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Relative Stability of Hydrogen and Deuterium Bonds

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Abstract: The relative energies of H and D bonds are due to differences in zero-point vibrational energy (ZPVE). Ab initio calculations are used to assess the changes in this quantity that accompany all possible substitutions of protium by deuterium in a number of complexes. The ZPVE of the D bond is lower than that of the H bond in the neutral dimer and trimer of water. This difference can be traced to one particular vibrational mode, the one which displaces the bridging atom away from the O···O axis. The heavier mass of D lowers the frequency, and hence the ZPVE associated with it. The situation reverses itself in ionic H bonds. The total ZPVE of the $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ complex is higher when a D occupies the bridging position, as compared to a terminal site. This difference is attributed to the intramolecular modes. Although replacement of the central H by D reduces the intermolecular ZPVE, the reduction of the intramolecular ZPVE is even larger when the substitution is made at a peripheral atom, so a D would tend to migrate away from a bridging location. This effect is noted also in the larger complex in which two methanol molecules are bound by a proton. The lower energy of a H bond as compared to a D bond is observed as well in the anionic $(HOH{\cdot\cdot}OH)^-$ system, although the magnitude of the preference is smaller here. In all cases, raising the temperature, and thus invoking thermal vibrational and entropic effects, tends to preferentially stabilize H over D bonds.

Introduction

The question sometimes arises as to whether a hydrogen bond is stronger or weaker than the equivalent deuterium bond.[1,2] For example, studies of protein folding dynamics, which depend upon the exchange rate of H bonded atoms, are affected by the relative strength of these interactions.[3−6] Since H and D are electronically identical, the electronic part of the total energies of the related complexes will be equal. The differences are associated with the masses, and thence primarily to the vibrational energies. One means of addressing this question experimentally is through the measurement of isotope fractionation factors which take into account statistical issues as well.[7−9]

The HF dimer is perhaps the simplest system for which this question is relevant. It might be posed as follows: Will FH···FD be higher or lower in total energy than FD···FH? The total vibrational energy of the D-bonded complex is computed to be lower than that of the H bond by about 100 cm^{-1}.[10,11] This difference is traced to the two intermolecular bending modes that represent primarily the wagging motion of the bridging hydrogen. In the case of the D bond, i.e. FD···FH, it is a heavy D nucleus which is moving, so the frequency is reduced, relative to FH···FD where it is protium that acts as the bridge. There are also differences in the intramolecular stretching vibrations, but the changes in these two modes cancel one another so that their sum is nearly equal in the two isotopomers. These computational findings are consistent with experimental data which are not based on a harmonic force field. Analysis of high-resolution near-IR data for the Cl analogue[12] is consistent with a “stronger” D bond here as well: ClD···ClH is more stable than ClH···ClD by 16 ± 4 cm^{-1}.

Changing the subunit from HX to H_2Y adds a number of new vibrational modes to the dimer. Nonetheless, the D-bonded form of the water dimer is more stable than the H bonded complex. An energy difference of 60 cm^{-1} was measured in the Kr matrix.[13] This effect was attributed chiefly to the out-of-plane motion that shears the bond, which is of higher frequency for a proton than a deuteron, consistent with the observations for the HF dimer.

Consonant with these ideas, when HDO is paired with NH_3, HOH, formaldehyde, or formamide, it is the D atom of the former molecule which acts as the bridge rather than the protium.[14−16] The same holds true for complexes between HDO and olefins, where there is some question as to whether there is a true H bond present.[17] In the latter case, the preference for D acting as a bridge rather than H is quite small, inasmuch as both isotopomers are observed. The difference in energy is estimated as less than 0.1 kcal/mol. An even smaller preference is noted between NCH···NCD and NCD···NCH, both of which have been observed in the gas phase, leading to the suggestion that their energy difference is only several cm^{-1} at most.[18]

The preference for D-bonding vs placement of a protium in the bridging position appears to reverse in ionic H bonds. Calculations at the SCF and MP2 levels of various isotopomers of the $H_2O{\cdot\cdot}H^+{\cdot\cdot}OH_2$ system[19] indicate that any D atoms would

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tend to migrate away from the bridging position, and toward one of the four peripheral sites. The equilibrium constant for this preference lies in the neighborhood of 2−3, based upon a strict harmonic treatment of the ab initio force field. Using a temperature of 298 K, an equilibrium constant of 2 translates into a free energy preference for H to act as a bridging atom of 0.4 kcal/mol. These results confirm an earlier experimental study based on fractionation factors in the gas phase.[20] Using collision-induced dissociation techniques, partially deuterated proton hydrates were formed in a flowing-afterglow-triple-quadrupole instrument and their reactions examined; D atoms prefer terminal and H atoms bridging positions. A similar preference for H bonds has also been noted in anions such as $(CH_3O{\cdot\cdot}H{\cdot\cdot}OCH_3)^-$ [21] and $(Cl{\cdot\cdot}H{\cdot\cdot}Cl)^-$.[22]

There thus appear to be a number of interesting questions that remain unanswered. In the first place, why is the D bond stronger than a H bond in the case of a neutral complex; what causes this trend to reverse when the bond acquires an overall charge? Does it matter whether this charge is positive or negative? And what happens to these patterns as more and more H atoms are replaced by D? These points have important implications for studies that are aimed at elucidating the molecular mechanism of charge migration in solvent or within the context of protein molecules. Another intriguing issue has to do with the cooperativity of H bonds. It is well known that a chain of several molecules, bound together by H bonds, tends to be more strongly bound than would be indicated simply by the sum of pairwise interactions in the dimers.[23−27] What is not well understood is how the relative stability of H and D bonds is affected by such cooperativity.

These questions are probed in some detail here. Using the water dimer as a starting point, the normal modes are evaluated at both the SCF and correlated MP2 ab initio levels to test for any influence of electron correlation upon the results. The D atom is substituted for a protium on each of the three symmetrically distinct locations on the water dimer. This study also extends beyond the earlier work in replacing more than one protium with deuterium, considering 2, 3, and 4 substitutions. Another goal of this project is to investigate the effects of D substitution upon the cooperativity of H bonding. For this purpose, the trimer of water is considered. Again, all possible combinations of protium and deuterium are considered. The scope of the work is extended to the apparent reversal in the strengths of H vs D bonding in charged vs neutral systems. The proton-bound water dimer and the anionic equivalent $(HO{\cdot\cdot}H{\cdot\cdot}OH)^-$ are used as prototypes, so as to facilitate direct comparison with the neutral dimer. Also considered is the effect of enlargement of the system beyond the simple hydrides like H_2O.

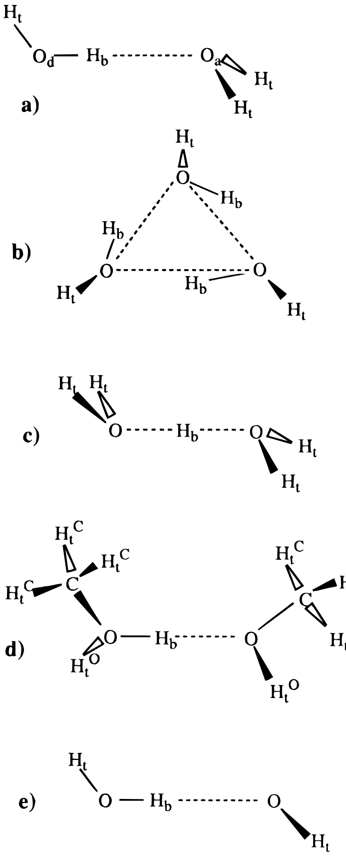

Figure 1. Equilibrium configurations of (a) water dimer, (b) water trimer, (c) $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$, (d) $(CH_3OH{\cdot\cdot}H{\cdot\cdot}OHCH_3)^+$, and (e) $(HOH{\cdot\cdot}OH)^-$. H_b and H_t refer respectively to bridging and terminal atoms. The geometry of $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ is illustrated with a centrosymmetric H bond, as observed in its MP2 structure. Equilibrium geometries are unaffected by isotopic substitution.

Methods and Results

Ab initio calculations were carried out using the Gaussian-94[28] and -90[29] packages of programs. The neutral complexes were studied with the 6−31G** basis set; 6-31+G** was employed for the ions.[30] Results were obtained at both the SCF and correlated MP2 levels. Vibrational modes and frequencies are based on a harmonic force field; no empirical scaling factors were used. The equilibrium configurations of the systems examined are illustrated in Figure 1. As equilibrium structures, these geometries are unaffected by replacement of H by its heavier isomer.

