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Application of the independent molecule model to the calculation of free energy and rigid-body motions of water heptamers and octamers

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Abstract

Stabilization of clusters of water heptamer and octamer in the gas phase is studied with the independent molecule model. As indicators of stabilization, the H-bonding strength, the H-bonding lifetime and the free energy are calculated. For both the heptamers and octamers, clusters with one oxygen-ring and some branching H-bonded waters are more stable than clusters with multi-oxygen-rings. Both the heptamer and octamer prefer a shape intermediate between planar and polyhedral; the branched waters are highly fluctuating and consequently contribute to increasing the entropy of the cluster. As the temperature increases from 0 to 300 K, the entropy contributes to the differentiation in free energy of the cluster geometries.
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1. Introduction

In a previous article [1], stabilities of the five water hexamers (cyclic, boat, book, prism, cage) in the gas phase were studied using the independent molecule model (MM). As indicators of stabilization, we chose three factors: the free energy, hydrogen bonding (H-bonding) strength and also H-bonding lifetimes for each hexamer. Our study showed that the more planar hexamers (cyclic and boat) are more stable than the three-dimensional hexamers (cage and prism), and that the most stable is the boat, and the least stable is the prism.

So far, there is general agreement that the global minima of the trimer, tetramer and pentamer of water are simple cyclic structures and that the octamer and the larger clusters prefer three-dimensional (polycyclic) structures [2–14]. However, do the larger clusters really prefer polycyclic structures?

In this article we investigate with the independent MM which heptamer and octamer structures are most stable in the gas phase.

As in our work on hexamer clusters, we examine the free energy, H-bonding strength and H-bonding lifetime for the

heptamers and octamers. In the independent MM, we can independently treat each water molecule in the cluster, and we can also obtain an energy minimum conformation for each cluster structure. Around the minimum point, each water in the cluster has six vibrational frequencies as a rigid-body motion besides its three internal frequencies. Then we can calculate the free energy assuming harmonic oscillators, and also calculate an H-bonding lifetime using the uncertainty relation $\Delta\tau\Delta E \sim \hbar$ between a lifetime $\Delta\tau$ and an energy difference ΔE of the vibrating rigid-body. For obtaining H-bonding strength, we use the geometrical position of hydrogen and oxygen H-bonding of each water in the minimized conformation. For a description of the independent MM method, see ref. [1]. In Section 2, the results on water heptamer are described, and in Section 3, the results on water octamer are given. Discussion and conclusion constitute Section 4.

2. Water heptamer

2.1. Methods

Starting geometries for heptamer clusters must be generated before an energy minimization can be done. The heptamer can be generated in several ways. In one method, we build up seven waters by considering the geometry of waters

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H-bonding to each other; we generated a cluster by using a compass and a ruler as tools on a basis of solid geometry taking account of both a form of water molecule and a distance between H-bonding waters. Thus, clusters like a cyclic heptamer are formed by this method. In a second method, we bind a water near any of three waters in a tetramer by considering an H-bonding distance, and we can form a heptamer with branching waters. Likewise we place a water near any of two waters in a pentamer, and we can make the other clusters of the branching heptamer. In a third method, positioning a water near any water in a hexamer, we can form many three-dimensional starting conformations for a heptamer; we placed a water, in some ways considering the direction, above a centre of a cyclic hexamer, boat hexamer or book hexamer, and so on. We formed 22 starting conformations, ranging in shape from roughly planar to polyhedral.

The independent variables describing the movement of each water in the heptamer are a translational vector and Eulerian angles expressing motions of a rigid body, and two bond lengths and one bond angle expressing internal motion of water: a total of nine variables per water (see ref. [1]). The force field parameters for calculating the potential energy between waters, for H-bonding, and for intra-water energy contributions are also given in ref. [1]. The Hessian matrix for total potential energy expressed in terms of the nine variables making a total of 63 (9×7) is also presented in ref. [1]; this matrix is necessary for an energy minimization and normal mode analysis.

2.2. Results

2.2.1. Energy minimization

Energy of each heptamer cluster was minimized, as was done previously for the hexamers, using Newton's method based on a modified Cholesky factorization [15] of the Hessian. To achieve positive eigenvalues in the Hessian, the mutual positions of water molecules in the heptamer, and the positions of constituent atoms in each water were forced to change by altering 9×7 variables in such a way that the energy of the heptamer reduces. Energy minimization was stopped when the energy difference between the current step and the earlier step becomes to be less than 1×10^{-8} kcal/mol. At the energy minimum point of each heptamer, the subset of the Hessian whose elements are expressed in terms of the six variables describing a rigid-body motion, has six positive eigenvalues for each water in the heptamer, and also the subset whose elements are expressed in terms of the three variables describing internal motion, has three positive eigenvalues for each water.

Ten of the 22 heptamer clusters were selected as representatives for detailed analysis. We named them in according to their shapes. They are fancifully called airplane, skier, turtle, wreath, knight, cap, cave, mailbox, crane and crab heptamer in this article.

2.2.2. Normal mode analysis

At the energy minimum point, normal mode analysis is done with the subset of the Hessian (the force constant matrix) and the kinetic energy matrix expressed in refs. [16,17], both for rigid-body motion and for internal motions for each water in the heptamer. The six vibrational frequencies of a rigid-body motion for each water are shown in Table 1 for the 10 heptamer clusters. With the mean-square displacement of the atom caused by the rigid-body motions of each water, anisotropic thermal vibrations for all hydrogens and oxygens in the heptamer are calculated in the method described in ref. [17]. On the other hand, the mean-square displacement of the atom caused by the internal motions are negligible compared to the rigid-body motions, since the former frequencies range from about $1500\,\mathrm{cm}^{-1}$ to about $3800\,\mathrm{cm}^{-1}$. So, hereinafter we will not consider the internal motions of water molecules. The anisotropic thermal ellipsoid of hydrogen and oxygen atoms reflecting the rigid-body motions of each water are depicted in Fig. 1(a)–(j) for each of the 10 heptamer clusters, respectively [18]. In these figures as well as in subsequent figures, the displacements that would be caused when each of the six vibrational mode is excited at 300 K are calculated.

2.2.3. Classification of H-bond

From Fig. 1(a)–(j), we can see that the 10 heptamer clusters are comprised of some multi-membered oxygen-rings and some branching H-bonded waters, or only multi-membered oxygen-rings. The former are airplane, skier, turtle, knight, crane and the latter are wreath, cap, cave, mailbox, crab. In addition, we can see each cluster has different H-bonding patterns; say, in airplane, the 105, 106 and 107 waters form non-donor single-acceptor H-bonds (n-D s-A), the 104 forms single-donor single-acceptor (s-D s-A), and the 101, 102 and 103 form double-donor single-acceptor (d-D s-A) and so on. We use the same criteria for defining an H-bond as before [1]; a hydrogen-acceptor distance must be less than 2.5 Å, and a donor-hydrogen-acceptor angle must be larger than 135°. In Table 2, we show what membered oxygen-ring is used to each cluster, and moreover describe how the seven water molecules in each cluster take part in H-bonding as donor and/or acceptor.

2.2.4. H-bonding strength and H-bonding lifetime

Using the methods of ref. [1], we can estimate an H-bonding strength and H-bonding lifetime of water molecule taking part in an H-bond. The former depends on the configuration of hydrogen of one water and oxygen of another water taking part in the H-bond. Lifetime $\Delta\tau$ depends on the frequency range of rigid-body motions (Table 1) via an uncertainty relationship $\Delta\tau = 2/[c(\nu_{\max} - \nu_{\min})]$, where c is the speed of light.

In Fig. 2, we show H-bonding strengths and H-bonding lifetimes for each of the H-bonding patterns formed in the 10 heptamers. For example, with the n-D s-A H-bonding pattern of the airplane, the values are averaged over the 105,

Table 1
Vibrational frequencies for each of the seven rigid water molecules within the heptamer (cm^{-1})

Airplane						
101	85	244	287	348	483	555
102	96	238	320	352	429	584
103	97	249	285	340	449	609
104	29	66	231	258	326	578
105	15	18	18	125	179	321
106	13	16	18	129	179	311
107	14	17	18	132	168	319
Skier						
201	54	253	303	335	439	473
202	25	68	207	250	355	540
203	27	79	216	231	363	406
204	80	257	302	323	416	472
205	25	55	227	276	367	375
206	16	19	20	125	172	318
207	15	18	19	125	178	313
Turtle						
301	23	69	223	241	345	420
302	42	264	304	363	380	435
303	26	78	211	255	337	417
304	23	72	204	277	332	407
305	22	62	233	264	347	393
306	24	75	210	240	368	420
307	16	20	21	126	170	313
Wreath						
401	24	66	214	243	315	420
402	25	80	199	244	355	410
403	25	84	205	253	345	401
404	25	81	200	265	337	408
405	26	82	184	278	353	403
406	25	84	184	259	347	428
407	22	75	190	246	334	447
Knight						
501	156	200	252	318	356	963
502	23	90	221	270	357	426
503	26	86	207	253	326	437
504	43	252	293	347	405	487
505	101	194	289	348	502	731
506	32	48	213	256	352	699
507	16	17	20	113	172	317
Cap						
601	159	197	329	375	585	790
602	26	71	198	307	335	554
603	195	225	234	282	366	715
604	178	229	242	323	355	861
605	23	84	235	293	324	377
606	24	84	222	262	315	433
607	137	227	344	423	611	733
Cave						
701	34	111	207	273	354	885
702	187	239	330	424	822	942
703	31	42	205	247	356	715
704	131	203	307	428	567	711
705	177	225	245	297	401	834
706	141	207	323	457	710	761
707	187	231	238	314	355	668
Mailbox						
801	143	196	333	376	613	840
802	25	58	209	322	326	450
803	203	237	263	315	366	713

