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On the Contribution of Vibrational Anharmonicity to the Binding Energies of Water Clusters

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The second-order vibrational perturbation theory method has been used together with the B3LYP and MP2 electronic structure methods to investigate the effects of anharmonicity on the vibrational zero-point energy (ZPE) contributions to the binding energies of $(H_2O)_n$, $n = 2-6$, clusters. For the low-lying isomers of $(H_2O)_6$, the anharmonicity correction to the binding energy is calculated to range from -248 to -355 cm^{-1}. It is also demonstrated that although high-order electron correlation effects are important for the individual vibrational frequencies, they are relatively unimportant for the net ZPE contributions to the binding energies of water clusters.

1. Introduction

It has long been appreciated that vibrational anharmonicity is important in water clusters and other H-bonded systems.[1−28] For example, anharmonicity is important for accounting in a quantitative manner for the spectral shifts in the OH stretch vibrations in going from an isolated water monomer to the H-bonded environments of the monomers in a water cluster and for the appearance of various overtone and combination bands in the vibrational spectra of the clusters.[29−32] Anharmonicity also makes an important contribution to the vibrational zero-point energies, for example, contributing about 0.23 kcal/mol to the dissociation energy (D_0) of $(H_2O)_2$.[18]

One of the major challenges in experimental and theoretical studies of water clusters is the rapid growth in the number of possible isomers with an increasing number of water monomers.[33] For example, $(H_2O)_6$ has been predicted to have four isomers lying within 0.2 kcal/mol of the global potential energy minimum[34] and 23 isomers lying within 2 kcal/mol of the global minimum.[35] In such a case, the relative stabilities of the various isomers could be altered significantly by anharmonicity corrections to the ZPEs. Clary and Gregory have concluded that the energy ordering of the low-lying isomers of $(H_2O)_6$ is altered upon inclusion of corrections for ZPE that are calculated including vibrational anharmonicity.[3,36] However, these authors did not separate the harmonic from anharmonic contributions to the ZPEs, so the importance of the anharmonicity corrections for the relative energies is not clear. We note also that Losada et al. have argued that because the number of the low-frequency OH flipping modes changes from one isomer of $(H_2O)_6$ to another, these highly anharmonic vibrations could play an important role in determining the relative stabilities of the low-energy isomers.[34]

Despite the obvious importance of vibrational anharmonicity on the properties of water clusters, few of the theoretical studies of these clusters have included anharmonicity effects. Moreover, those studies that have included vibrational anharmonicity have employed approximations that introduce considerable uncertainty in the magnitudes of the calculated anharmonicity contributions. For example, the diffusion Monte Carlo calculations of Gregory and Clary[3,36] were carried out assuming rigid water monomers and employing a modified version of the ASP water model[37] for describing the intermolecular interactions. Thus, the resulting vibrational ZPEs have errors due to the neglect of intramolecular degrees of freedom and due to the limitations of the water model.

In recent years, the vibrational SCF (VSCF) method[38−42] and the second-order vibrational perturbation theory method (VPT2)[43−48] have been coupled with electronic structure codes, allowing for the calculation of anharmonic vibrational frequencies and vibrational ZPEs using ab initio potential energy surfaces. These approaches do not require the use of rigid monomers and avoid other problems associated with model potentials. The vibrational SCF method has been applied in conjunction with ab initio or density functional electronic structure methods to the water dimer,[9] but, because of the steep computational cost, this approach has not been applied to clusters as large as $(H_2O)_6$. As implemented by Chaban et al.,[42] a VSCF calculation on a single isomer of $(H_2O)_6$ would require nearly 290 000 energy evaluations when using 16 grid points, which is computationally prohibitive with reasonably large basis sets. (We note, however, that Gordon and co-workers have recently introduced variants of the VSCF method that reduce the computational effort by about 1 order of magnitude.[49]) The VPT2 method is much less computationally demanding, and, at the time we initiated this study, had not been applied to water clusters. However, Bouteiller et al. have published a paper recently in which they employed the VPT2 method to calculate the frequencies of the water dimer.[50]

