to 4.85 mdyn/Å (compare with monomer-water value of 8.45 mdyn/Å). The value is found to increase to 5.09 mdyn/Å when the lone-pair electrons on the oxygen atom are involved in hydrogen-bonding with neighbouring water molecules (structure IV). This is contrary to the observations

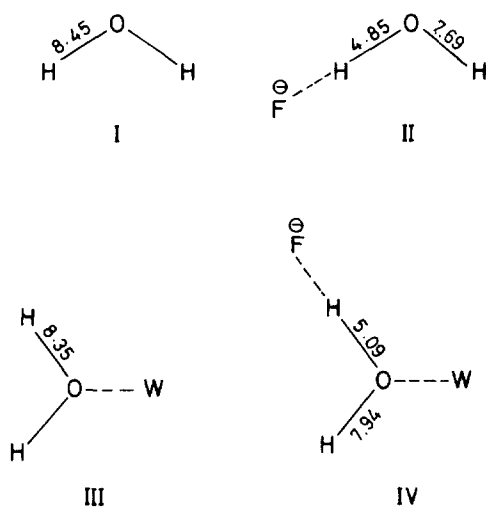


Figure 7. Effect of F^- on the O-H stretching force constants for H_2O and $(H_2O)_2$.

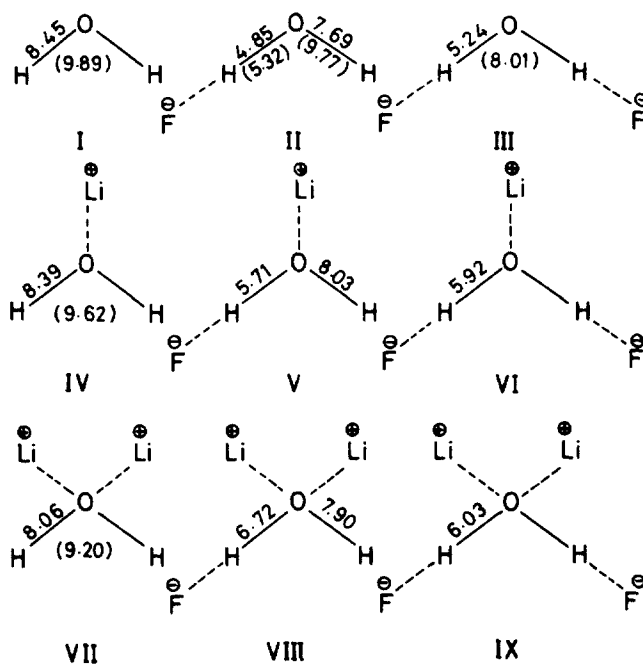


Figure 8. Variations in the O-H stretching force constants for water-lithium fluoride complexes. The values in parentheses are the corresponding *ab initio* values reported by Falk *et al* (1986).

made for similar systems when water, acetonitrile, dimethylether are used as electron donors instead of F^- (structure V in figures 1 to 3). While the cooperativity effect reduces the hydrogen-bonded O-H stretching force constant in the latter cases, it is found to increase in the case of interactions with F^- ions.

In figure 8 are shown the hydrogen-bonded O-H stretching force constants for 9 structures involving interaction of water with Li^+ and/or F^- ions. The *ab initio*

force constants for limited structures exhibiting interaction of water with Li^+ and F^- as reported by Falk *et al* (1986) are also given in the figure for comparison. The *ab initio* force constant values are nearly 15% higher than those obtained in the present studies. However the trends in the variation in the force constants for structures I to III and for structures I to IV to VII are similar in both cases. It may be noticed that the effect of interaction of Li^+ ions with one water molecule on the O–H stretching force constants is not significant although it is more than that obtained for interaction of water with one or two neighbouring water molecules (structures IV and V of figure 3). As found above (figure 7) the cooperativity effect on the hydrogen-bonded O–H stretching force constants for $\text{H}_2\text{O}\dots\text{F}^-$ complexes through the involvement of lone-pair electrons on the oxygen atom with Li^+ ions is in the reverse order to that observed in cases where organic bases are considered instead of F^- ions.