Table 1 (Continued)

804	29	78	240	311	323	443
805	208	244	265	348	357	614
806	30	63	220	291	368	537
807	191	208	311	412	540	684
Crane						
901	201	208	237	285	470	715
902	182	207	265	276	491	704
903	139	193	356	415	614	761
904	32	69	222	269	381	587
905	36	59	216	228	395	841
906	119	214	350	387	636	760
907	214	229	353	439	715	814
Crab						
1001	206	239	355	450	711	976
1002	30	84	193	287	396	676
1003	208	243	251	301	441	636
1004	203	235	256	301	401	687
1005	141	202	334	431	721	824
1006	33	77	214	281	368	616
1007	147	229	315	449	610	786

106, 107 waters. Fig. 2 indicates that higher values on the axes have higher H-bonding strength and longer H-bonding lifetime. We see that the n-D s-A H-bonds (in red letters) of airplane, skier, turtle and knight bind more tightly, and keep their H-bonds longer. Whereas the s-D n-A H-bonds (in aqua letters) of crane, and d-D d-A in crane and in crab bind weakly and do not last long. The relationship between H-bonding strength and H-bonding lifetime is pronounced in some clusters (airplane, skier, knight, mailbox and crab), but less so in the others.

2.2.5. Free energy

We estimate Helmholtz free energy as the third indicator of stabilization in the water clusters. We assume a water heptamer is composed of independent harmonic oscillators with their respective eigenfrequencies. Therefore, the partition function for water heptamer can be expressed in terms of 6×7 harmonic oscillators for the rigid-body motions in the following:

$$Z = e^{-\beta \Phi_0} \prod_{j=1}^{6 \times 7} \frac{1}{2 \sinh(\beta h \nu_j / 2)} \tag{1}$$

where $\beta = 1/k_B T$ (k_B is the Boltzmann constant, T the absolute temperature), Φ_0 the potential energy of the heptamer at the energy minimum point, and ν_j is the jth eigenfrequency ($j = 1 \sim 6 \times 7$). With the partition function Z, the free energy is $F = -k_B T \log Z$, the internal energy is $U = -\partial \log Z / \partial \beta$, and the entropy is $S = -(\partial F / \partial T)_\nu$. Thus, the internal energy is given as follows:

$$U = \begin{cases} \Phi_0 + \sum_{j=1}^{6 \times 7} \left\{ \dfrac{h \nu_j}{2} + \dfrac{h \nu_j}{e^{\beta h \nu_j} - 1} \right\} \\ \Phi_0 + \varepsilon_{\text{zero}}^{\text{rigid}} + \varepsilon_{\text{osci}}^{\text{rigid}} \end{cases} \tag{2}$$

where the first term in the braces is the zero-point vibrational energy, and the second term is the average harmonic
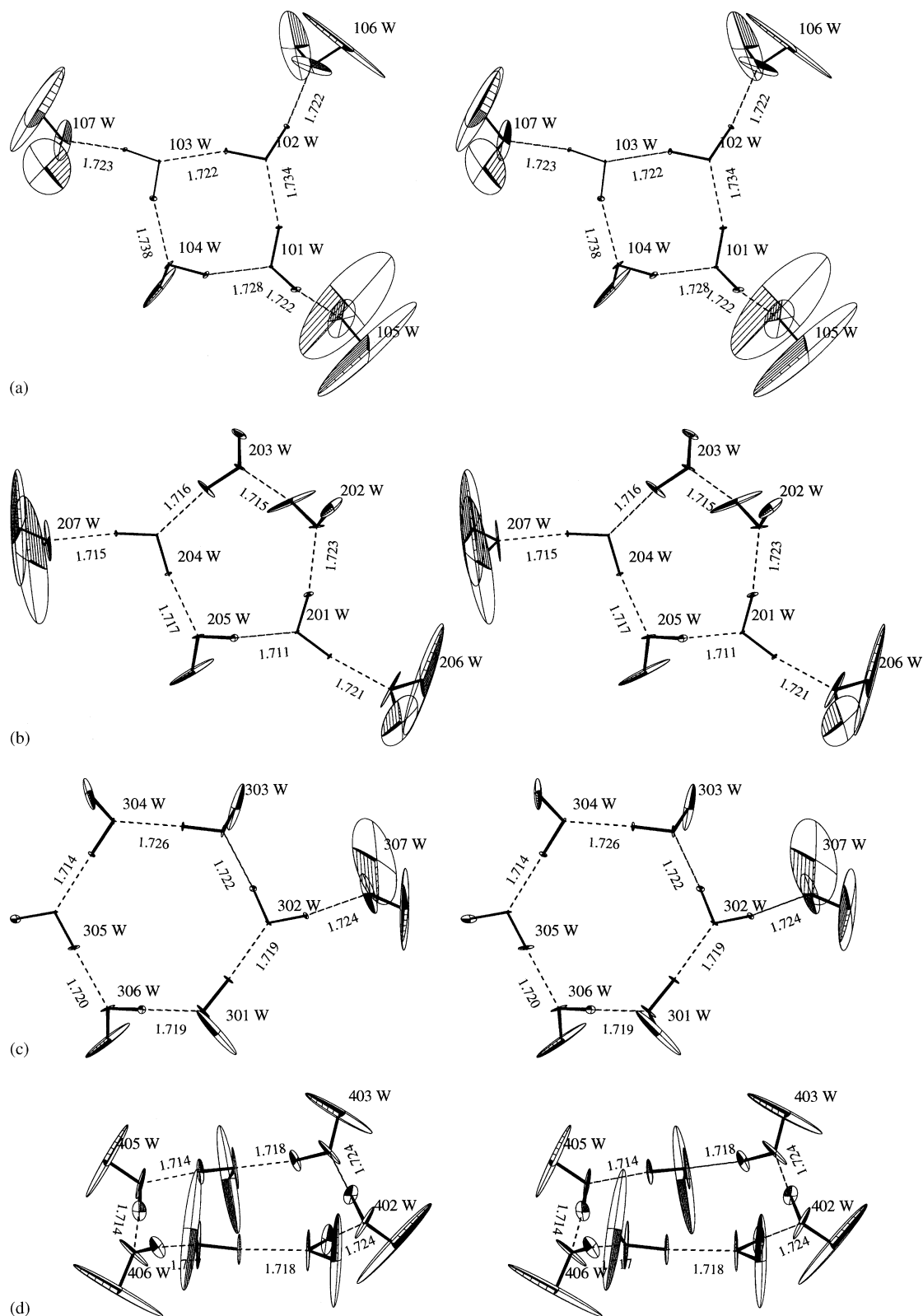
Fig. 1. Stereo view of rigid-body motions of each water molecule in the heptamer. The thermal ellipsoids of atoms (at 70 or 97%) are drawn in ORTEP. A 70% probability ellipsoid means that the nucleus has a 70% probability of being inside. In order to make viewing easier, the percent probability varies according to the cluster being plotted. Dashed lines show the H-bonds. The numerical values are the distances (Å) between donor and acceptor. (a) Airplane (70%), (b) skier (70%), (c) turtle (70%), (d) wreath (97%), (e) knight (70%), (f) cap (97%), (g) cave (97%), (h) mailbox (97%), (i) crane (97%) and (j) crab (97%).
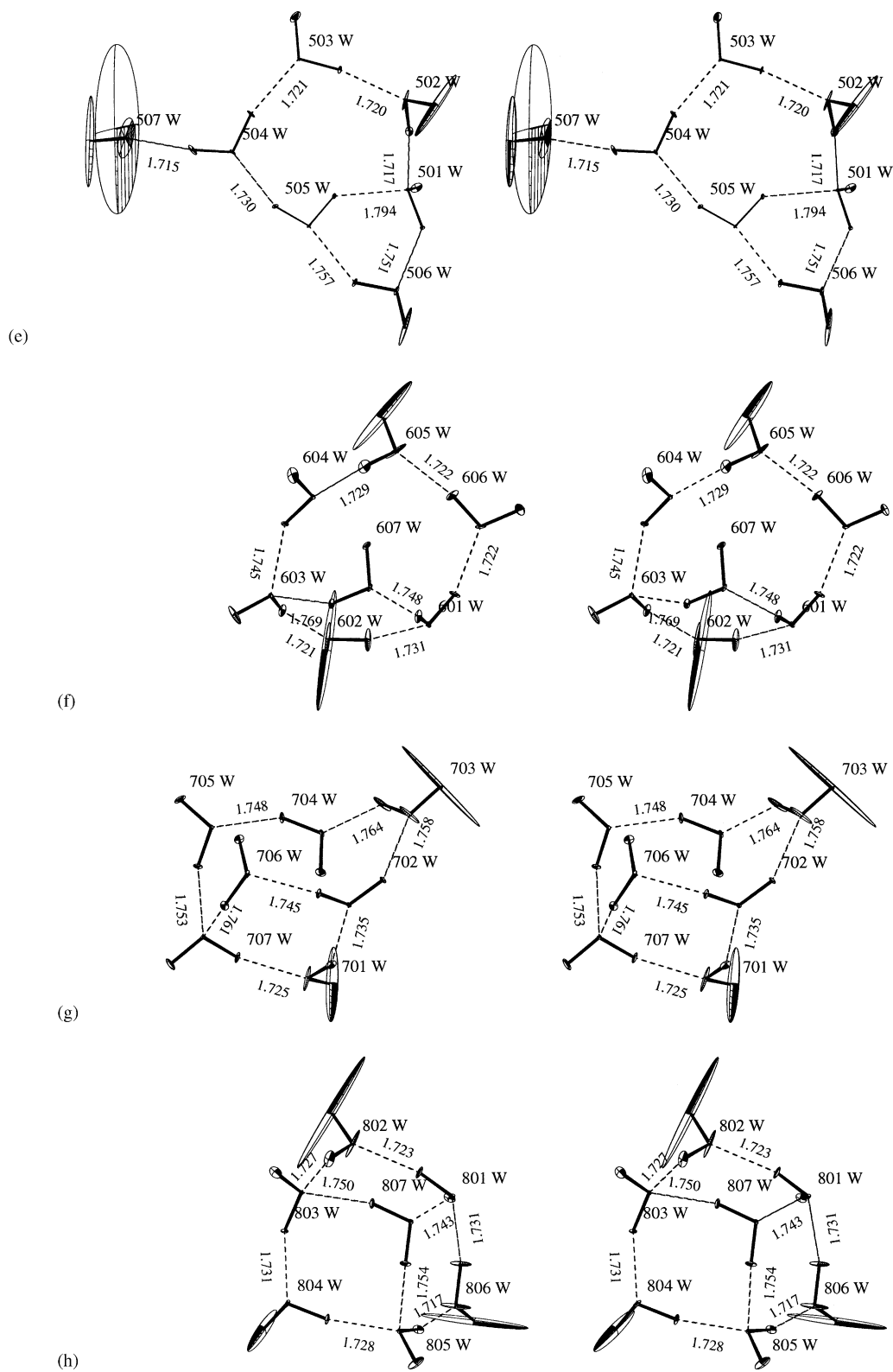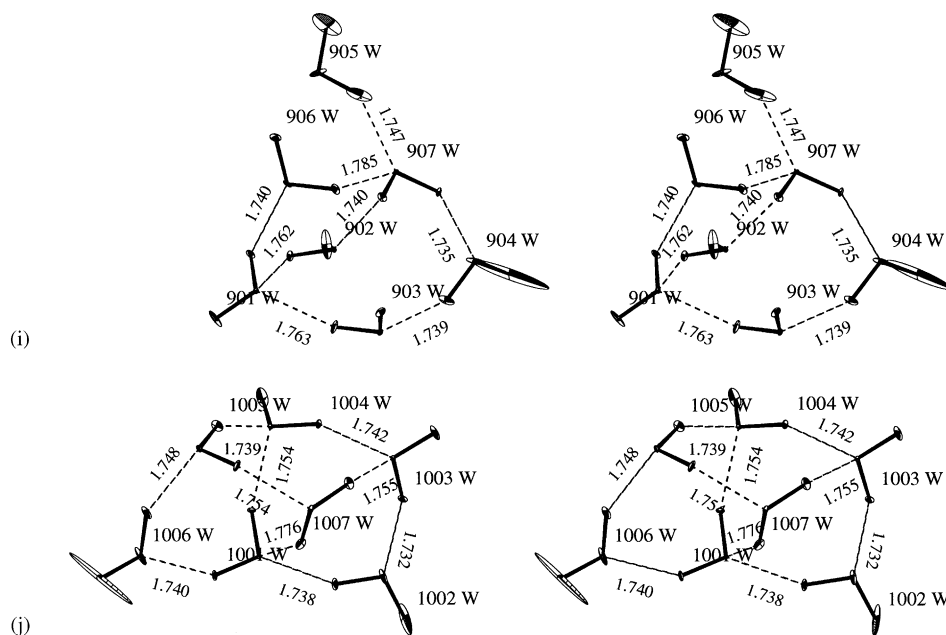
(e)