The VPT2 method is analogous to the MP2 method for electronic structure calculations, with the harmonic approximation being used to generate the zeroth-order vibrational wave functions and energies needed for the perturbation corrections involving the cubic force constants and semidiagonal quartic force constants. As implemented by Barone et al.[51] and incorporated in the Gaussian 03 code,[52] the necessary cubic and quartic force constants are calculated by numerical differentiation of the analytical Hessians. For $(H_2O)_6$, a VPT2 calculation requires evaluating 97 Hessians to obtain the necessary cubic

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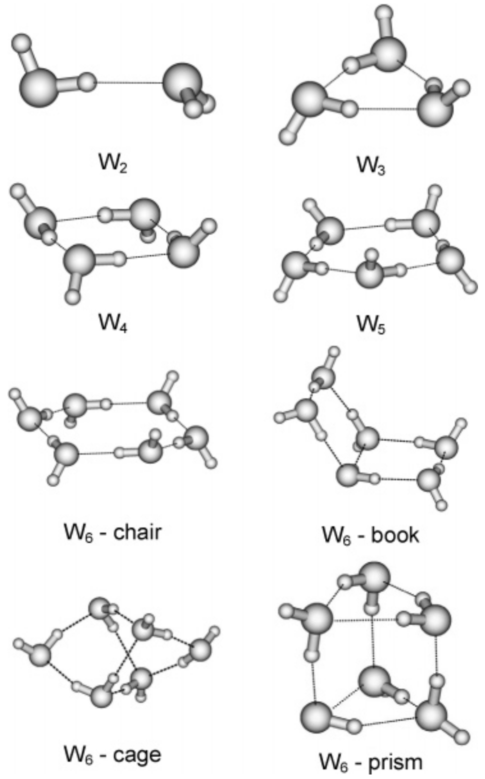

Figure 1. Water clusters studied in this work.

and quartic force constants. This requires about 2 orders of magnitude less computational time than would vibrational SCF calculations, as implemented by Chaban et al.

In the present study, we apply the vibrational perturbation theory method to the $(H_2O)_n$, $n = 1-6$, clusters. For the $n = 2-5$ clusters, only the lowest energy isomers are considered, whereas for $(H_2O)_6$, the lowest energy chair, cage, prism, and book isomers[34,53−56] (see Figure 1) are considered. In the figures and tables, the $(H_2O)_n$ clusters are referred to as W_n for short. The anharmonicity corrections were calculated using the Becke3LYP[57] method for all of the clusters considered and the MP2 method for the clusters up to $n = 4$ in size. The aug-cc-pVDZ[58] basis set was employed. For the monomer and dimer, calculations are also performed with the larger aug-cc-pVTZ[58] basis set. Here we focus our attention on the vibrational zero-point energies; the trends in the vibrational frequencies will be considered in a separate publication.[59]

2. Methodology

All of the calculations were performed using the Gaussian 03 program.[52] The geometries were optimized using the "tight" criterion, and the Becke3LYP calculations were carried out using the ultrafine grid. The Hessians were calculated analytically, and a step size of 0.025 Å was used for the numerical differentiations to produce the required third and fourth derivatives.

In applying the vibrational perturbation theory to polyatomic systems, it is essential to have a suitable strategy for dealing with Fermi resonances. Barone's VPT2 code screens for Fermi resonances and treats them via a strategy proposed by Martin et al.[60] A second issue that arises in applying the VPT2 approach to water clusters is that it is unable to treat shifts in frequencies due to tunneling between local minima separated by small barriers, as occurs, for example, upon flipping the H atoms of free OH groups of water clusters. As shown by Losada and Leutwyler,[61] the tunneling associated with the OH flipping degrees of freedom can lead to large reductions in the associated vibrational transition energies but is much less important for the ZPEs, the primary quantities of interest here.

3. Results

Although the focus of this study is on vibrational ZPEs, it is instructive to compare the calculated and experimentally observed anharmonic vibrational frequencies in the case of $(H_2O)_2$ (Table 1). Overall, the Becke3LYP and MP2 anharmonic frequencies are in fairly good agreement, although with the aug-cc-pVTZ basis set the OH stretch frequencies are 21−48 cm^{-1} lower at the Becke3LYP level. For the most part, these differences are also found for the harmonic frequencies, with the result that anharmonicity corrections are comparable in the Becke3LYP and MP2 approximations. The average absolute difference between the calculated (MP2/aug-cc-pVTZ) and measured anharmonic frequencies for the OH stretch and HOH bending vibrations is only 12 cm^{-1}. For the intermolecular vibrations, the average difference between theory and experiment is only 19 cm^{-1}, but it should be noted that there is considerable uncertainty in the experimental frequencies of some of these modes.