1. Water Dimer. The water dimer adopts the well-known geometry illustrated in Figure 1a wherein the H bond is very nearly linear. The proton−acceptor molecule is oriented so as to form a pyramidal arrangement of the three hydrogens around this oxygen atom.[31,32] The harmonic frequencies computed for the intramolecular modes of the water dimer are listed in the first row of Table 1. The A and D designations at the head of

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Table 1. Harmonic Intramolecular Vibrational Frequencies (cm^{-1}) of Water Dimer with Varying Degrees of Isotopic Substitution[a]

			bend		sym stretch		asym stretch		ZPVE, kcal/mol
	n_b	n_t	A	D	D	A	D	A	
SCF									
HOH··OH$_2$	0	0	1768	1798	4098	4143	4237	4257	29.00
$n_b+n_t=1$									
HOH··OHD	0	1	1550	1798	4099	3051	4237	4203	27.05
DOH··OH$_2$	0	1	1768	1603	3059	4146	4125	4257	27.08
HOD··OH$_2$	1	0	1768	1552	2998	4142	4213	4257	27.04
$n_b+n_t=2$									
HOH··OD$_2$	0	2	1294	1798	4100	2986	4237	3122	25.05
DOH··OHD	0	2	1550	1603	3059	3051	4128	4203	25.13
DOD··OH$_2$	1	1	1768	1314	2959	4143	3102	4257	25.06
HOD··OHD	1	1	1550	1552	2998	3051	4213	4202	25.09
$n_b+n_t=3$									
DOH··OD$_2$	0	3	1294	1602	3059	2986	4129	3122	23.13
DOD··OHD	1	2	1550	1314	2959	3051	3103	4202	23.11
HOD··OD$_2$	1	2	1294	1551	3000	2984	4213	3122	23.09
$n_b+n_t=4$									
DOD··OD$_2$	1	3	1294	1314	2959	2986	3103	3122	21.11
MP2									
HOH··OH$_2$	0	0	1682	1717	3820	3879	4002	4010	27.30
$n_b+n_t=1$									
HOH··OHD	0	1	1475	1716	3822	2863	4002	3947	25.46
DOH··OH$_2$	0	1	1682	1538	2886	3882	3847	4010	25.49
HOD··OH$_2$	1	0	1682	1474	2796	3877	3978	4010	25.45
$n_b+n_t=2$									
HOH··OD$_2$	0	2	1231	1716	3823	2795	4001	2938	23.58
DOH··OHD	0	2	1475	1538	2886	2863	3852	3948	23.66
DOD··OH$_2$	1	1	1682	1254	2762	3877	2926	4010	23.59
HOD··OHD	1	1	1472	1476	2795	2864	3978	3947	23.62
$n_b+n_t=3$									
DOH··OD$_2$	0	3	1231	1538	2886	2795	3853	2938	21.77
DOD··OHD	1	2	1475	1254	2761	2863	2926	3947	21.75
HOD··OD$_2$	1	2	1231	1474	2804	2786	3978	2938	21.73
$n_b+n_t=4$									
DOD··OD$_2$	1	3	1230	1254	2760	2796	2926	2938	19.86

[a] n_b and n_t refer respectively to the number of bridging and terminal positions occupied by D; the acceptor and donor molecules are represented by A and D, respectively.

Table 2. Harmonic Intermolecular Vibrational Frequencies (cm^{-1}) and Zero-Point Vibrational Energy of Water Dimer with Varying Degrees of Isotopic Substitution

									ZPVE, kcal/mol	
	n_b	n_t	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	inter	total
SCF										
HOH··OH$_2$	0	0	116	135	142	176	377	613	2.23	31.23
$n_b+n_t=1$										
DOH··OH$_2$	0	1	98	128	134	169	339	612	2.11	29.20
HOH··OHD	0	1	101	120	138	175	361	598	2.13	29.19
HOD··OH$_2$	1	0	108	126	140	172	342	480	1.95	28.99
$n_b+n_t=2$										
HOH··OD$_2$	0	2	94	110	124	174	346	585	2.05	27.10
DOH··OHD	0	2	91	105	131	168	321	597	2.02	27.15
DOD··OH$_2$	1	1	94	119	128	166	321	479	1.87	26.93
HOD··OHD	1	1	94	116	135	171	322	460	1.85	26.95
$n_b+n_t=3$										
DOH··OD$_2$	0	3	86	104	106	167	302	585	1.93	25.06
DOD··OHD	1	2	87	102	124	165	299	459	1.77	24.88
HOD··OD$_2$	1	2	89	105	124	170	304	442	1.76	24.85
$n_b+n_t=4$										
DOD··OD$_2$	1	3	83	101	104	164	279	441	1.67	22.78
MP2										
HOH··OH$_2$	0	0	94	147	164	205	430	667	2.44	29.74
$n_b+n_t=1$										
DOH··OH$_2$	0	1	82	139	155	195	388	667	2.32	27.82
HOH··OHD	0	1	85	129	155	204	407	651	2.33	27.79
HOD··OH$_2$	1	0	88	137	161	198	395	526	2.15	27.60
$n_b+n_t=2$										
HOH··OD$_2$	0	2	79	122	136	202	387	633	2.23	25.80
DOH··OHD	0	2	75	120	145	195	362	650	2.21	25.87
DOD··OH$_2$	1	1	77	129	149	191	371	525	2.06	25.65
HOD··OHD	1	1	81	123	150	198	365	506	2.03	25.65
$n_b+n_t=3$										
DOH··OD$_2$	0	3	70	117	121	194	338	632	2.10	23.87
DOD··OHD	1	2	71	115	138	191	340	505	1.94	23.69
HOD··OD$_2$	1	2	75	116	135	197	343	480	1.92	23.65
$n_b+n_t=4$										
DOD··OD$_2$	1	3	67	111	120	190	315	479	1.83	21.70

each column indicate whether the particular molecule serves as proton acceptor or donor, respectively. The last column of Table 1 sums the six frequencies to yield a total intramolecular zero-point vibrational energy (ZPVE) of 29.00 kcal/mol at the SCF level, 27.30 kcal/mol at MP2. (The smaller correlated frequencies are typical of most molecules and complexes.)

Listed in the succeeding rows of Table 1 are the harmonic frequencies computed for all the different permutations of one, two, three, or four D atoms substituted for H in the water dimer. In this table, the number of deuterium atoms that is placed in the single bridging position (zero or one) is represented by n_b, and n_t refers to the number of D atoms in terminal, i.e. non-bridging, positions. The sum of n_b plus n_t of course indicates the total number of D atoms in the complex. The upper portion of Table 1 presents the data computed at the SCF level, followed in the lower half by the MP2 results.

The vibrational modes of the monomer carry over into the dimer with some fidelity. So for both the donor and acceptor molecules (D and A in Table 1), the bending motion is recognized, as well as the symmetric and asymmetric stretches. One may note from the first row of Table 1 that the frequency of the donor molecule is consistently smaller than that of the acceptor for each of the two intramolecular stretching modes; the reverse is true for the bend.

The second through fourth rows replace one of the protiums by a deuterium, in each of three symmetrically distinct locations. With respect to the total intramolecular zero-point energy, there seems little difference where this deuterium is placed. In each case, this quantity is smaller by almost 2 kcal/mol than the water dimer containing no deuterium at all. In fact, this trend continues as the number of deuteriums is increased: Each substitution of a protium by a deuterium lowers the intramolecular zero-point energy by almost 2 kcal/mol, with no real sensitivity to where these replacements are made.

Analysis of the individual modes illustrates that each is altered by substitution. For example, the SCF bending frequency of the proton donor molecule is 195 cm^{-1} higher in HOH··OHD than in DOH··OH$_2$. On the other hand, the situation reverses in the proton acceptor molecule where the frequency of DOH··OH$_2$ exceeds that of HOH··OHD by 218 cm^{-1}. It is this sort of compensation which results in the very small differences in total intramolecular zero-point energy, and its insensitivity to the location of the deuterium. The frequencies of a given molecule appear insensitive also to any isotopic substitution on its partner. For example, the SCF symmetric stretching frequency of the proton donor HOH is 4098 cm^{-1} in the fully protiated dimer. This frequency remains constant to within only 2 cm^{-1} as the proton acceptor molecule is changed to OHD and then to OD$_2$. These trends are noted at both the SCF and MP2 levels.

The analogous data for the six intermolecular modes are reported in Table 2. The frequencies span a range from about 100 to 600 cm^{-1}. There is a general tendency for each frequency to lower as the number of deuteriums in the complex increases. However, these decreases are rather small for the first four modes. For example, ν_1 drops by about 30 cm^{-1} at the SCF level upon changing all four protiums to deuterium. ν_5 is somewhat more sensitive, diminishing by about 100 cm^{-1}.