(f)

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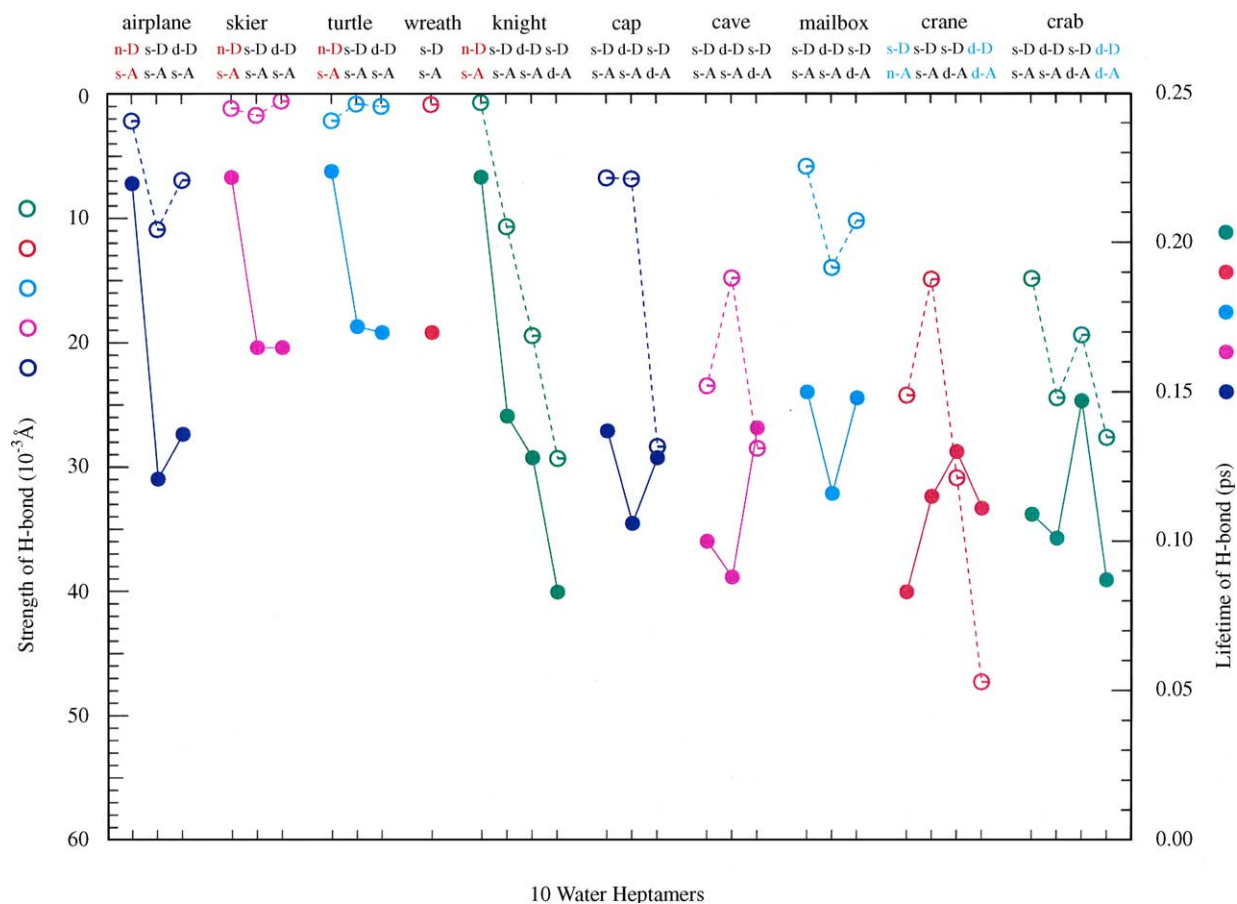Fig. 1. (*Continued*).

Fig. 1. (*Continued*).

Fig. 2. H-bond strength (open circles) and H-bond lifetime (solid circles) for H-bond patterns formed in the 10 heptamers. The left ordinate exhibits H-bond strength (in Å); the values becomes less positive as one goes up the axis; less positive means a stronger H-bond. The right ordinate describes H-bond lifetime (in ps).

Table 2
Classification of H-bonding

	n-A	s-A		d-A
Airplane: one 4-membered oxygen-ring				
n-D		105, 106, 107		
s-D		104		
d-D		101, 102, 103		
Skier: one 5-membered oxygen-ring				
n-D		206, 207		
s-D		202, 203, 205		
d-D		201, 204		
Turtle: one 6-membered oxygen-ring				
n-D		307		
s-D		301, 303, 304, 305, 306		
d-D		302		
Wreath: one 7-membered oxygen-ring				
n-D				
s-D		401, 402, 403, 404, 405, 406, 407		
d-D				
Knight: one 3-membered oxygen-ring, one 5-membered oxygen-ring				
n-D		507		
s-D		502, 503, 506		501
d-D		504, 505		
Cap: one 4-membered oxygen-ring, two 6-membered oxygen-rings				
n-D				
s-D		602, 604, 605, 606, 607		603
d-D		601		
Cave: one 4-membered oxygen-ring, two 6-membered oxygen-rings				
n-D				
s-D		701, 703, 704, 705, 706		707
d-D		702		
Mailbox: three 4-membered oxygen-rings, one 6-membered oxygen-ring				
n-D				
s-D		802, 804, 806		803, 805
d-D		801, 807		
Crane: one 4-membered oxygen-ring, two 5-membered oxygen-rings				
n-D				
s-D	905	902, 903, 904, 906		901
d-D				907
Crab: five 4-membered oxygen-rings				
n-D				
s-D		1002, 1006		1003, 1004
d-D		1005, 1007		1001