From Table 1 it can also be seen that, with the exception of the OH stretch vibrations, the MP2 frequencies, both harmonic and anharmonic, calculated with the aug-cc-pVDZ and aug-cc-pVTZ basis sets agree within 10 cm^{-1}. The sensitivity of the

TABLE 1: Harmonic and Anharmonic Vibrational Frequencies and Zero-Point Energies (cm^{-1}) of $(H_2O)_2$

	calculated[a]								
	harmonic				anharmonic				
	MP2		B3LYP		MP2		B3LYP		experimental anharmonic
	aVDZ	aVTZ	aVDZ	aVTZ	aVDZ	aVTZ	aVDZ	aVTZ	
	3925	3935	3895	3890	3737	3753	3710	3711	3745[b]
	3904	3915	3874	3870	3722	3745	3696	3697	3735[c]
	3796	3814	3789	3791	3615	3648	3617	3627	3660 ± 5[c]
	3704	3719	3672	3675	3554	3583	3531	3542	3601[c]
	1643	1650	1637	1647	1592	1595	1585	1592	1611[d]
	1624	1629	1617	1628	1580	1585	1576	1583	1593[d]
	639	630	634	625	505	502	507	499	520[e]
	358	360	360	362	309	310	322	287	290[d]
	184	184	184	187	148	138	137	117	108[f]
	151	155	157	157	106	114	132	102	103[f]
	148	147	156	155	112	113	103	117	103[f]
	127	127	130	130	60	60	69	37	87[f]
ZPE	**10 101**	**10 133**	**10 053**	**10 059**	**9860**	**9898**	**9820**	**9806**	

[a] aVDZ and aVTZ denote aug-cc-pVDZ and aug-cc-pVTZ, respectively. [b] Reference 62. [c] Reference 7. [d] In Ar matrix, ref 63. [e] In N_2 matrix, ref 63. [f] Reference 64.

TABLE 2: Harmonic and Anharmonic ZPEs and ZPE Contributions to the Binding Energies (cm^{-1}) of the $(H_2O)_n$, $n = 1-6$, Clusters Calculated at the B3LYP/aug-cc-pVDZ Level of Theory[a]

	W_1	W_2	W_3	W_4	W_5	W_6 chair	W_6 book	W_6 cage	W_6 prism
					ZPE				
harm.	4659	10 053	15 855	21 503	26 893	32 316	32 553	32 669	32 715
anh.-corr.[a]	−75	−233	−346	−464	−612	−730	−699	−771	−805
total	4584	9820	15 509	21 039	26 281	31 586	31 854	31 898	31 910
				ZPE contrib. to D_0					
harm.	−	735	1879	2867	3599	4363	4600	4716	4762
anh.-corr.[a]	−	−83	−121	−163	−236	−279	−248	−321	−355
total	−	652	1758	2704	3363	4084	4352	4395	4407

[a] Anh.-corr. denotes the anharmonicity correction to the vibrational ZPE and to the ZPE contribution to D_0.

TABLE 3: Harmonic and Anharmonic ZPEs and ZPE Contributions to the Binding Energies (cm^{-1}) of the $(H_2O)_n$, $n = 1-6$, Clusters Calculated at the MP2/aug-cc-pVDZ Level of Theory[a]

	W_1	W_2	W_3	W_4	W_5	W_6 chair	W_6 book	W_6 cage	W_6 prism
					ZPE				
harm.	4682	10 101	15 913	21 607	27 056	32 520	32 731	32 864	32 933
anh.-corr.[b]	−76	−241	−374	−470	−612	−730	−699	−771	−805
total	4606	9860	15 539	21 137	26 444	31 790	32 032	32 093	32 128
				ZPE contrib. to D_0					
harm.	-	738	1868	2881	3648	4430	4642	4774	4843
anh.-corr.[b]	-	−89	−146	−166	−236	−279	−248	−321	−355
total	-	649	1722	2715	3412	4151	4394	4453	4488

[a] For the $n = 5$ and 6 clusters, the anharmonicity corrections are from Becke3LYP/aug-cc-pVDZ calculations. [b] Anh.-corr. denotes the anharmonicity correction to the vibrational ZPE and to the ZPE contribution to D_0.

frequencies to the basis set is greater for the OH stretch vibrations with the frequency differences being as large as 18 cm^{-1} in the harmonic approximation and 33 cm^{-1} in the anharmonic approximation. However, as noted below, the basis set dependence is much less important for the anharmonicity contributions to the binding energy.