Most sensitive of all is ν_6, and it is on this mode that we focus our attention. In the fully protiated dimer, this frequency

Table 3. Vibrational Frequencies (cm^{-1}) of Isotopomers of Water and Total Zero-Point Vibrational Energy

	bend	sym stretch	asym stretch	ZPVE, kcal/mol
		SCF		
HOH	1769	4147	4264	14.54
HOD	1551	3055	4208	12.59
DOD	1295	2989	3126	10.59
		MP2		
HOH	1557	4081	4276	14.16
HOD	1360	3031	4187	12.25
DOD	1142	2935	3141	10.31

is 613 cm^{-1} at the SCF level. There is little change noted when a deuterium is placed on one of the terminal positions, but this frequency drops down to 480 cm^{-1} when the bridging position is occupied by a D. In fact, this conclusion pertains in the other cases as well, with two, three, and four deuteriums. ν_6 lies in the 600−610-cm^{-1} range when a protium acts as the bridging atom but drops down below 500 cm^{-1} when deuterium acts as the bridge. This finding is consistent with the identification of ν_6 as a wagging motion of the proton donor molecule, coordinated with some similar motion of the acceptor, albeit by a small amount. Replacement of H with D will hence appreciably raise the effective mass for the mode.

The approximate 120 cm^{-1} drop in ν_6 corresponds to a lowering of its zero-point energy by 0.2 kcal/mol. Taking into account the near independence of the other five modes to the location of the deuterium substitution, it becomes possible to explain the total intermolecular zero-point vibrational energies in the penultimate column of Table 2. For each degree of substitution ($n_b + n_t$), there is a clear pattern evident: The vibrational energy is smaller by 0.2 kcal/mol when the bridging position is occupied by D as compared to a bridging H. This rule is carried over unchanged into the total zero-point vibrational energy (intramolecular + intermolecular) in the last column of Table 2, since the intramolecular quantity is insensitive to the location of the D atom. It is notable also that the MP2 and SCF sets of data are entirely consistent with one another. Moreover, a previous set of computations of intermolecular frequencies, based upon a different ab initio force field, arrived at a similar conclusion that it is ν_6 which is primarily responsible for differences in ZPVE between the various isotopomers.[13]

The hydrogen-bond energy of a complex formed by the reaction A + B → A··B subtracts the energies of the two monomers A and B from that of the complex. The last column of Table 2 reports the vibrational energy of each complex. From this must be subtracted the zero-point vibrational energies of its constituent monomers, whether they be HOH, HOD, or DOD. The computed frequencies of each of these monomers are exhibited in Table 3, along with their total zero-point vibrational energy.

After subtraction of the zero-point vibrational energy of the isolated monomers from that of the complex, one arrives at a vibrational correction to the binding energy. These corrections are reported as ΔZPVE in Table 4. As an example, the first row of the table indicates that the HOH··OH$_2$ complex contains 2.14 kcal/mol more SCF zero-point energy than the pair of isolated HOH monomers. Consequently, the H bond energy is smaller by this amount than the purely electronic contribution which is 4.55 kcal/mol at the SCF level, leaving a value of 2.41 kcal/mol.

The last column of Table 4 reports the complexation energy of each of the various complexes. There are a number of interesting trends in the data. The "weakest" complex is the fully protiated one with a H bond energy of 5.39 kcal/mol at the MP2 level. Each progressive replacement of a protium by deuterium yields a further enhancement of the binding energy of the complex. Consequently, the perdeuterated complex is the strongest, more tightly bound than HOH··OH$_2$ by 0.34 kcal/mol (by 0.53 kcal/mol at the SCF level). There is a notable difference in the effects of substitution upon whether the atom replaced is a bridging or terminal atom. If the bridging hydrogen of HOH··OH$_2$ is replaced by a D, the binding energy is increased by some 0.2 kcal/mol. (This increment varies between 0.19 and 0.25 over the full range of substitutions in Table 4.) Substitutions of the terminal atoms add only very small increments, on the order of 0.02 kcal/mol. There does not seem to be much difference in whether these terminal positions occur on the donor or acceptor molecule. These patterns are true also at the SCF level, although the magnitudes of the increments are slightly larger.

Table 4. Difference in Zero-Point Vibrational Energy between Complexes and Constituent Monomers and the Resulting Complexation Energy (in kcal/mol)

	n_b	n_t	ΔZPVE	$-(\Delta E$[a] $+ \Delta$ZPVE)
		SCF		
HOH··OH$_2$	0	0	2.14	2.41
HOH··OHD	0	1	2.05	2.50
DOH··OH$_2$	0	1	2.06	2.49
HOD··OH$_2$	1	0	1.86	2.69
HOH··OD$_2$	0	2	1.97	2.59
DOH··OHD	0	2	1.97	2.59
DOD··OH$_2$	1	1	1.80	2.76
HOD··OHD	1	1	1.77	2.79
DOH··OD$_2$	0	3	1.88	2.67
DOD··OHD	1	2	1.70	2.85
HOD··OD$_2$	1	2	1.68	2.88
DOD··OD$_2$	1	3	1.61	2.94
		MP2		
HOH··OH$_2$	0	0	1.41	5.39
HOH··OHD	0	1	1.38	5.42
DOH··OH$_2$	0	1	1.40	5.40
HOD··OH$_2$	1	0	1.18	5.62
HOH··OD$_2$	0	2	1.33	5.47
DOH··OHD	0	2	1.36	5.44
DOD··OH$_2$	1	1	1.17	5.63
HOD··OHD	1	1	1.14	5.66
DOH··OD$_2$	0	3	1.31	5.49
DOD··OHD	1	2	1.13	5.67
HOD··OD$_2$	1	2	1.09	5.71
DOD··OD$_2$	1	3	1.07	5.73

[a] The electronic contribution to the binding energy is equal to −4.55 and −6.80 kcal/mol at the SCF and MP2 levels, respectively, following counterpoise correction of the BSSE.

One expression of the question as to the relative strength of H vs D bonds would be a pairing of DOD with HOH. The complex is more strongly bound when the first molecule acts as donor, as compared to the reverse situation, by some 0.16 kcal/mol at the MP2 level. An alternative phrasing of the question pairs HOD with OH$_2$ and compares the geometries in which the H or D of the first molecule acts as the bridging atom. HOD··OH$_2$ is computed to be more strongly bound than DOH··OH$_2$ by 0.22 kcal/mol. Still another posing of a similar question might be the pairing of two HOD monomers. Again, the complex is more stable than the constituent monomers by 0.2 kcal/mol in the case of a D bridge as compared to a H bond. And in the situation of full substitution, either H or D, the binding energy of DOD··OD$_2$ exceeds that of HOH··OH$_2$ by some 0.3 kcal/mol.

In summary, the greater strength of the D as compared to the H bond in the water dimer can be traced primarily to the intermolecular ν_6 mode which can be characterized as a bending motion of the proton donor molecule. The heavier D imparts a higher effective mass to this mode, and lowers its frequency such that the zero-point energy is reduced by 0.2 kcal/mol.

Table 5. Harmonic Intermolecular Vibrational Frequencies and Zero-Point Vibrational Energy of Water Trimer with Varying Degrees of Isotopic Substitution, Computed at the MP2 Level

		freq, cm^{-1}	ZPVE, kcal/mol		
n_b	n_t	$\nu_{10} + \nu_{11} + \nu_{12}$	inter	intra	total
0	0	2412	7.27	40.19	47.46
n_b+n_t=1					
0	1	2402 ± 6	7.05	38.41	45.45
1	0	2214 ± 3	6.87	38.38	45.25
n_b+n_t=2					
0	2	2387 ± 6	6.81	36.63	43.44
1	1	2198 ± 14	6.64	36.60	43.24
2	0	2006 ± 8	6.46	36.58	43.04
n_b+n_t=3					
0	3	2377	6.58	34.85	41.43
1	2	2181 ± 11	6.44	34.76	41.20
2	1	1991 ± 15	6.27	34.73	41.01
3	0	1791	6.07	34.76	40.83
n_b+n_t=4					
1	3	2167 ± 5	6.22	32.98	39.20
2	2	1971 ± 18	6.05	32.95	39.00
3	1	1775 ± 8	5.88	32.92	38.80
n_b+n_t=5					
2	3	1955 ± 6	5.84	31.11	36.96
3	2	1754 ± 9	5.68	31.08	36.76
n_b+n_t=6					
3	3	1741	5.49	29.24	34.73

2. Water Trimer. The trimer of water is known to adopt a cyclic equilibrium geometry.[33−37] As indicated in Figure 1b, there are three very nearly equivalent H bonds, each with a bridging hydrogen H_b. Two of the terminal hydrogens (H_t) are on one side of the interoxygen plane and the third is on the other. Note that the three water molecules are not precisely equivalent and the three R(OO) distances are not equal. The three H bonds are all distorted from linearity, with θ(O··OH) approximately 18°, caused by the strain imposed in forming a small ring. There are 21 normal vibrational modes in all. The twelve of lowest frequency correspond to intermolecular modes, and the nine highest are intramolecular. The latter refer to the symmetric and antisymmetric stretches or bends of the individual subunits, or combinations thereof.