oscillator energy. The $\varepsilon_{\text{zero}}^{\text{rigid}}$ and the $\varepsilon_{\text{osci}}^{\text{rigid}}$ are the total zero-point vibrational energy and the total average harmonic oscillator energy for rigid-body motions, respectively. The entropy term $-TS$ is also given below:

$$-TS = -\frac{1}{\beta}\sum_{j=1}^{6\times 7}\left[\frac{\beta h \nu_j}{2}\coth\frac{\beta h \nu_j}{2} - \log\left\{2\sinh\frac{\beta h \nu_j}{2}\right\}\right]$$

$$= -(TS)^{\text{rigid}} \tag{3}$$

where $-(TS)^{\text{rigid}}$ is the total vibrational entropy term for rigid-body motions. Thus, the free energy F is expressed as $F = U - TS$, which is calculated as a sum of four contributions. In Table 3, we show the free energies with the four terms for each heptamer cluster at the temperature 300 K, the free energy at 0 K (F_{zero}) and the number of H-bond for each. We see that the minimized energy Φ_0 corresponding to binding energy of the heptamer decreases in order from top to bottom in Table 3. (As in our previous papers, we use the terms "increases" and "decreases" in the algebraic sense, not necessarily in terms of the magnitudes.) The binding energies Φ_0 of the airplane, skier, turtle and wreath (7 H-bonds) are −33.0 to −35.3 (kcal/mol), the Φ_0 of the knight, cap, cave and crane (8 H-bonds) are −35.7 to −41.4 (kcal/mol) and the mailbox (9 H-bonds) and the crab (10 H-bonds) have −41.1 and −43.2 (kcal/mol), respectively. As the number of H-bonds increases, the value of Φ_0 decreases as would be expected. But the free energy does not monotonically depend on the variation of the number of H-bonds.

2.2.6. Stabilizing factors

We are now in a position that we can estimate which of the 10 clusters is the most stable or the least stable, considering the three indicators we calculated. Fig. 3 compares the H-bonding strength, the H-bonding lifetime and the free energy. From this figure, we discern that the variations of the three values against the 10 heptamers are similar. This figure indicates that a cluster with a higher value on the ordinate axes for any of three values would be more stable than a cluster with a lower value. Therefore, we see that the clusters with one oxygen-ring and 7 H-bonds (airplane, skier, turtle and wreath) are more stable than the clusters with multi-oxygen-rings and 8, 9 or 10 H-bonds. Among the four clusters, the skier and the turtle would be a bit more stable than the other two, although the difference is variable. The cave and crane with three oxygen-rings and 8 H-bonds would belong to the least stable group of heptamers analysed in this article. The crab with five oxygen-rings and 10 H-bonds, though this is the most complex structure among the 10 clusters, is the third least stable. The cap and the cave cluster are comprised of the same topology as shown in Table 2, but their stability differs. We see that even if topology is the same, the stability of clusters depends on the structure as depicted in Fig. 1(f) and (g).

Although the relationship between H-bonding strength and H-bonding lifetime for H-bonding pattern in each cluster is good in some clusters and not so clear in the others based on Fig. 2, the relationship is clearly shown in the blue and green curves of Fig. 3.

2.2.7. Temperature dependence of free energy

Among three stabilizing factors, we can estimate a temperature dependence of free energy. We pick 3 of the 10 heptamer clusters; the skier for stable H-bonding, knight for middle and crab for less stable. In Fig. 4, we show the

Table 3
Free energy for the 10 heptamers at 300 K, free energy at 0 K (F_{zero}) and the number of H-bond in the each

	HB	Φ_0	$+\varepsilon_{zero}^{rigid}$	$+\varepsilon_{osci}^{rigid}$	$-(TS)^{rigid} = F$	(F_{zero})
Airplane	7	−32.97	+13.63	+15.06	−38.05 = −42.33	(−19.34)
Skier	7	−34.15	+13.04	+15.18	−37.08 = −43.01	(−21.11)
Turtle	7	−34.80	+12.95	+15.11	−35.90 = −42.65	(−21.85)
Wreath	7	−35.30	+13.12	+14.94	−33.97 = −41.21	(−22.18)
Knight	8	−35.68	+16.01	+13.79	−31.26 = −37.15	(−19.67)
Cap	8	−39.92	+18.96	+12.05	−24.04 = −32.96	(−20.96)
Cave	8	−40.93	+22.15	+10.93	−20.90 = −28.74	(−18.78)
Mailbox	9	−41.07	+18.99	+11.88	−23.55 = −33.76	(−22.08)
Crane	8	−41.40	+21.81	+10.90	−20.80 = −29.49	(−19.59)
Crab	10	−43.20	+22.18	+10.70	−20.13 = −30.44	(−21.02)

Units of kcal/mol.

temperature dependence of the free energy with respective contributions. We see that, near 0 K, though both the harmonic oscillator energy and the entropy term are nearly zero, the free energy is almost the same for all three heptamers, since the more negative a binding energy is, the more positive the corresponding zero-point vibrational energy is, as shown in Fig. 4. Hence, it would be possible that three different clusters would exist at the almost same abundance. As the temperature goes up, the harmonic oscillator energy is also going up, whereas the entropy term rapidly goes down,

leaving the binding energy and the zero-point energy constant. Consequently, as temperature goes up the free energy goes down from its value at 0 K. As temperature changes, one cluster may prefer to exist, while another may not. This difference derives from a difference of cluster structure, and it related to the difference in entropy. The simpler a water cluster is, the more the structure is fluctuating, and the vibrational entropy becomes larger. On the other hand, the more complex a cluster is, the less the structure is fluctuating, and the entropy becomes smaller. At 300 K, the differences in
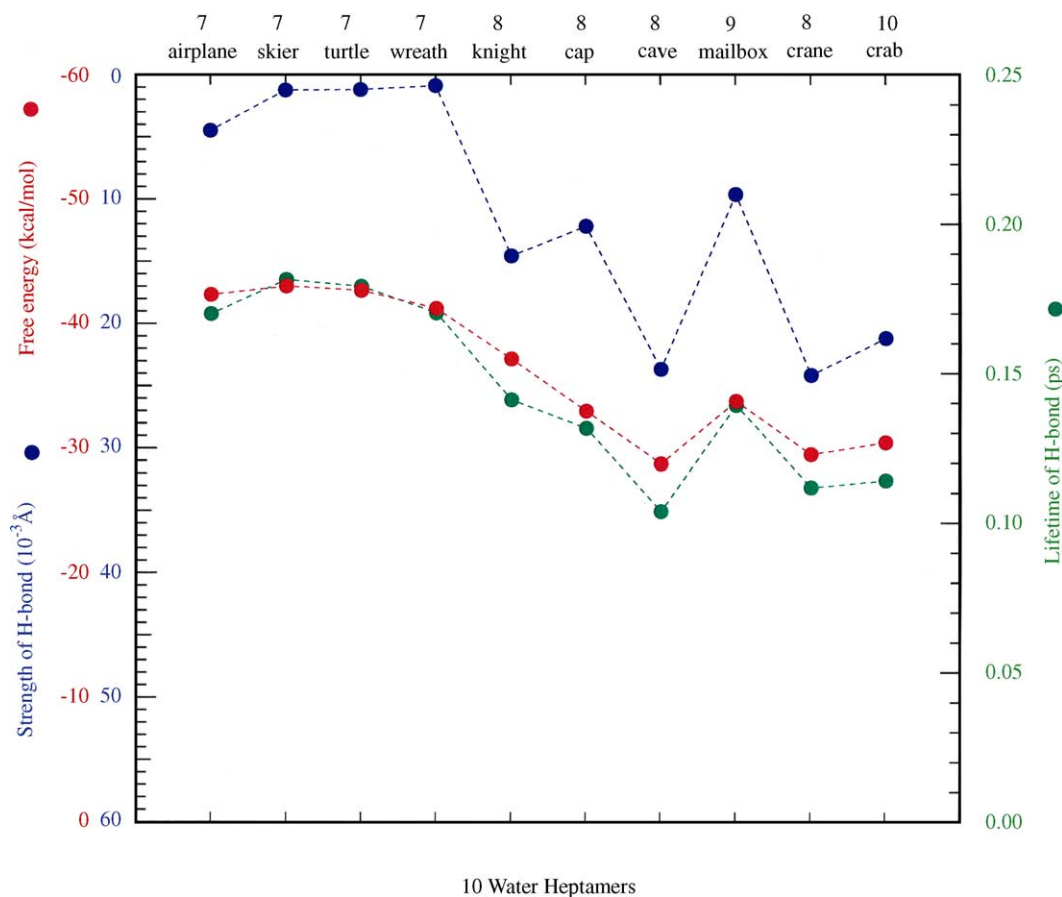