Tables 2 and 3 report for the $n = 2-6$ clusters the calculated harmonic and anharmonic ZPEs, as well as the ZPE contributions to the cluster binding energies, calculated by subtracting n times the ZPE of the monomer from the ZPE of the $(H_2O)_n$ cluster of interest. For $(H_2O)_2$, the ZPE contribution to the binding energy is calculated at the MP2/aug-cc-pVDZ level to be 738 cm^{-1} in the harmonic approximation and 649 cm^{-1} when allowing for vibrational anharmonicity. These values are reduced by only 3 and 6 cm^{-1}, respectively, upon adoption of the aug-cc-pVTZ basis set. The corresponding ZPE contributions to the binding energy at the Becke3LYP/aug-cc-pVDZ level, 735 and 652 cm^{-1}, are close to the MP2 values. The calculated anharmonicity contributions to the binding energy of $(H_2O)_2$ (89 and 83 cm^{-1} at the MP2/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels, respectively) are in excellent agreement with a prior estimate[18] (80 cm^{-1}) of this quantity.

Figure 2 plots the calculated harmonic and anharmonic ZPE contributions per monomer to the binding energies for the $n = 2-6$ clusters. The two curves are roughly parallel, with the difference ranging from 42 to 59 cm^{-1} (see Table 4). For the four $(H_2O)_6$ isomers considered, the calculated total anharmonicity corrections to the binding energies range from −248 cm^{-1} (book) to −355 cm^{-1} (prism). Thus, vibrational anharmonicity changes the relative energies of these isomers by up to 107 cm^{-1} (0.3 kcal/mol).

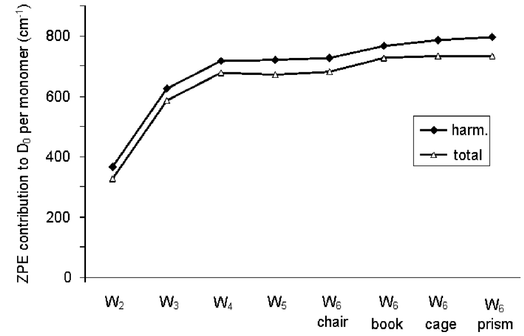

Figure 2. Vibrational ZPE contributions per monomer (cm^{-1}) to the dissociation energies of the $(H_2O)_n$, $n = 2-6$, clusters.

TABLE 4: Vibrational ZPE Contributions (cm^{-1}) to the Binding Energies Reported Per Monomer and Calculated at the B3LYP/aug-cc-pVDZ Level of Theory

	W_2	W_3	W_4	W_5	W_6 chair	W_6 book	W_6 cage	W_6 prism
harm.	368	626	717	720	727	767	786	794
anh.	−42	−40	−41	−47	−46	−42	−53	−59
total	326	586	676	673	681	725	733	735

Calculations at the MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ level of theory, including corrections for BSSE and vibrational ZPEs, calculated in the harmonic approximation, give relative energies of 0.00, 0.02, 0.05, and 0.15 kcal/mol for the chair, cage, book, and prism isomers of the water hexamer, respectively.[34] When these results are combined with the anharmonicity corrections calculated here, we find that the cage isomer is predicted to be the most stable, followed by the prism (+0.04 kcal/mol), chair (+0.10 kcal/mol), and book (+0.24 kcal/mol) isomer. The relative ordering stays the same upon deuteration, with the exception that in $(D_2O)_6$ the prism isomer is predicted to be 0.02 kcal/mol more stable than the cage. Obviously, when dealing with isomers this close in energy, the calculated energy ordering cannot be taken as definitive.