Of greatest interest are the three intermolecular vibrations of highest frequency. ν_{10}, ν_{11}, and ν_{12} correspond to the three modes which consist primarily of the bending motion of the three bridging hydrogens. As such, it is this collection of modes which were found to be most sensitive to the identity of the bridging atom. The sum of these three frequencies is listed in the appropriately labeled column of Table 5. The first row of Table 5 refers to the undeuterated trimer, from which it may be seen that these three frequencies sum to 2412 cm^{-1} in $(H_2O)_3$.

Calculations were performed in which all combinations of hydrogens of the water trimer were replaced by D. The data are organized in much the same way as for the dimer. The second and third rows refer to the monodeuterated complex, wherein the deuterium may replace either a terminal or bridging H atom. Since there are three separate terminal positions (the three water molecules are not quite equivalent), there are three such complexes. The entry of 2402 ± 6 cm^{-1} in Table 5 indicates that the frequency sums in these three complexes all fall within this range. Similarly, these frequencies sum to 2211−2217 cm^{-1} when the single D is located at one of the three bridging positions. The difference between placing the deuterium on a terminal or bridging atom is 188 cm^{-1}, which accounts for 0.27 kcal/mol lower zero-point vibrational energy in this triad of modes when D acts as a bridge.

Table 6. Difference in Zero-Point Vibrational Energy between Trimers and Constituent Monomers and the Resulting Complexation Energy (in kcal/mol), All Calculated at the MP2 Level

n_b	n_t	ΔZPVE	$-(\Delta E^a + \Delta$ZPVE)
0	0	4.97	7.92
0	1	4.87	8.02
1	0	4.67	8.22
0	2	4.77	8.12
1	1	4.57	8.32
2	0	4.37	8.52
0	3	4.67	8.22
1	2	4.47	8.42
2	1	4.27	8.62
3	0	4.07	8.82
1	3	4.38	8.51
2	2	4.18	8.71
3	1	3.98	8.91
2	3	4.09	8.80
3	2	3.88	9.01
3	3	3.79	9.10

[a] The electronic contribution to the binding energy is equal to −12.89 kcal/mol at the MP2 level following counterpoise correction of the BSSE.

The next column in Table 5 illustrates that when all intermolecular modes are combined, the complex contains 0.18 kcal/mol more intermolecular zero-point energy when the D is in a terminal as compared to a bridging position. There is little if any distinction in the intramolecular energy. The last column of Table 5 indicates that the D-bridging position is favored over the H bridge by 0.20 kcal/mol. Hence, one can attribute the lower energy of the D-bridged complex to the vibrational modes involving a motion of the bridging atom perpendicular to the H bond axis.

Progression to higher degrees of deuteration reiterates these same trends. Each replacement of a H with a D lowers the total zero-point energy by 2.0 kcal/mol. But most important, within any class of deuteration, e.g. di or tri, one may observe that each change in position of the D atom from terminal to bridging lowers the total ZPVE of the complex by 0.20 kcal/mol. This difference is wholly attributed to the intermolecular component, and in particular to the three of highest frequency. The lower energy of the D bonds can hence be traced to the vibrational modes wherein the bridging atom is displaced from the D bond axis. This decrement of 0.2 kcal/mol is the same as was noted above for exchanging the bridging H atom in the dimer for a deuterium.

Table 6 lists data similar to that in Table 4. ΔZPVE refers to the difference in MP2 zero-point vibrational energy between the trimer and the sum of the three constituent monomers. ΔE has a comparable meaning: this quantity indicates the electronic contribution to the binding energy of the trimer (relative to three isolated monomers), with an appropriate counterpoise correction of the superposition error. The MP2 binding energies of the dimers listed in Table 4 were all in the neighborhood of 5.5 kcal/mol. Since the trimer contains three H bonds, one might expect a total binding energy of three times this amount. However, each of the H bonds in the trimer is significantly weakened by its distortion from a linear O−H··O arrangement.

The influence of deuteriosubstitution upon the H bond energies in the last column of Table 6 is consistent with the trends noted above for the dimer. For any given total number of deuterium atoms within the trimer, the total binding energy is increased by 0.2 kcal/mol for each D atom in a bridging position. For example, moving the single D atom from a terminal to a bridging position increases the binding energy from 8.0 to 8.2 kcal/mol. When there are two D atoms in the dimer,

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Table 7. MP2 Harmonic Vibrational Frequencies and Zero-Point Vibrational Energy of $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ with Varying Degrees of Isotopic Substitution

			frequency, cm^{-1}				ZPVE, kcal/mol		
			inter		intra				
	n_b	n_t	ν_7	$\nu_8 + \nu_9$	$\nu_{12} + \nu_{13}$	$\nu_{14} + \nu_{15}$	inter	intra	total
$H_2O{\cdot\cdot}H{\cdot\cdot}OH_2$	0	0	920	3099	7604	7840	4.88	31.51	36.39
	n_b+n_t=1								
$HDO{\cdot\cdot}H{\cdot\cdot}OH_2$	0	1	902	2978	6605	7788	4.66	29.71	34.37
$H_2O{\cdot\cdot}D{\cdot\cdot}OH_2$	1	0	715	2427	7603	7840	4.47	30.39	34.86
	n_b+n_t=2								
$D_2O{\cdot\cdot}H{\cdot\cdot}OH_2$	0	2	872	2799	5619	7722	4.46	27.87	32.33
$HDO{\cdot\cdot}H{\cdot\cdot}OHD$	0	2	888	2908	5607	7736	4.45	27.90	32.35
$HDO{\cdot\cdot}D{\cdot\cdot}OH_2$	1	1	705	2368	6604	7788	4.28	28.55	32.83
	n_b+n_t=3								
$D_2O{\cdot\cdot}H{\cdot\cdot}OHD$	0	3	859	2745	5543	6748	4.25	26.06	30.31
$D_2O{\cdot\cdot}D{\cdot\cdot}OH_2$	1	2	690	2330	5619	7721	4.11	26.68	30.79
$HDO{\cdot\cdot}D{\cdot\cdot}OHD$	1	2	693	2310	5606	7736	4.09	26.71	30.82
	n_b+n_t=4								
$D_2O{\cdot\cdot}H{\cdot\cdot}OD_2$	0	4	832	2586	5479	5759	4.05	24.22	28.27
$D_2O{\cdot\cdot}D{\cdot\cdot}OHD$	1	3	678	2277	5542	6748	3.93	24.84	28.77
	n_b+n_t=5								
$D_2O{\cdot\cdot}D{\cdot\cdot}OD_2$	1	4	662	2250	5479	5759	3.76	22.96	26.72

the binding energies are 8.1, 8.3, and 8.5 kcal/mol respectively for 0, 1, and 2 of these atoms acting as bridges. For this reason, one can claim that a D bond is stronger than a H bond by 0.2 kcal/mol within the context of the trimer, just as was noted for the dimer. There is a smaller increment of about 0.1 kcal/mol that is related to the total number of D atoms. For example, changing a terminal H to a D atom increases the binding energy from 7.9 to 8.0 kcal/mol in $(H_2O)_3$.

As a result of both of these trends, the perdeuterated trimer is most strongly bound of all, with a total binding energy of 9.1 kcal/mol, as compared to 7.9 kcal/mol for $(H_2O)_3$. If one considers a trimer of monodeuterated monomers, i.e. $(HDO)_3$, the D-bonded complex in which the three deuteriums act as bridges is bound by 8.82 kcal/mol, stronger by 0.6 kcal/mol than the same trimer in which the three protiums serve as bridges. This difference is also consistent with a greater strength of 0.2 kcal/mol for each D vs H bond.

The results presented in Tables 5 and 6 were all gathered at the MP2 level. As in the case of the dimer, the trends are reproduced extremely well at the SCF level as well, even the quantitative aspects of H/D substitution.

3. Hydron-Bound Dimer. The proton-bound water dimer, $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$, differs from the neutral complex in a number of important respects. In the first place, the ionic H bond is much stronger. That is, it takes severalfold more energy to dissociate this complex to its constituents, OH_3^+ and OH_2, than to break apart the neutral water dimer.[38,39] Another important distinction has to do with the potential in which the bridging hydrogen moves. In the neutral complex, the bridging hydrogen occupies a single-well potential, with its equilibrium position quite clearly on the proton donor molecule. The potential in the cationic complex is much flatter. At the correlated MP2 level, the minimum is located equidistant between the two oxygen atoms so the H bond is centrosymmetric, consistent with earlier findings.[19,38,40−44]

The MP2 equilibrium geometry of the $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ complex is illustrated in Figure 1c where it may be seen that the two water molecules are symmetrically equivalent. The $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ complex belongs to the C_2 point group. The interoxygen distance is 2.39 Å. The bridging hydrogen does not lie precisely along the O··O axis; the θ(OHO) angle is 177°. The two hydrogens on each water are symmetrically inequivalent, with slightly different r(OH) bond lengths and angles. The torsion angle between hydrogens on the two waters is 45.5°.