Fig. 3. Free energy (red), H-bond strength (blue) and H-bond lifetime (green) for the each of 10 heptamers. The data points in blue and green are averaged over each heptamer. The values of both ordinates mean that a heptamer becomes more stable as one goes up the axis. The integer at top of each position is the number of H-bond formed in that heptamer.
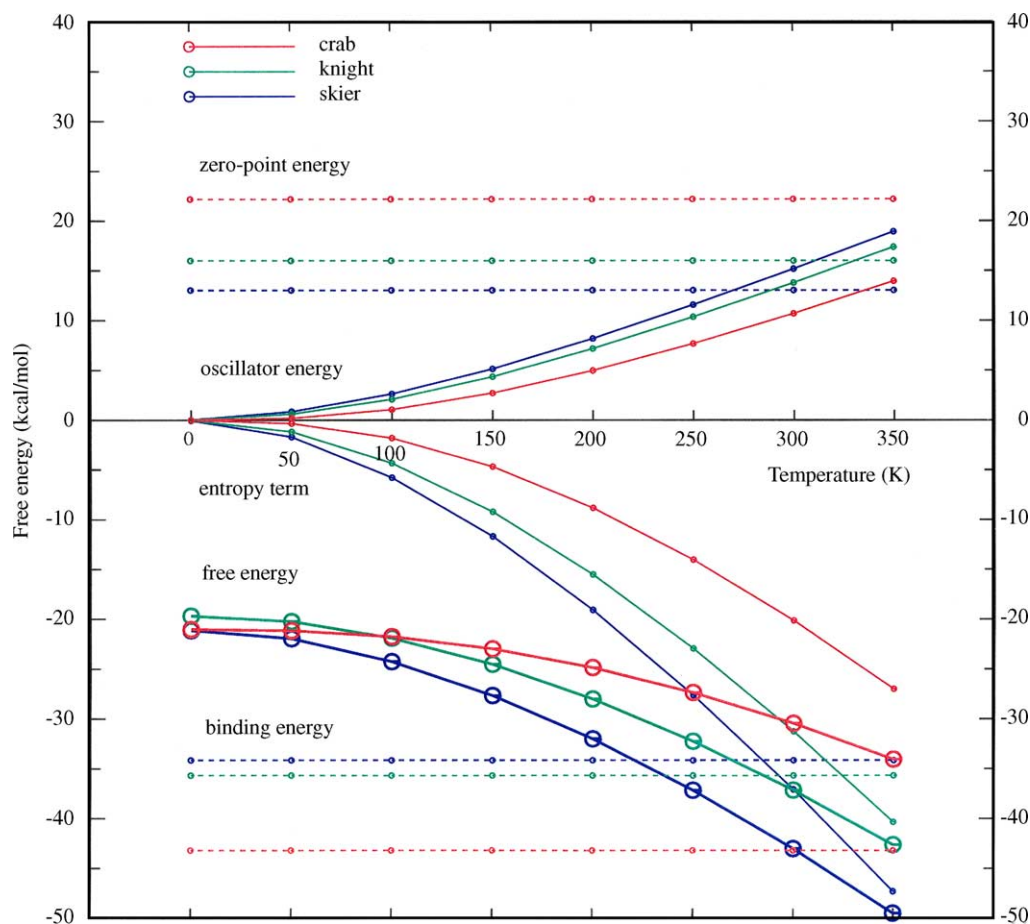
Fig. 4. Temperature dependence of free energy for the three heptamer. The blue, green and red colours indicate the quantities relative to the skier, knight and crab heptamers, respectively. The figure shows the binding energy Φ_0 (lower dashed lines), the zero-point vibrational energy $\varepsilon_{zero}^{rigid}$ (upper dashed lines), the average harmonic oscillator energy $\varepsilon_{osci}^{rigid}$ (upper curves), the vibrational entropy term $-(TS)^{rigid}$ (lower curves) and the free energy (thick curves with large open circles).

free energy of the three clusters is large: the skier is more stable than the knight, and the knight is more stable than the crab.

3. Water octamer

3.1. Methods

The method for generating starting structures of octamer clusters is similar to what was done for the heptamers. We created 28 starting conformations ranging from roughly planar to polyhedral. The independent variables for each water are six for rigid-body motion and three for internal motions; hence the total for a water octamer is 72 (9×8).

3.2. Results

3.2.1. Energy minimization

An energy minimization for each of the 28 octamer clusters was performed, and we selected 10 of these as representatives for further analysis. They are called clover, pentagon, bib, balloon, crown, chair, seal, diamond, coal and d2d according to each shape except for the last. The d2d cluster is a cubic structure of D_{2d} symmetry [8].

3.2.2. Normal mode analysis

At the energy minimum point, normal mode analysis is done for each water in the octamer. The six vibrational frequencies of rigid-body motion for each water of the 10 octamers are given in Table 4. The thermal ellipsoids of hydrogen and oxygen atoms reflecting the rigid-body motions of each water octamer are also depicted in Fig. 5(a)–(j) for each of the 10 octamer clusters, respectively.

3.2.3. Classification of H-bond

From Fig. 5(a)–(j), we learn that the clusters are comprised of some multi-membered oxygen-rings and some branched H-bonding waters, or only multi-membered oxygen-rings. The former are clover, pentagon, bib, balloon and chair and the latter are crown, seal, diamond, coal and d2d. In addition, we can also discern each cluster has different H-bonding patterns. In Table 5, we list the size of the oxygen-ring for each cluster, and how the eight water

Table 4
Vibrational frequencies for each of the eight rigid water molecules within the octamer (cm^{-1})

Clover						
101	109	233	289	313	504	634
102	106	231	310	350	464	605
103	108	248	270	300	470	722
104	107	237	313	339	435	631
105	15	17	18	121	181	324
106	15	17	18	125	180	316
107	15	17	19	127	168	321
108	16	17	18	123	170	322
Pentagon						
201	90	232	287	327	491	536
202	112	225	300	361	436	479
203	23	73	209	246	367	457
204	54	263	295	327	418	463
205	27	69	230	240	366	446
206	14	20	20	118	172	324
207	14	17	18	130	185	318
208	16	18	20	133	169	314
Bib						
301	23	69	218	241	354	423
302	44	262	310	359	385	438
303	26	81	204	260	344	415
304	23	69	203	280	326	415
305	44	261	295	347	385	454
306	26	81	199	241	369	431
307	15	20	21	126	170	314
308	15	18	21	136	170	313
Balloon						
401	24	85	195	237	350	435
402	22	72	202	249	337	421
403	42	259	302	334	371	456
404	26	82	180	273	351	400
405	24	84	186	276	342	412
406	25	81	188	263	350	421
407	26	82	196	242	355	433
408	15	20	22	125	170	310
Crown						
501	23	95	180	251	345	407
502	23	94	180	240	346	424
503	23	95	173	238	347	447
504	23	95	165	247	346	453
505	23	96	160	264	347	438
506	23	96	161	277	348	416
507	23	96	166	275	348	404
508	23	95	174	263	343	402
Chair						
601	43	156	205	337	561	624
602	63	164	168	299	306	593
603	27	80	204	305	332	522
604	177	243	275	307	334	798
605	29	84	244	292	330	448
606	194	248	270	326	350	736
607	27	55	238	305	352	421
608	157	229	317	411	461	501
Seal						
701	167	190	338	403	462	820
702	20	224	249	272	307	387
703	176	214	302	386	554	946
704	167	247	297	359	587	719
705	206	252	261	317	456	537

Table 4 (*Continued*)

706	32	66	217	293	339	623
707	177	227	295	397	643	716
708	215	255	271	348	356	505
Diamond						
801	173	193	323	410	492	798
802	184	215	246	305	404	856
803	192	230	247	299	468	589
804	131	173	345	434	521	748
805	201	218	250	292	443	813
806	191	226	246	294	508	588
807	144	217	367	437	575	723
808	152	233	261	352	765	837
Coal						
901	212	217	246	317	453	525
902	196	207	269	288	437	744
903	144	209	349	422	639	740
904	207	241	281	308	388	746
905	179	212	230	285	508	703
906	136	197	374	381	609	755
907	171	208	354	411	491	564
908	183	220	277	389	497	1030
d2d						
1001	220	248	268	304	519	551
1002	190	212	299	406	653	710
1003	207	239	264	297	545	598
1004	186	211	305	391	663	728
1005	166	203	305	408	663	819
1006	222	238	260	308	528	568
1007	209	256	258	299	522	590
1008	178	211	305	396	658	761

molecules in each cluster take part in each H-bond as donor and/or acceptor.

3.2.4. H-bonding strength and H-bond lifetime

H-bonding strengths and H-bonding lifetimes for each of the H-bonding patterns formed in the 10 octamer clusters are plotted in Fig. 6. Analogous to Fig. 2, we see that the H-bonds (n-D s-A in red letters) of clover, pentagon, bib and balloon tend to be stronger and last longer than the others. But we cannot generalize about the relative strength of other types of H-bonds. In the case of heptamer, we could say more. In going from the heptamer to the octamer, the structure becomes more complex, and it is difficult to discern which H-bond patterns are advantageous. Also unlike the heptamer, the relationship between H-bonding strength and H-bonding lifetime in each cluster is blurred in the octamers.