Next, we consider the contributions of various types of vibrations to the ZPEs of the water clusters. Table 5 decomposes the calculated harmonic ZPE contributions to the binding energies into contributions from the OH stretch, HOH bend, and intermolecular degrees of freedom. Here, we focus on the harmonic results because the anharmonic ZPE corrections do

TABLE 5: ZPE Contributions (cm^{-1}) of Various Classes of Vibrations to the Binding Energies of the $(H_2O)_n$, $n = 2-6$, Clusters Calculated in the Harmonic Approximation at the B3LYP/aug-cc-pVDZ Level

	W_2	W_3	W_4	W_5	W_6 chair	W_6 book	W_6 cage	W_6 prism
OH stretch	−84	−398	−859	−1160	−1410	−1405	−1324	−1259
bending modes	9	22	53	90	104	105	119	130
intermolecular modes	811	2256	3673	4669	5669	5901	5921	5891
total	735	1879	2867	3599	4363	4600	4716	4762

TABLE 6. ZPE Contributions (cm^{-1}) of Various Classes of Vibrations to the Binding Energies of the $(H_2O)_n$, $n = 2-4$, Clusters Calculated in the Harmonic Approximation at the QCISD/aug-cc-pVDZ Level[a]

	W_2	W_3	W_4
OH stretch	−49 (−84, −76)	−239 (−398, −347)	−544 (−859, −766)
bending modes	11 (9, 11)	27 (22, 28)	62 (53, 65)
intermolecular modes	776 (811, 803)	2091 (2256, 2187)	3400 (3673, 3582)
total	737 (735, 738)	1879 (1879, 1868)	2919 (2876, 2881)

[a] Becke3LYP/aug-cc-pVDZ and MP2/aug-cc-pVDZ results are reported in parentheses, with the Becke3LYP results given first.

not depend on the frequency values alone.[65] As expected, the most important class of vibrations for the ZPE contributions to the binding energies is that of the intermolecular vibrations. However, the contributions due to the OH stretch degrees of freedom are also sizable, being 11−24% as large in magnitude as the contributions due to intermolecular vibrations. The ZPE contributions due to the HOH bending vibrations are about 1 order of magnitude smaller still. Although the ZPE contributions from the intermolecular vibrations and the intramolecular bending vibrations make positive contributions to D_0, the net ZPE contributions due to the OH stretching degrees of freedom make negative contributions to D_0.

A rough estimate of the anharmonicity contributions from different classes of vibrations to the ZPEs can be obtained by using eq 47 from ref 51, which expresses the ZPE in terms of the harmonic and anharmonic frequencies as well as the anharmonicity constants. On the basis of this approach, it is found that the anharmonicity corrections to the intermolecular vibrations dominate the net anharmonicity corrections to the binding energies of the $(H_2O)_n$, $n = 2-6$, clusters. However it should be noted that the anharmonic frequencies of the individual intermolecular vibrations include contributions that couple the intermolecular and intramolecular normal modes.

Both the B3LYP and MP2 methods give OO distances that are too short and single- and double-donor OH bond lengths that are too long compared to those from calculations including high-order electron correlation effects. These geometrical errors translate into errors in the calculated vibrational frequencies. This leads naturally to the question as to whether the limitations of these theoretical methods have significant consequences for the ZPE contributions to the binding energies. To examine this issue, we have optimized the geometries and calculated the harmonic frequencies for the $(H_2O)_n$, $n = 2-4$, clusters at the QCISD[66]/aug-cc-pVDZ level of theory. The ZPE contributions due to both the OH stretch and the intermolecular vibrations are altered significantly in going from the MP2 (or B3LYP) to the QCISD level of theory (Table 6). However, the net ZPEs are essentially unchanged upon the inclusion of high-order correlation effects. Thus, we conclude that both the B3LYP and MP2 methods are suitable for calculating the contributions of vibrational ZPE to the binding energies of water clusters.