The symmetry of the $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ complex leads to vibrational modes that are nearly paired. The six highest frequencies correspond to intramolecular vibrations within the H_2O units. The two highest, ν_{14} and ν_{15} at 3920 cm^{-1}, are asymmetric stretches within each monomer which are in and out of phase with each other, respectively. Frequencies of 3798 and 3806 cm^{-1} correspond to the ν_{12} and ν_{13} symmetric stretches within the monomers and the two bends, ν_{10} and ν_{11}, occur at 1721 and 1796 cm^{-1}. The remaining bands are of intermolecular type. ν_8 and ν_9 occur at 1524 and 1575 cm^{-1}, and represent the wagging of the two water monomers, with a large displacement of the bridging proton perpendicular to the H bond axis. Another mode which is important for our purposes here is the motion of the bridging hydrogen between the two O atoms, along the H bond axis. The frequency associated with this proton transfer coordinate, ν_7, is 920 cm^{-1}. The other modes occur between 180 and 630 cm^{-1} and are relatively insensitive to isotopic substitution.

The first row of Table 7 reports these frequencies in the unsubstituted complex. Note that six of these frequencies are reported as a sum over a pair, since the two modes are similar in type. The effects of monosubstitution are visible in the next two rows of Table 7, in which the deuterium can occur on either a terminal or bridging position. Comparison with the first row reveals that replacement of a terminal atom drops the (ν_{12} + ν_{13}) sum by a full 1000 cm^{-1}. This reduction is understandable in light of the characters of these modes which involve internal stretching in the water molecules. The other frequencies are only slightly affected by the terminal substitution. In contrast, replacement of the bridging hydrogen leaves the intramolecular frequencies virtually unchanged. The reduction is seen instead in the intermolecular modes. The proton transfer frequency, ν_7, is lowered by 200 cm^{-1}; a drop of 570 cm^{-1} occurs in the pair of H bond bending modes, ν_8 and ν_9.

The implications of these frequency changes have immediate parallels in the zero-point vibrational energies. Deuteriosubstitution of a terminal hydrogen lowers the total intermolecular ZPVE by 0.2 kcal/mol, as compared to 0.4 kcal/mol for bridging

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substitution. This 0.2 kcal/mol greater reduction for the case of bridge replacement is consistent with the results for the neutral water dimer and trimer. But the situation for the intramolecular modes is quite different here. Recall that the total intramolecular ZPVE of each neutral complex was lowered by about 2 kcal/mol for each change of a H atom to D, but was quite insensitive to the particular location of the D atom. In the case of the $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ ion, the intramolecular ZPVE is lower by 0.7 kcal/mol when the D atom is located at a terminal as compared to bridging position. This difference is larger than the 0.2 kcal/mol lower intermolecular ZPVE for the bridge. Consequently, the total ZPVE, in the last column of Table 7, is lower for the terminal substitution than for bridging, by 0.5 kcal/mol.

These trends are repeated for the disubstituted case. Whereas the $\nu_{14} + \nu_{15}$ sum is unaffected by substitution, there is a large change in $(\nu_{12} + \nu_{13})$. This reduction amounts to 1000 cm^{-1} for one terminal D, and twice that amount for two deuteriums. The intermolecular frequencies are lowered somewhat by terminal substitution, but by much more when it is the bridging atom that is replaced. The difference between these two cases is 180 cm^{-1} in the case of ν_7, and 500−600 cm^{-1} for $(\nu_8 + \nu_9)$. As in the case of monosubstitution, the intermolecular ZPVE favors the bridging position by 0.2 kcal/mol, but this is overshadowed by the intramolecular term which is lower by 0.7 kcal/mol when it is a protium that occupies this position.

The latter is true for higher degrees of deuteriosubstitution as well. In all cases, the total ZPVE is lower by 0.5 kcal/mol when the bridging position is occupied by H as compared to D. This preference is traced to the intramolecular modes which favor a H bridge. The energetic manifestation of this preference is larger in magnitude than that shown by the intermolecular frequencies which favor the D bridge. To probe more deeply, it is the $(\nu_{12} + \nu_{13})$ pair which accounts for the preference for H bridging for mono- and disubstitution. But when the number of D atoms exceeds 2, the $(\nu_{12} + \nu_{13})$ sum remains approximately constant at 5500−5600 cm^{-1}, whereas the $(\nu_{14} + \nu_{15})$ pair provides the bulk of the preference. It may be noted from Table 7 that this pair of frequencies is lower by 1000 cm^{-1} when the bridging position is occupied by H, as compared to D for $n_b + n_t = 3$ or 4.

The influence of these zero-point vibrational energies upon the complexation energies is reported in Table 8. The first row indicates that the $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ complex contains 0.76 kcal/mol more ZPVE than its constituents H_3O^+ and OH_2, leading to a binding energy of 33.74 kcal/mol. Turning now to single deuteriosubstitution, the $(HDO{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ complex can dissociate to two different sets of products, depending upon whether the central hydrogen departs with the HDO or OH_2 molecule. As indicated by the next two rows of Table 8, these two dissociations differ slightly in ΔZPVE. Regardless of which dissociation path is followed, one finds that replacement of a terminal protium by a deuterium atom leads to a complex that is bound by slightly more (0.1−0.2 kcal/mol) than the unsubstituted complex. On the other hand, replacement of the bridging atom results in a more weakly bound complex: $(H_2O{\cdot\cdot}D{\cdot\cdot}OH_2)^+$ is bound by 0.4 kcal/mol less than $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$. From another perspective, if a single H atom is going to be deuterated, there is a 0.5−0.6 kcal/mol energetic preference that this atom be in a terminal position.

Turning now to higher degrees of substitution, there are more possibilities to consider. Nonetheless, the same patterns persist. Substitution of the terminal hydrogens strengthens the H bond by a small amount (between 0.1 and 0.5 kcal/mol) whereas D substitution of the bridging atom weakens the interaction by up to 0.4 kcal/mol. Multiple terminal substitutions can cancel the effects of a replacement of the bridging atom. Consequently, the binding energy of the fully deuterated $(D_2O{\cdot\cdot}D{\cdot\cdot}OD_2)^+$ is essentially identical to that of $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$. So from this perspective there is little difference in energy between H and D bonds. But for any given number of D atoms, there is a 0.3−0.8 kcal/mol preference that the bridging position retain a proton. As a typical example of the preference for the H bond in these cations, when H_2DO^+ is combined with OH_2, $HDO{\cdot\cdot}H^+{\cdot\cdot}OH_2$ is found to be more strongly bound than $H_2O{\cdot\cdot}D^+{\cdot\cdot}OH_2$ by 0.5 kcal/mol.

Table 8. Difference in Zero-Point Vibrational Energy between Isotopomers of the $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ Complex and Constituent Monomers and the Resulting Complexation Energy (in kcal/mol), All Calculated at the MP2 Level

	n_b	n_t	ΔZPVE	$-(\Delta E^a + \Delta ZPVE)$	constituents
$H_2O{\cdot\cdot}H{\cdot\cdot}OH_2$	0	0	0.76	33.74	$H_3O^+ + H_2O$
	$n_b{+}n_t{=}1$				
$HDO{\cdot\cdot}H{\cdot\cdot}OH_2$	0	1	0.70	33.80	$H_2OD^+ + H_2O$
			0.57	33.93	$H_3O^+ + HOD$
$H_2O{\cdot\cdot}D{\cdot\cdot}OH_2$	1	0	1.19	33.32	$H_2OD^+ + H_2O$
	$n_b{+}n_t{=}2$				
$D_2O{\cdot\cdot}H{\cdot\cdot}OH_2$	0	2	0.65	33.85	$HOD_2{}^+ + H_2O$
			0.40	34.10	$H_3O^+ + OD_2$
$HDO{\cdot\cdot}H{\cdot\cdot}OHD$	0	2	0.50	34.00	$H_2OD^+ + HOD$
$HDO{\cdot\cdot}D{\cdot\cdot}OH_2$	1	1	1.15	33.35	$HOD_2{}^+ + H_2O$
			0.98	33.52	$H_2OD^+ + HOD$
	$n_b{+}n_t{=}3$				
$D_2O{\cdot\cdot}H{\cdot\cdot}OHD$	0	3	0.45	34.05	$HOD_2{}^+ + HOD$
			0.33	34.17	$H_2OD^+ + OD_2$
$D_2O{\cdot\cdot}D{\cdot\cdot}OH_2$	1	2	1.13	33.37	$OD_3{}^+ + H_2O$
			0.81	33.69	$H_2OD^+ + OD_2$
$HDO{\cdot\cdot}D{\cdot\cdot}OHD$	1	2	0.95	33.55	$HOD_2{}^+ + HOD$
	$n_b{+}n_t{=}4$				
$D_2O{\cdot\cdot}H{\cdot\cdot}OD_2$	0	4	0.28	34.22	$HOD_2{}^+ + OD_2$
$D_2O{\cdot\cdot}D{\cdot\cdot}OHD$	1	3	0.93	33.57	$OD_3{}^+ + HOD$
			0.78	33.73	$HOD_2{}^+ + OD_2$
	$n_b{+}n_t{=}5$				
$D_2O{\cdot\cdot}D{\cdot\cdot}OD_2$	1	4	0.76	33.74	$OD_3{}^+ + OD_2$

[a] The electronic contribution to the binding energy is equal to −34.50 kcal/mol following counterpoise correction of the BSSE.