3.2.5. Free energy

The partition function for water octamer can be expressed by 6×8 harmonic oscillators for rigid-body motions. Thus, the free energy F is calculated as a sum of four contributions as in the case of the heptamer. In Table 6, we show the free energies with the four contributions for each octamer cluster at 300 K, the free energy at 0 K (F_{zero}), and the
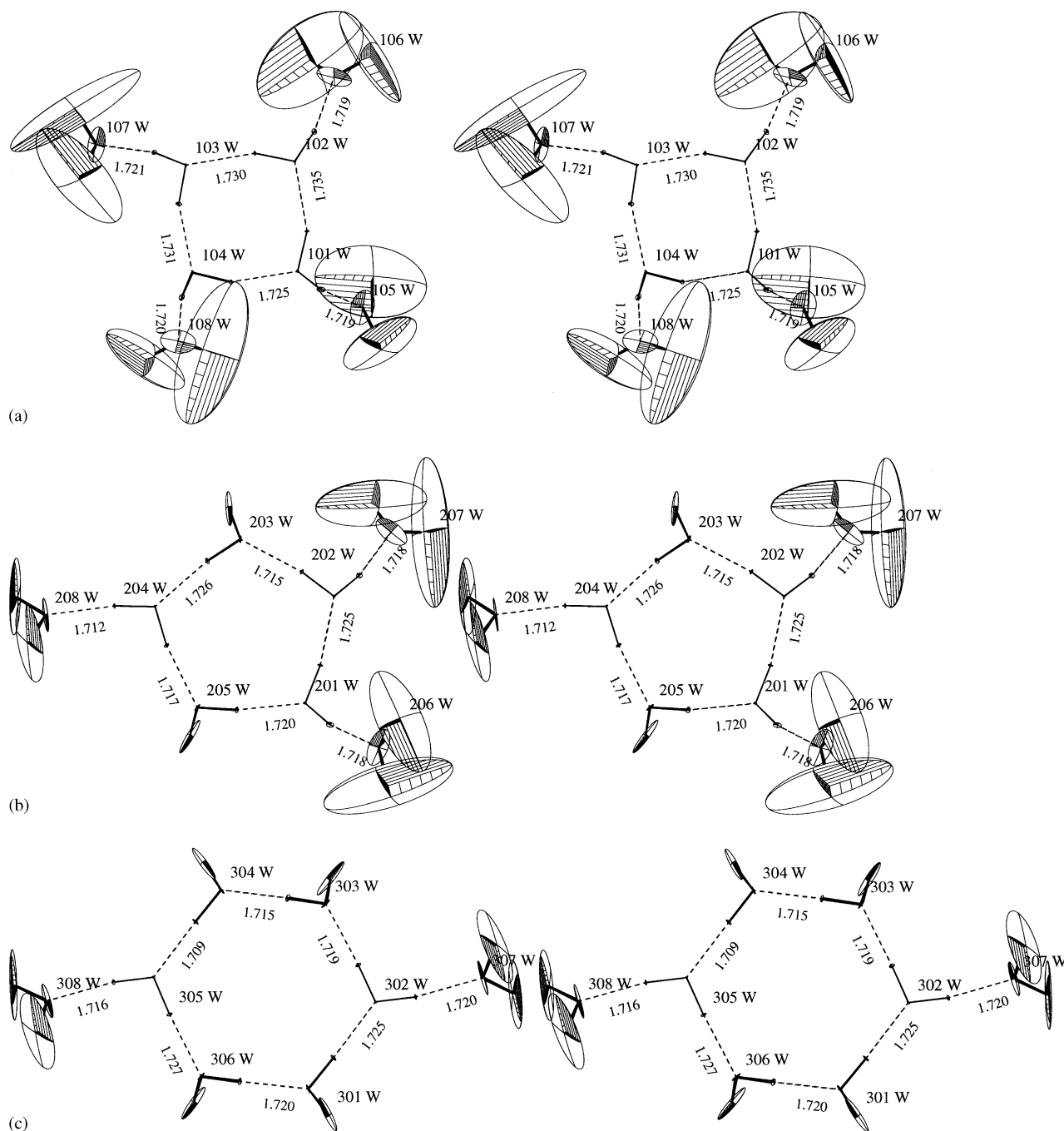
Fig. 5. Stereo view of rigid-body motions of each water molecule in the octamer. The thermal ellipsoids of atoms (at 50 or 70 or 97%) are drawn in ORTEP. (a) Clover (50%), (b) pentagon (50%), (c) bib (50%), (d) balloon (70%), (e) crown (97%), (f) chair (97%), (g) seal (97%), (h) diamond (97%), (i) coal (97%) and (j) d2d (97%).

number of H-bond in each. We see that the binding energy Φ_0 decreases in order from top to bottom in Table 6. Along with the increase of H-bond, the binding energy generally decreases, though the order of the decrease is somewhat different because of the structure of the cluster.

3.2.6. Stabilizing factors

In Fig. 7, we show the three stabilization indicators for each octamer cluster. We see that the slopes of the indicators are roughly the same. In addition, we can point out that the 10 clusters are divided into three zones: The first is comprised of five clusters with 8 H-bonds, the second has the chair and the seal, and the third has the diamond, the coal and the d2d. In the first zone, trends for both the free energy (red) and the lifetime (green) agree well, while in the third, the correspondence of the strength (blue) and the lifetime (green) is quite good, although these clusters have different numbers of H-bonds.
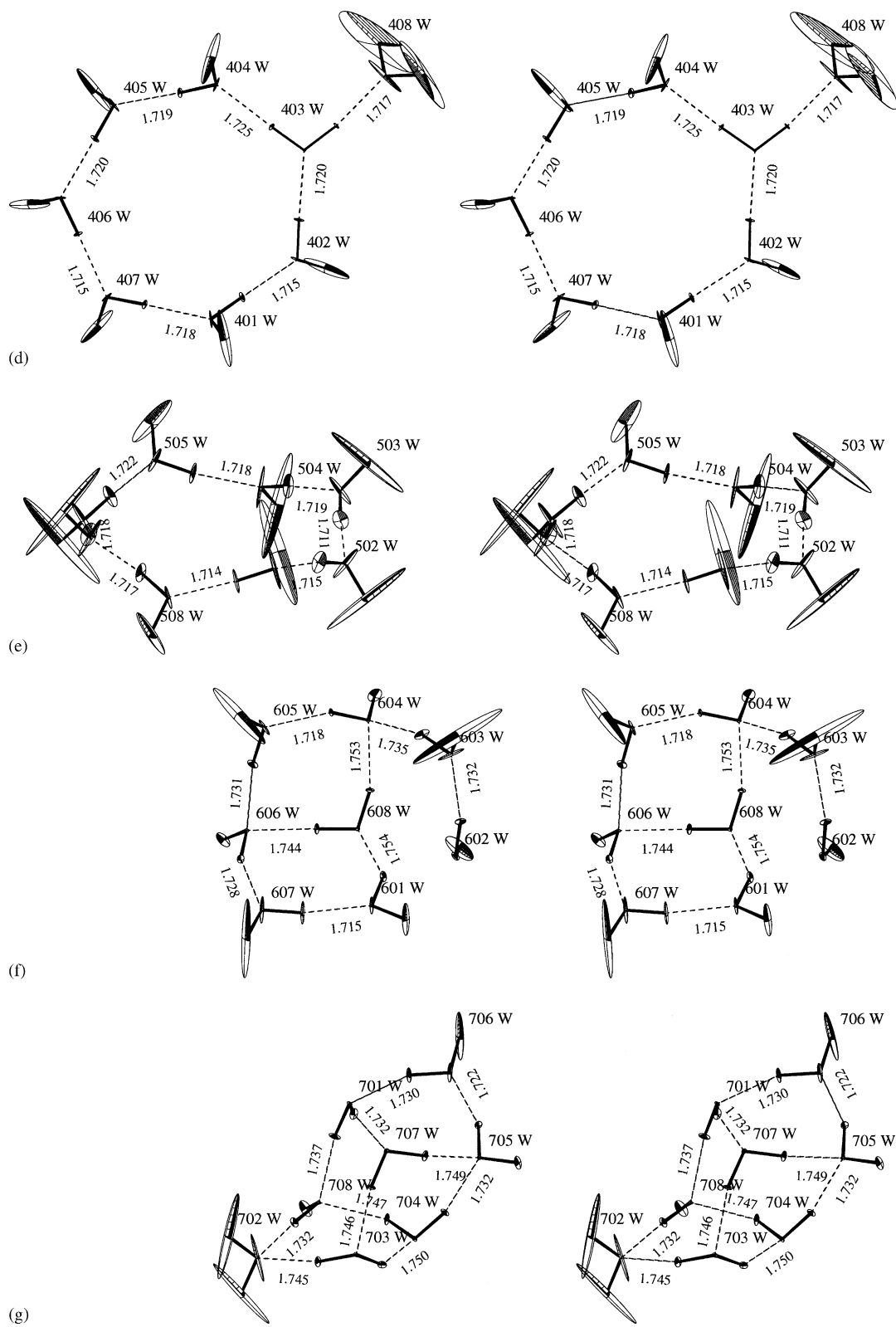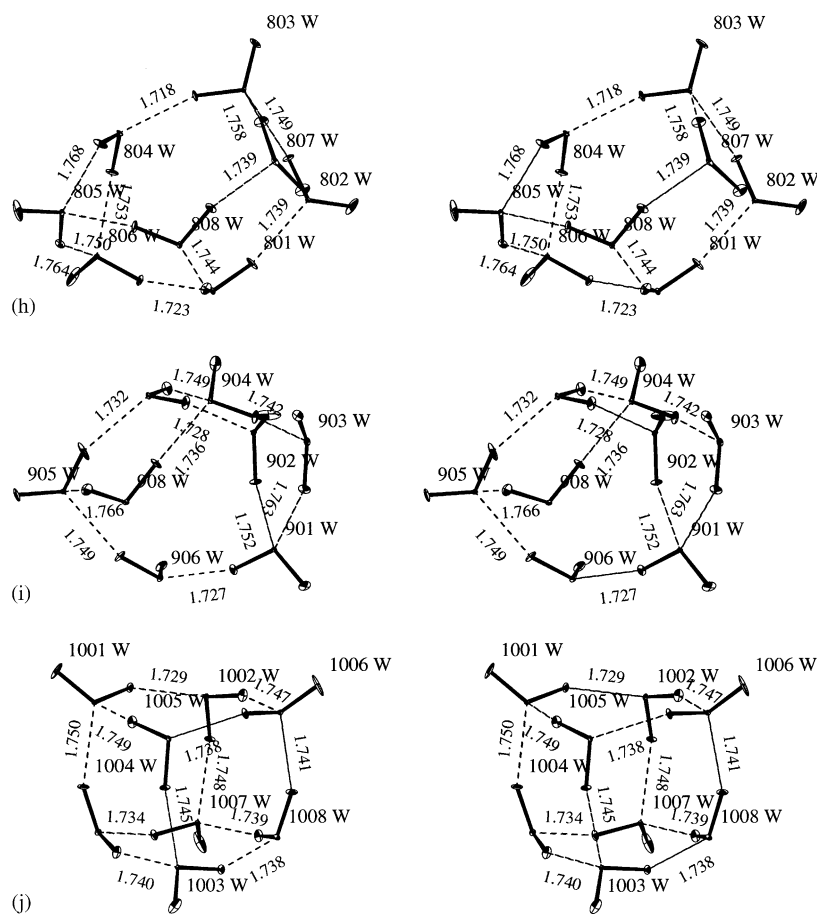
(d)

(e)

(f)

(g)

Fig. 5. (*Continued*).