2.4 Quantification of the cooperativity effect

We can define the cooperativity effect (CE) as the *reduction in the force constant (ΔF) of the hydrogen-bonded O–H stretching mode when the lone-pair electrons on the oxygen atom of the water molecule are involved in hydrogen-bonding, divided by the hydrogen-bonded O–H stretching force constant (F) of the species when the lone-pair electrons are free, and multiplying the fraction by 100. That is*

$$\text{CE} = (\Delta F/F) 100.$$

For example CE for structure IV in figure 4 may be calculated as

$$\text{CE} = (7.64 - 6.36) 100/7.64 = 16.8.$$

The values thus calculated for all the systems are given in table 3. In the case of symmetrical and unsymmetrical H-bonded water complexes, the cooperativity effect is, in general, found to increase in structures $\text{A}\dots\text{O}-\text{H}\dots\text{D}$ with increasing basicity of D for the same electron-acceptor molecule A as well as with increasing electron-acceptor power of A for the same electron donor D. For linear water polymers, $\text{A}_m\dots\text{O}-\text{H}\dots\text{D}_n$ the cooperativity is found to increase with increasing values of m and n . The value is also found to increase with increasing values of n for cyclic polymers $(\text{H}_2\text{O})_n$. The cooperativity effect is found to be negative for a cyclic dimer, perhaps because of a strain in the ring.

3. Conclusions

It is observed from the above studies that involvement of a lone-pair of electrons on the oxygen atom of water molecule with an electron acceptor A ($\text{A} = \text{Li}^+$ or H_2O) decreases the force constant of the stretching mode of its O–H bond hydrogen-bonded to an electron donor D ($\text{D} = \text{H}_2\text{O}$, DME, AN) in the structures $\text{A}\dots\text{O}-\text{H}\dots\text{D}$. The extent of reduction depends upon the nature of the electron donor D and the electron acceptor A. When A represents Li^+ ions and D represents acetonitrile molecules the reduction is found to be maximum for the species considered. On the basis of these observations it may be envisaged that the reduction in the O–H stretching force constant may be much more significant if A is replaced by a bivalent or a trivalent cation like Be^{2+} , Mg^{2+} and Al^{3+} and D is

Table 3. Cooperativity effect for water complexes.a) *Unsymmetric and symmetric hydrogen-bonded water complexes*

System	Cooperating agent					
	H ₂ O		(H ₂ O) ₂		Li ⁺	
	Unsym	Sym	Unsym	Sym	Unsym	Sym
W-DME	3.2	4.5	5.8	4.9	15.7	12.7
W-W	4.1	2.8	5.3	4.9	16.8	12.7
W-AN	4.9	3.1	5.5	6.0	17.5	15.2
W-F ⁻	-5.0	-	-	-	-6.1	-

b) *Linear polymers A_m...O-H...D_n*

m	n				
	1	2	3	4	5
0	0	0.52	0.65	1.61	2.00
1	1.94	3.91	5.51	5.61	
2	2.51	5.91	6.32		
3	4.41	6.12			
4	4.53				

c) *Cyclic polymers (H₂O)_n*

Bonded	n				
	2	3	4	5	6
	-0.9	1.16	5.8	8.19	10.26

replaced by a strong base like DMSO, pyridine etc. The recent experimental studies of Kleeberg *et al* (1986) show that the O-H stretching force constants are found to have significant reduction when such systems are considered. On the basis of the present studies it is found that dimethylether and water have similar basicities. The experimental gas phase proton affinities of water, dimethylether and acetonitrile are respectively 173, 193, 191 kcal/mole (Bowers 1979). It is not clear whether our force constant values have not been exactly predicted by the CNDO method or contributions of some other parameters like off-diagonal force constants and vibrational coupling are lacking in our calculations. However, *ab initio* calculation on these systems may be beneficial for such studies. Studies on variation in O-H stretching force constants in linear and cyclic water polymers also demonstrate an interesting cooperativity effect when the values of *m* and *n* increase from 1 to 5 in the structures A_{*m*}...O-H...D_{*n*} and also when the value of *n* increases from 2 to 6 in the cyclic (H₂O)_{*n*} structures.

When F^- is used as the electron donor the calculations show a reversal of cooperativity effect on addition of A in the $A...O-H...F^-$ structures. It is observed that the *ab initio* force constant calculations show similar trends as observed in the present studies for the limited number of $(H_2O)F^-$ and $(H_2O)Li^+$ complexes considered by Falk *et al* (1986). Therefore it seems that the reversal of cooperativity effect noticed in these calculations for $(H_2O)F^-$ complexes may not be an artifact of the semi-empirical method used in the present studies. The idea of negative cooperativity or anti-cooperativity is not new. It was first put up by Flory (1969) on the basis of theoretical models and more recently by Kleeberg (1986, 1987) and Kocak *et al* (1987) on the basis of their experimental results. It is observed (Kleeberg 1987) that the hydrogen-bonded asymmetric O–H stretching band for water–anion complexes in dichloromethane shifts to higher frequencies with increasing concentration of water, thus showing a reverse order of cooperativity. It is, however, found that the stabilization energies of these complexes do not follow trends similar to those observed in force constants and do not show the so called anticooperativity (M C Shivaglal and S Singh, unpublished results). More detailed studies in this direction are in progress and will be published later.

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