Hence, the pattern in the cationic complex is opposite to that noted in the neutral dimer and trimer. Whereas the D bonds are more stable in the latter cases, the opposite is true for the hydron-bound water dimer where it is the H bond that is preferred. This behavior, predicted on the basis of harmonic frequencies, is consistent with deuterium isotope fractionation measurements[20] which indicate a preference of D atoms to occupy positions on the periphery of charged complexes containing water, i.e. terminal sites.

Unlike the previous two cases of the neutral water dimer and trimer where SCF and MP2 geometries are fairly similar, there is a fundamental distinction between the SCF and MP2 optimized structures of $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$. Whereas the MP2 geometry contains a centrosymmetric H bond, the SCF proton transfer potential contains a pair of minima. As a result, the equilibrium position of the proton is much closer to one water molecule than to the other. More specifically, the bridging hydrogen is located 1.065 Å from one O atom and 1.346 Å from the other, when the geometry is optimized at the SCF level. Despite this important difference in structure, the trends in vibrational energies are reproduced surprisingly well, even quantitatively, at the SCF level. As for the MP2 results, for any given degree of D substitution, the system contains 0.5 kcal/mol more ZPVE when the bridging position is occupied by D as compared to H. This distinction is attributed to the intramolecular vibrations which show a preferential stabilization of the H bond by 0.6−0.7 kcal/mol, lowered by the intermolecular ZPVE which favors the D bond by 0.1−0.2 kcal/mol.

Table 9. Zero-Point Vibrational Energies of $(CH_3OH{\cdot\cdot}H{\cdot\cdot}OHCH_3)^+$ Complex and Its Deuterated Derivatives[a]

n_b	n_t^O	n_t^C	ZPVE	ΔZPVE	$-(\Delta E^b + \Delta ZPVE)$
0	0	0	78.15	0.66	27.95
$n_b + n_t^O + n_t^C = 1$					
1	0	0	76.17	0.92	27.69
0	0	1	75.97[c]	0.63	27.98
0	1	0	75.86	0.61	28.00
$n_b + n_t^O + n_t^C = 2$					
1	0	1	73.99	0.89	27.72
1	1	0	73.89	0.88	27.73
0	0	2	73.78	0.59	28.02
0	1	1	73.69	0.57	28.03
0	2	0	73.69	0.68	27.94
$n_b + n_t^O + n_t^C = 3$					
1	0	2	71.81	0.86	27.75
1	1	1	71.71	0.86	27.75
1	2	0	71.59	0.84	27.77
0	0	3	71.58	0.57	28.04
0	1	2	71.50	0.55	28.06
0	2	1	71.40	0.53	28.07

[a] ΔZPVE refers to the difference between the complex and its constituent subunits. The complexation energy is listed in the last column. All quantities are computed at the SCF level and reported in kcal/mol. [b] The electronic contribution to the binding energy is equal to −28.61 kcal/mol following counterpoise correction of the BSSE. [c] In this and other cases where there are several possible choices for the specific site(s) chosen, values listed represent an average.

Detailed analysis of the various vibrational modes reproduces the same patterns noted above for the MP2 modes and frequency trends.

Larger Complex. In an effort to consider the possible generalization of these trends to larger systems, calculations of a similar sort were carried out for the proton-bound methanol dimer, $(CH_3OH{\cdot\cdot}H{\cdot\cdot}OHCH_3)^+$. The optimized configuration of this complex at the SCF level is reported in Figure 1d from which it may be seen that the structure contains a noncentrosymmetric H bond at this level. The two r(OH) bond lengths involving the bridging hydrogen are 1.046 and 1.380 Å.

The analysis is impaired by an inability to clearly distinguish intermolecular from intramolecular vibrational modes in this complex. One of the features of the smaller systems above that enabled the categorization was that the intermolecular frequencies were considerably smaller in magnitude than the intramolecular quantities. The situation is different here in that both the isolated neutral CH_3OH and protonated $CH_3OH_2^+$ subunits contain low-frequency vibrations, some less than 400 cm^{-1}. A second factor is the complexity of the modes themselves. For example, mode number 9 in the unsubstituted $(CH_3OH{\cdot\cdot}H{\cdot\cdot}OHCH_3)^+$ contains elements of both an internal C−O stretch in one of the subunits and an intramolecular O··H··O stretching motion. A further complication is that each different D substitution changes the character of some of the modes and alters the frequency enough so that it becomes impossible to monitor the changes in the frequency of any given mode. For these reasons, the analysis of the effects of D substitution concentrates on the total zero-point vibrational frequencies, with no further separation into intermolecular and intramolecular types.

At the SCF level, the total ZPVE of the undeuterated $(CH_3OH{\cdot\cdot}H{\cdot\cdot}OHCH_3)^+$ complex is 78.15 kcal/mol, as reported in the first row of Table 9. Replacement of one hydrogen by deuterium lowers this quantity by about 2 kcal/mol. This reduction is of the smallest magnitude when it is the bridging hydrogen that is replaced. The total ZPVE of $(CH_3OH{\cdot\cdot}D{\cdot\cdot}OHCH_3)^+$ is 76.17 kcal/mol. The other two possible sites of D substitution comprise the methyl or hydroxyl groups of the methanol. The numbers of such replacements are indicated by the quantities n_t^C and n_t^O, respectively. As illustrated by the appropriate rows of Table 9, the total ZPVE of the complex is 75.97 kcal/mol if the replacement occurs on a methyl group and 75.86 kcal/mol if on a hydroxyl. In other words, the bridging D position results in the highest ZPVE, with a methyl position lower by 0.2 kcal/mol, and hydroxyl lower still by 0.1 kcal/mol.

This pattern repeats itself for the disubstituted complexes reported in the next section of Table 9. The two complexes with the highest ZPVE are those with a D occupying the bridging position; replacement of a methyl hydrogen as the second substitution leads to a higher vibrational energy than hydroxyl by 0.1 kcal/mol. Lower by another 0.1 kcal/mol is the complex wherein two methyl hydrogens are replaced by D. The last section of data reported in Table 9 concerns trisubstitution and exhibits a repetition of these same trends. The ZPVE is highest for a replacement of the bridging atom, followed by a methyl position. Each change from methyl to hydroxyl lowers the ZPVE by about 0.1 kcal/mol. Calculations were carried out for higher degrees of substitution (not listed in Table 9) and these patterns reproduce those in the table.

The total zero-point vibrational energies in Table 9 are followed by the difference between this quantity in each complex and the sum of constituent monomers. The last column of Table 9 is most revealing with regard to the relative strength of hydrogen and deuterium bonds. A glance down the first column illustrates that in all cases where the bridging position is occupied by a hydrogen atom, i.e. $n_b = 0$, the computed strength of the H bond is in the range between 27.9 and 28.1 kcal/mol. Upon replacing the bridging atom with a deuterium, the interaction energy decreases to 27.7−27.8 kcal/mol. In short, the D bond appears to be weaker than the H bond by some 0.2−0.3 kcal/mol. An example is the bond formed between CH_3OHD^+ and CH_3OH. The interaction energy is 28.0 kcal/mol if the protium of the former molecule acts as the bridge but only 27.7 kcal/mol if it is the deuterium in the bridging position. This trend is consistent with the simpler $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ system although the difference there was a little larger, perhaps 0.5 kcal/mol. Apparently then, it is valid to extrapolate the results of an analysis of H bonding between simple hydrides to larger systems like the methanol dimer, provided one expects certain quantitative differences.

4. $(HOH{\cdot\cdot}OH)^-$. The anionic analogue consists of a OH^- ion paired with a water molecule. At either the SCF or MP2 levels, the equilibrium geometry consists of a noncentrosymmetric H bond; the proton transfer potential is of the double-well type. Prior calculations[39,45−50] have indicated that any barrier to proton transfer in this system would be rather low. The equilibrium structure in Figure 1e has the bridging hydrogen 1.095 Å from one O atom and 1.397 Å from the other. The two terminal hydrogens are positioned such that the ϕ(HOOH) dihedral angle is 111°, and the entire complex has no elements of symmetry. The H bond is nearly linear with a θ(OHO) angle of 176°.