Fig. 5. (*Continued*).

Table 5
Classification of H-bonding

	n-A	s-A	d-A
Clover: one 4-membered oxygen-ring			
n-D		105, 106, 107, 108	
s-D			
d-D		101, 102, 103, 104	
Pentagon: one 5-membered oxygen-ring			
n-D		206, 207, 208	
s-D		203, 205	
d-D		201, 202, 204	
Bib: one 6-membered oxygen-ring			
n-D		307, 308	
s-D		301, 303, 304, 306	
d-D		302, 305	
Balloon: one 7-membered oxygen-ring			
n-D		408	
s-D		401, 402, 404, 405, 406, 407	
d-D		403	
Crown: one 8-membered oxygen-ring			
n-D			
s-D		501, 502, 503, 504, 505, 506, 507, 508	
d-D			
Chair: two 4-membered oxygen-rings			
n-D			

Table 5 (*Continued*)

|	n-A	s-A	d-A
s-D	602	601, 603, 605, 607	604, 606
d-D		608	
Seal: three 4-membered oxygen-rings, two 5-membered oxygen-rings			
n-D			702
s-D		706	705, 708
d-D		701, 703, 704, 707	
Diamond: one 3-membered oxygen-ring, one 4-membered oxygen-ring, three 5-membered oxygen-rings			
n-D			
s-D		802, 807	803, 805, 806
d-D		801, 804, 808	
Coal: one 4-membered oxygen-ring, two 5-membered oxygen-rings, one 6-membered oxygen-ring			
n-D			
s-D		902, 903, 906	901, 904, 905
d-D	908	907	
d2d: six 4-membered oxygen-rings			
n-D			
s-D			1001, 1003, 1006, 1007
d-D		1002, 1004, 1005, 1008	
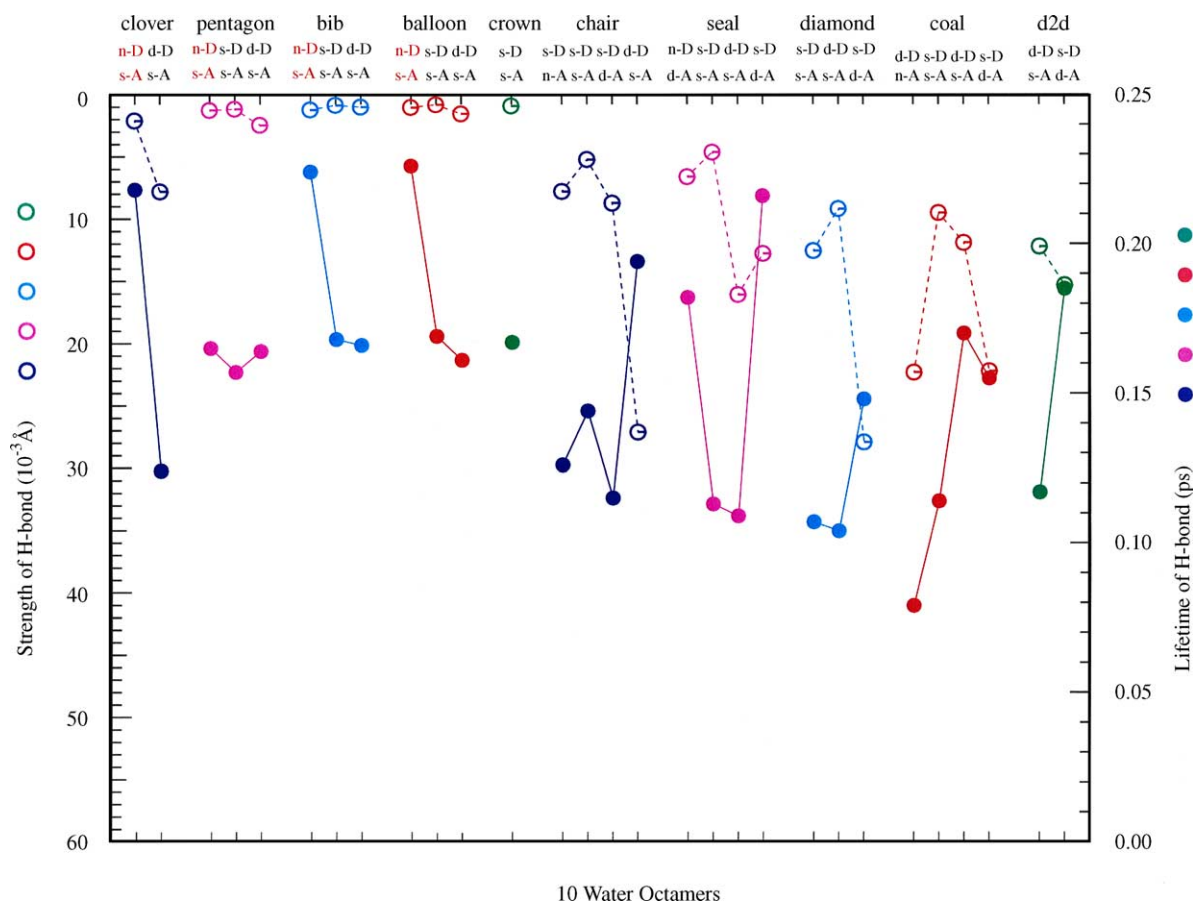
Fig. 6. H-bond strength (open circles) and H-bond lifetime (solid circles) for H-bond patterns formed in the 10 octamers. The legends are the same as in Fig. 2.

The clusters in the first zone with one oxygen-ring and 8 H-bonds are more stable than in the other zones with multi-oxygen-rings and more H-bonds. As for the seal and the diamond with the same 11 H-bonds, the stabilization is different owing to the difference of the structure. In addition, it might be surprising that the d2d (12 H-bond) is more stable than the coal (10 H-bonds) and the diamond (11 H-bonds).

3.2.7. Temperature dependence of free energy

As was done in the heptamer analysis, we select three clusters from the 10 octamers: the pentagon in the first zone, the seal in the second, and the d2d in the third (see Fig. 8). It seems that, near 0 K, the three clusters would be almost equally abundant, although the d2d is a little more likely. As the temperature rises forward 300 K, the entropy effect grows, and the pentagon becomes strongly preferred. The

Table 6
Free energy for the 10 octamers at 300 K, free energy at 0 K (F_{zero}) and the number of H-bond in the each

|	HB	Φ_0	$+\varepsilon_{zero}^{rigid}$	$+\varepsilon_{osci}^{rigid}$	$-(TS)^{rigid} = F$	(F_{zero})
Clover	8	−37.59	+15.71	+17.26	−44.04 = −48.66	(−21.88)
Pentagon	8	−38.82	+14.94	+17.38	−43.15 = −49.64	(−23.88)
Bib	8	−39.55	+14.62	+17.43	−42.34 = −49.83	(−24.93)
Balloon	8	−40.07	+14.78	+17.27	−40.53 = −48.56	(−25.29)
Crown	8	−40.52	+15.01	+17.07	−38.70 = −47.14	(−25.51)
Chair	9	−44.82	+20.20	+14.29	−28.79 = −39.13	(−24.62)
Seal	11	−48.92	+23.97	+12.41	−22.84 = −35.39	(−24.95)
Diamond	11	−50.82	+26.12	+11.53	−19.56 = −32.72	(−24.70)
Coal	10	−51.12	+25.90	+11.51	−19.37 = −33.09	(−25.22)
d2d	12	−53.26	+26.46	+11.11	−18.40 = −34.09	(−26.80)

Units of kcal/mol.
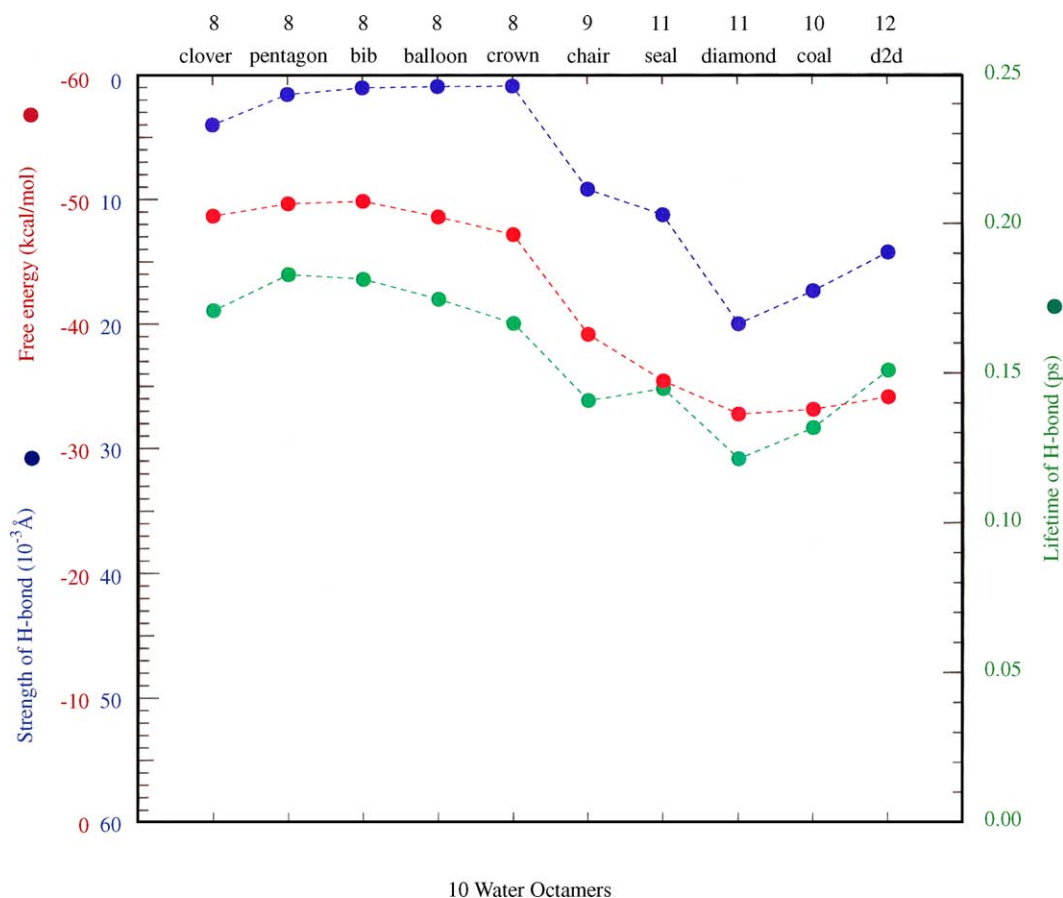
Fig. 7. Free energy (red), H-bond strength (blue) and H-bond lifetime (green) for the each of 10 octamers. The integer at top position is the number of H-bond formed in each octamer. The legends are the same as in Fig. 3.

seal and the d2d have almost the same probabilities of existence even as the temperature goes up, although they have different structures.

4. Discussion and conclusion

From Figs. 3 and 7, we see that the three quantities to track stabilization in the heptamers and octamers follow each other fairly well. In these figures, the free energies for both heptamers and octamers are calculated at 300 K. We cannot in principle estimate the temperature dependence of the H-bonding strength and H-bonding lifetime. We have estimated the strengths at the energy minimum point in each water cluster. Even at near 0 K, each water molecule is undergoing zero-point vibrations around an energy minimum point. Hence we cannot exactly judge the geometrical position of a hydrogen. At 300 K, water molecules in clusters are widely fluctuating as depicted in Figs. 1 and 5, so we cannot precisely calculate the H-bonding strength from the geometrical positions of hydrogen and oxygen H-bonding. The H-bonding strength estimated at an energy minimum point would have to be based on averaged positions of the water molecules fluctuating at 300 K. However, we expect

the trend of the values in Figs. 3 and 7 to roughly agree with the trend of the free energy calculated at 300 K.

The H-bonding lifetime is derived from the difference in the frequencies of a harmonic oscillator whose frequencies are given by force constants obtained as the second derivatives of potential field offered by water molecules in the cluster. Thus, H-bonding lifetime implicitly depends on temperature, since this value is dependent on the potential field produced by the water molecules. The potential field is dependent on the position of water, whose positions also depend on the temperature. The H-bonding lifetimes calculated at an energy minimum point would be the ones corresponding to the averaged positions of water molecules at 300 K, for the same reason as in the case of H-bonding strength.

Thus, H-bonding strength and lifetime implicitly depend on the temperature, whereas the free energy is explicitly dependent on the temperature. We can conclude that the free energy is the most valid indicator among these three. From Figs. 4 and 8, we can see that the probability of existence of each cluster is largely dependent on the temperature. Near 0 K, the probabilities do not differ greatly. But in the temperature range above about 150 K, with which we are concerned, the free energies gradually separate as depicted, as
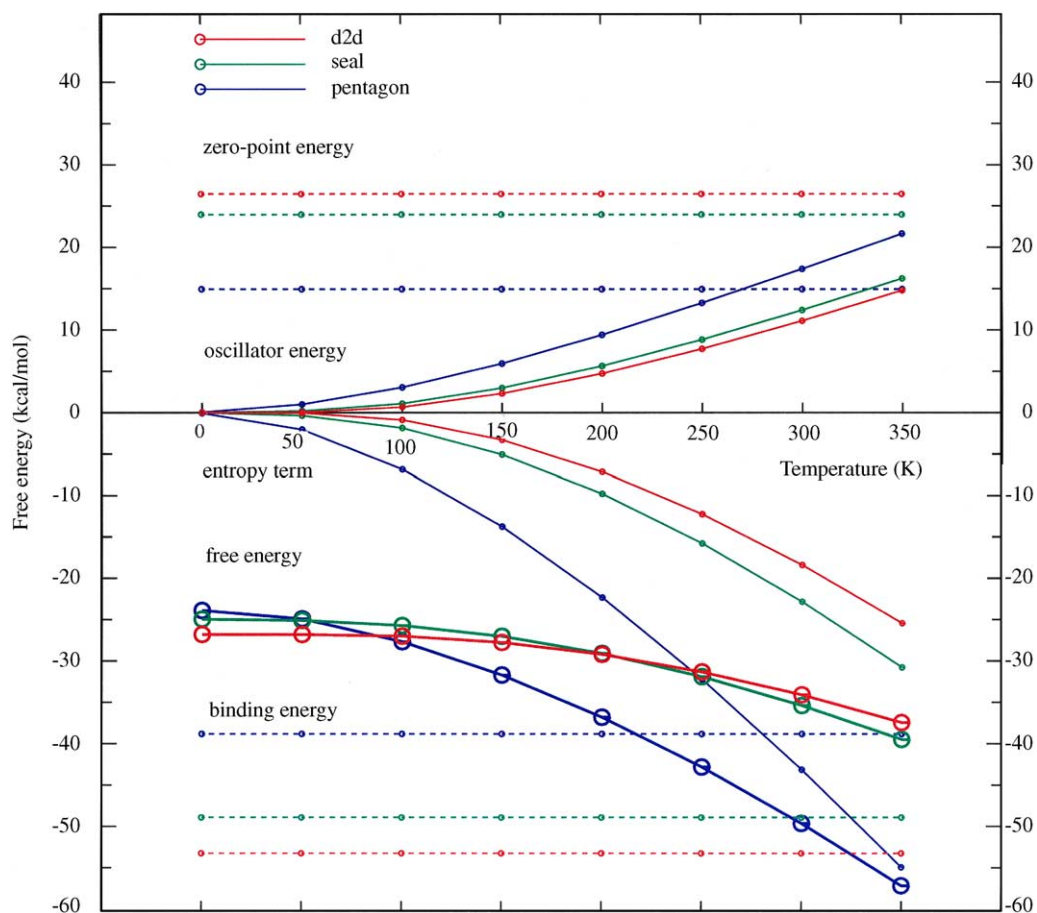
Fig. 8. Temperature dependence of free energy for the three octamers. The blue, green and red colours indicate the quantities relative to the pentagon, seal and d2d octamer, respectively. The legends are the same as in Fig. 4.

the temperature rises. In this temperature range, the relative populations of each cluster would depend on the free energy.

In conclusion, we could say, at 300 K, that of the 10 water heptamers, the airplane, the skier and the turtle belong to the more stable group, whereas the cave, the crane and the crab belong to the less stable group. The clusters in the more stable group are comprised of one oxygen-ring and some branched H-bonding waters, and their shapes are intermediate between planar and polyhedral. The clusters in the less stable group are comprised of multi-oxygen-rings, and their structures are polyhedral. Among the 10 water octamers, the clover, the pentagon and the bib belong to more stable group, while the diamond, the coal and the d2d belong to less stable group. As with the heptamers, the clusters in the more stable group are comprised of one oxygen-ring and some branching H-bonded waters, so they take form of structures intermediate between planar and polyhedral. The clusters in the less stable group are comprised of multi-oxygen-rings, and their structures are polyhedral.

By our calculations, water heptamer and octamer in the gas phase prefer structures intermediate between planar and polyhedral. Side-chain waters connected to an oxygen-ring fluctuate more than waters in an oxygen-ring. Vibrational entropies of the side-chain waters increase more, so the free energy of these structures decreases more as the temperature rises. The wreath in the heptamer and the crown in the octamer are, of course, not exactly planar; as one goes around the ring the oxygens go up or down. Although the d2d octamer is polyhedral, the compactness of this three-dimensional structure leads to a less entropic effects.

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