There are nine vibrational modes in the $(HOH{\cdot\cdot}OH)^-$ complex. The two of highest frequency lie at approximately 3900 cm^{-1}, and are reported as ν_8 and ν_9 in the first row of Table 10. They correspond to the stretches of the terminal hydrogen atoms away from the corresponding O atom. ν_5 and ν_7 refer to displacements of the bridging hydrogen perpendicular

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Table 10. MP2 Harmonic Vibrational Frequencies and Zero-Point Vibrational Energy of $(HO{\cdot\cdot}H{\cdot\cdot}OH)^-$ with Varying Degrees of Isotopic Substitution

			frequency, cm^{-1}							
			inter			intra		ZPVE, kcal/mol		
	n_b	n_t	ν_5	ν_6	ν_7	ν_8	ν_9	inter	intra	total
HOH··OH	0	0	1379	1603	1749	3879	3919	8.99	11.14	20.13
	$n_b+n_t=1$									
DOH··OH	0	1	1373	1586	1698	2853	3879	8.65	9.62	18.27
HOH··OD	0	1	1366	1595	1748	2823	3919	8.76	9.63	18.39
HOD··OH	1	0	1028	1228	1355	3879	3918	7.27	11.14	18.41
	$n_b+n_t=2$									
DOH··OD	0	2	1361	1576	1698	2823	2853	8.41	8.11	16.52
DOD··OH	1	1	1021	1223	1258	2851	3879	6.93	9.61	16.54
HOD··OD	1	1	1003	1222	1353	2823	3918	7.04	9.63	16.67
	$n_b+n_t=3$									
DO··D··OD	1	2	998	1213	1257	2823	2851	6.69	8.11	14.79

to the H bond axis, whereas ν_6 corresponds to its motion along this axis. As such, these three modes, in the 1380−1750-cm^{-1} range, can be considered to be of intermolecular type and would be expected to be most sensitive to the mass of the bridging atom. This expectation is borne out in that the four modes of lowest frequency are not changed much by isotopic substitution at any of the three sites.

The next several rows of Table 10 list the effect of monosubstitution on the various frequencies. Replacement of a terminal hydrogen reduces the corresponding intramolecular frequency by some 1000 cm^{-1}. The intermolecular frequencies are much less sensitive. Consequently, the total intramolecular ZPVE is reduced by 1.5 kcal/mol, as compared to a drop of only 0.3 kcal/mol in the intermolecular quantity. Replacement of the bridging hydrogen by deuterium has very nearly the opposite effect. The intramolecular frequencies are unchanged, whereas the various intermolecular modes each suffer a lowering by several hundred cm^{-1}. The cumulative result is a decrease of the intermolecular ZPVE by 1.7 kcal/mol. The last column of Table 10 reveals that there is very little to distinguish the various sites of substitution with respect to total ZPVE. Within ±0.1 kcal/mol, this quantity is reduced by 1.7 kcal/mol regardless of the specific site of substitution.

This same pattern repeats itself for disubstitution in that the intermolecular and intramolecular frequencies are affected respectively by replacement of the bridging and terminal hydrogens. The intramolecular frequencies ν_8 and ν_9 are lowered by 1000 cm^{-1} for each replacement of a terminal hydrogen. The intermolecular quantities are each reduced by several hundred cm^{-1} when the bridging H is replaced by D. The net results are about the same. That is, for each degree of substitution, there is little difference in total ZPVE between the situation where the bridging position is occupied by H as compared to D.

After subtraction of the total ZPVE of the constituent monomers, one may note the effects of these results upon the H bond energies, as listed in Table 11. The total interaction energies are all in the range of 20.5−20.9 kcal/mol. There is a tendency for the D bonds to be slightly weaker than the H bonds. For example, the binding energy of $HOD{\cdot\cdot}OH^-$ is 20.5 kcal/mol, as compared to 20.7 for $DOH{\cdot\cdot}OH^-$. In other words, when HOD is paired with OH^-, there is a 0.2-kcal/mol preference for the H atom of the former molecule to act as the bridge, as compared to D. Similarly, the binding energy of $HOD{\cdot\cdot}OD^-$ is slightly smaller than that of $DOH{\cdot\cdot}OD^-$. On the other hand, the binding energy of the fully deuterated $DOD{\cdot\cdot}OD^-$ is slightly greater than that of $HOH{\cdot\cdot}OH^-$.

Table 11. Difference in Zero-Point Vibrational Energy between Isotopomers of the $(HOH{\cdot\cdot}OH)^-$ Complex and Constituent Monomers and the Resulting Complexation Energy (in kcal/mol), All Calculated at the MP2 Level

	n_b	n_t	ΔZPVE	$-(\Delta E^a + \Delta\text{ZPVE})$
HOH··OH	0	0	1.07	20.64
	$n_b+n_t=1$			
DOH··OH	0	1	1.03	20.68
HOH··OD	0	1	0.82	20.89
HOD··OH	1	0	1.18	20.53
	$n_b+n_t=2$			
DOH··OD	0	2	0.77	20.93
DOD··OH	1	1	1.18	20.53
HOD··OD	1	1	0.92	20.79
	$n_b+n_t=3$			
DOD··OD	1	2	0.92	20.79

[a] The electronic contribution to the binding energy is equal to −21.71 kcal/mol following counterpoise correction of the BSSE.

A prior study addressed a similar question in a related anion. The H bond in $(CH_3O{\cdot\cdot}H{\cdot\cdot}OCH_3)^-$ was compared to the complex in which the bridging atom was replaced by deuterium.[21] Ion cyclotron measurements indicated that the equilibrium constant for the reaction

$$(CH_3O{\cdot\cdot}H{\cdot\cdot}OCH_3)^- + CH_3OD \leftrightarrow (CH_3O{\cdot\cdot}D{\cdot\cdot}OCH_3)^- + CH_3OH$$

is less than unity, approximately 0.3. In other words, the protium prefers the bridging position in the complex to the hydroxyl location on the CH_3OH monomer, as compared to the D atom. Although limited to the SCF level with a 4-31G basis set, the accompanying calculations[21] verified the preference for a H bond in the anion and provided a surprisingly accurate reproduction of the energetics. This coincidence adds further confidence that our correlated computations with a more flexible basis set are capable of representing the system accurately.

One should probably conclude that in the pairing of two hydroxide anions via a hydron, there appears to be a weak but significant preference for H over D bonds, based upon a harmonic treatment of the vibrational modes. This trend is present also in the SCF data.

Conclusions and Discussion

Deuterium bonds would appear to be stronger than H bonds in complexes pairing neutral molecules. This effect is due largely to the zero-point vibrational energy associated with one of the intermolecular modes. While there are changes occurring in other intermolecular modes upon isotopic substitution, as well as in the intramolecular frequencies, these changes tend to cancel one another. The intermolecular mode of highest frequency can be characterized as a bending motion of the proton donor molecule which distorts the linearity of the H bond. The heavier mass of D imparts this mode with a higher effective mass, thereby lowering its frequency and the accompanying zero-point energy. The same principle extends to the trimer of water where it is again the bending motion that takes the bridging hydron away from the H bond axis that controls the energetic difference between H and D bonds. The trend also retains its quantitative aspect: D bonds pairing water molecules are computed to be stronger than H bonds by 0.2 kcal/mol. It might be supposed that adding additional water molecules to the trimer would yield no further changes to these results. This contention is supported by recent calculations of oligomers of formamide, up to $n = 6$, where the fractionation factors were little affected by n.[51]

The situation reverses itself for ionic H bonds, such as $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$. Similar to the neutral H bonds, the ZPVE associated with the intermolecular modes is smaller by about 0.2 kcal/mol when the bridging position is occupied by D as compared to H. But quite unlike the neutral H bonds, the intramolecular frequency sums are dramatically affected by the mass of the bridging atom. Placement of a deuterium on either of the water molecules of $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ reduces the total intramolecular ZPVE by 0.7 kcal/mol more than this quantity is reduced if the D resides on the bridging site. The latter trend is larger by 0.5 kcal/mol than the preference for a D bond on the part of the intermolecular modes. Consequently, it is the H bond that is favored over the D bond in $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ by 0.5 kcal/mol. Although the MP2 and SCF optimized geometries of this complex differ fundamentally in that the H bond is centrosymmetric in the former case but the proton transfer potential contains two distinct wells at the latter level, the same principles apply, quantitatively as well as qualitatively, in either case. Enlargement of the system to a proton-bound pair of methanol molecules suggests the above conclusions are valid also for molecules larger than water. Although it becomes difficult to disentangle intramolecular from intermolecular modes, it is nonetheless apparent that the H bond is stronger than the D bond in such cationic complexes.

The preference of the cationic complexes for a protium to occupy the bridging position is repeated in the anionic analogue $(HOH{\cdot\cdot}OH)^-$, albeit by a smaller amount. This energetic preference in the contribution of ZPVE to the binding energy is on the order of 0.2 kcal/mol.

It is unlikely that the results discussed here would be modified in any meaningful way by application of a higher level of ab initio theory in order to extract the force field. While a larger basis set might certainly affect the magnitudes of some of the binding energies or vibrational frequencies, what is of most importance here is the *differences* between systems with protium or deuterium in certain sites of the complex. These differences would appear to be rather insensitive to particulars of the ab initio approach. It is notable in this regard that while the inclusion of correlation had a substantial impact upon the binding energies and vibrational frequencies of the systems examined, the effects upon the differences between H- and D-bonded systems were surprisingly minor. Indeed, even though the SCF and MP2 equilibrium geometries of the $(H_2O{\cdot\cdot}H{\cdot\cdot}OH_2)^+$ cation were fundamentally distinct in that the latter contains a centrosymmetric H bond and the former does not, the two methods yielded remarkably similar isotope effects. Further confirmation of the insensitivity of the fractionation factors to basis set comes from a recent detailed study of more than a dozen small molecules.[52]

A more likely source of error in these calculations is the assumption of a harmonic force field. Anharmonic corrections to vibrational frequencies can be significant, particularly in weakly bound complexes, or in those where the proton transfer potential is a shallow one.[53-61] On the other hand, it is again expected that the various errors incurred by the harmonic approximation are likely to cancel one another when focusing on the difference in ZPVE between systems containing protium and deuterium in different sites. This expectation is in fact confirmed by a recent set of computations that incorporated the effects of third-order anharmonicity into a semiempirical PES for the water dimer[62] as well as a number of other complexes. The authors found that anharmonic contributions to the energy made negligible contributions to the energy differences between various isotopomers.

The data reported in this work for interaction energies are the sum of electronic and zero-point vibrational terms and thus pertain specifically to the gas phase at very low temperature. As the temperature climbs near 298 K, another factor that becomes more important is the rotational energy of the various species. At room temperature, translational and rotational motions each contribute $^3/_2RT$ to the total energy. Since formation of a H bond brings together two reactants to form a single product complex, each type of motion contributes $-^3/_2RT$ to the complexation energy. Thus a more complete value for the gas-phase interaction energies would add $-3RT$ (-1.78 kcal/mol at 298 K) to those listed above. A further correction of $-RT$ (-0.6 kcal/mol) converts ΔE to ΔH.

ΔE becomes complete when corrected for the "thermal energy", which arises from population of excited vibrational levels. This quantity is typically negligible for a simple molecule such as H_2O since the vibrational levels are far enough apart that even at room temperature there is little occupation above the ground vibrational level. But the lower intermolecular frequencies that occur in H-bonded complexes result in levels close enough together that significant populations occur in excited states. This thermal energy amounts to some 2 kcal/mol in the water dimer. Hence, the interaction energies in the last column of Table 4 would be reduced by this amount when computing the full $-\Delta E$. (It is coincidental that this reduction in magnitude is similar in amount to the $-3RT$ increase that is associated with translational and rotational energies indicated above.)

What is most important to our purposes here, however, is the *difference* in thermal energies between those complexes in which the bridging atom is D as compared to H. This difference was found to be quite small, such that these thermal energies have negligible effect on the trends described above. For example, in the case of the neutral water dimer, the thermal energy of the complex is higher by 0.03 kcal/mol when D acts as the bridging atom, as compared to H. Similarly small sensitivity to the specific site of substitution, i.e. ±0.02 kcal/mol, is common also to the other systems examined here.

Equilibrium measurements deal not with ΔE or ΔH, but rather with ΔG. Comparison with the equilibrium constants or

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fractionation factors must therefore include considerations of entropy. The formation of a single H bonded complex from a pair of free molecules necessarily involves a loss of entropy. In the case of the water dimer, this entropy change due to complexation is some -20 cal mol^{-1} deg^{-1}. But, most importantly for our purposes here, there is a small difference in this quantity, depending upon whether the bridging atom is a H or D. The computed entropy of the D-bridged water dimer is consistently more negative than in the case of the H bridge by 0.2$-$0.3 cal mol^{-1} deg^{-1}. Hence, as the temperature rises, the preference of the water dimer to contain a D vs a H bond will diminish as the $-T\Delta S$ term becomes more important. At 298 K, the latter term translates into a 0.06$-$0.09 kcal/mol less negative contribution to ΔG in the case of the D bond, washing out some of the 0.2 kcal/mol preference for the D bond in ΔH. A similar entropic pattern accompanies the water trimers. A more negative value of ΔS (by about 0.35 cal mol^{-1} deg^{-1}) occurs when the D atoms occupy bridging as opposed to terminal positions. So as in the case of the dimer, the preference for D bonds in the trimer will be lessened as the temperature rises.

The same pattern persists in the ions as well. In these cases, the entropic effect acts to reinforce the enthalpic preference for protium in the bridging position, as compared to deuterium. Hence, despite the rather small preference of the anion for a H vs a D bond on enthalpic grounds alone, the H bond will much more clearly be favored when factors of temperature are considered. This conclusion is supported by the aforementioned equilibrium disproportionation for H bonds vs D bonds in the anionic $(CH_3O{\cdot\cdot}H{\cdot\cdot}OCH_3)^-$ complex.[21]

The results presented here are strictly applicable only to the complexes and their constituent monomers in the gas phase. The situation becomes much more difficult to analyze in solution. In the first place, many of the vibrational modes can be affected by the bath of solvent molecules. For example, wagging motions of either water molecule in the dimer that occur freely in the gas phase must overcome specific interactions with neighboring molecules in solution. The translational and rotational motions of the pertinent entities are lost in solution, replaced by motions that can better be described as vibrational modes that involve the surrounding molecules. A detailed treatment of the question of H vs D bonding in solvent must await dynamical studies, using a highly accurate force field that can adequately evaluate specific vibrational modes and the effect of isotopic substitution.

Nonetheless, it is tempting to speculate as to what some of the solvent effects might be. In the case of the neutral oligomers of water, the dominating component of the preference for D vs H bonds was found to be the bending of the bridging atom away from the H bond axis. One might expect this particular mode to be relatively unaffected by solvent molecules which interact directly with the oxygen atoms and peripheral hydrogens. For this reason, it is not unlikely that the preference for a D bond might persist in solution. In the case of the hydron-bound cations, the primary factor which leads to a preference for H over D bonds was found to arise from the intramolecular vibrational modes. Due to their intramolecular nature, these modes are less subject to external forces than are the intermolecular vibrations. It would hence not be surprising to see the preference for the H bond persist in solution. Predictions regarding the anionic complexes are more problematic since the gas-phase preference for the H bond is smaller in magnitude. On the other hand, entropic effects also favor H bonds over D bonds so any lingering small enthalpic preference is likely to be reinforced as the temperature rises.

In terms of fractionation factors, which refer to the preference of a given site to be occupied by a D as compared to H,[63] our data indicate that in electrically neutral complexes, the fractionation factor for a bridging site will be greater than that of a nonbridge; the opposite is true when the system is cationic or anionic. This point applies not only to a solute but to the bulk solvent as well. That is, our results on the water dimer and trimer suggest that the component of the fractionation factor related to the bulk solvent should be considered some sort of weighted average between bridging and nonbridging sites. The distinction between these two types of site is confirmed by the experimental results mentioned above.[20]

We note finally that the results are consistent with a simple picture: as the proton transfer potential becomes deeper, the zero-point vibrational energy level of D sinks progressively lower than that for the proton. Thus, the preference for D over H, on the basis of vibrational energy, increases as the potential deepens. The transfer potential of the bridging hydron in the ionic systems is very shallow, much less steep than the potential for stretching of the nonbridging hydrogens. One is consequently not surprised to observe a preference for H over D in the bridging site. The transfer potential of the bridging hydron is much steeper in the case of the neutral water dimer or trimer, which can be used to rationalize the preference for D in this case. It must be understood, however, that the above picture is an oversimplification, which takes no account of other modes, and can consequently lead to incorrect conclusions if applied injudiciously.

Intermediate between the gas phase, to which these calculations apply explicitly, and solution, where many more effects must be considered, is the environment of the low-temperature matrix. Based on spectroscopic measurements, it would appear that the surrounding inert molecules exert surprisingly little influence on many of the vibrational modes that occur in the gas phase.[14−17,64] Prior work has indicated that the preference established in the gas phase for a D bond, as compared to a H bond, remains true when the complex is placed in such a matrix.[13,65] Hence, it is anticipated that some of the conclusions derived from the calculations described herein may survive when tested in low-temperature matrices.

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