4. Conclusions

The VPT2 method has been combined with the Becke3LYP and MP2 electronic structure methods to calculate anharmonic contributions to the ZPEs of the $(H_2O)_n$, $n = 1-6$, clusters. The anharmonic contribution to the ZPE correction to the binding energy is calculated to be −83, −121, −163, and −236 cm^{-1} for $(H_2O)_2$, $(H_2O)_3$, $(H_2O)_4$, and $(H_2O)_5$, respectively. For the four low-energy isomers considered, the anharmonic contribution to the ZPE correction to the binding energy of $(H_2O)_6$ ranges from −248 to −355 cm^{-1}, being larger in magnitude for the cage and prism than for the chair and book isomers. Allowing for the effects of vibrational anharmonicity, we predict the most stable isomer of $(H_2O)_6$ to be the cage isomer, followed by the prism, chair, and book isomers, in order of increasing energy, with all four isomers lying within 0.2 kcal/mol of one another. The cage, chair, and book isomers have been observed experimentally to date, the cage in the microwave experiments of Liu et al.,[67,68] the chair in the Helium droplet experiments of Nauta et al.,[69] and the book isomer in the IR studies of Steinbach et al.[70] and Diken et al.[31]

High-order correlation effects, although important for the frequencies of individual vibrational modes, are found to be relatively unimportant for the net vibrational zero-point energies. In other words, the success of the Becke3LYP and MP2 methods for calculating the vibrational ZPEs is a consequence of a near cancellation of errors. The origin of this cancellation is well understood in that these theoretical methods underestimate the frequencies of the OH groups engaged in H bonding and tend to overestimate the frequencies of the intermolecular vibrations. The present study also reveals that there are sizable differences between the ZPE contributions to the binding energies calculated considering only the intermolecular degrees of freedom and those calculated including all degrees of freedom. This suggests that rigid monomer water models are of limited use for the calculation of ZPE contributions to the binding energies of water clusters.

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References and Notes

(1) Kim, K. S.; Mhin, B. J.; Choi, U.-S.; Lee, K. *J. Chem. Phys.* **1992**, *97*, 6649.
(2) Xantheas, S. S.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 8774.
(3) Gregory, J. K.; Clary, D. C. *J. Phys. Chem.* **1996**, *100*, 18014.
(4) Jung, J. O.; Gerber, R. B. *J. Chem. Phys.* **1996**, *105*, 10332.
(5) Munoz-Caro, C.; Nino, A. *J. Phys. Chem. A* **1997**, *101*, 4128.
(6) Sabo, D.; Bacic, Z.; Graf, S.; Leutwyler, S. *J. Chem. Phys.* **1998**, *109*, 5404.
(7) Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863.
(8) Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A.; Mas, E. M.; Bukowski, R.; Szalewicz, K. *J. Chem. Phys.* **2000**, *113*.

(9) Wright, N. J.; Gerber, R. B. *J. Chem. Phys.* **2000**, *112*, 2598.

(10) Del Bene, J. E.; Jordan, M. J. T. *J. Mol. Struct.: THEOCHEM* **2001**, *573*, 11.

(11) Keutsch, F. N.; Brown, M. G.; Petersen, P. B.; Saykally, R. J.; Geleijns, M.; van der Avoird, A. *J. Chem. Phys.* **2001**, *114*, 3994.

(12) Park, C. Y.; Kim, Y.; Kim, Y. *J. Chem. Phys.* **2001**, *115*, 2926.

(13) Rekik, N.; Valcescu, A.; Blaise, P.; Henri-Rousseau, O. *Chem. Phys.* **2001**, *273*, 11.

(14) Smit, M. J.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A.; Bukowski, R.; Szalewicz, K. *J. Phys. Chem. A* **2001**, *105*, 6212.

(15) Tobias, D. J.; Jungwirth, P.; Parrinello, M. *J. Chem. Phys.* **2001**, *114*, 7036.

(16) Atamas, N. A.; Yaremko, A. M.; Bulavin, L. A.; Pogorelov, V. E.; Berski, S.; Latajka, Z.; Ratajczak, H.; Abkowicz-Bienko, A. *J. Mol. Struct.* **2002**, *605*, 187.

(17) Chaban, G. M.; Gerber, R. B. *Spectrochim. Acta, Part A* **2002**, *58*, 887.

(18) Dykstra, C. E.; Shuler, K.; Young, R. A.; Bacic, Z. *J. Mol. Struct.: THEOCHEM* **2002**, *591*, 11.

(19) Goldman, N.; Fellers, R. S.; Brown, M. G.; Braly, L. B.; Keoshian, C. J.; Leforestier, C.; Saykally, R. J. *J. Chem. Phys.* **2002**, *116*, 10148.

(20) Sandorfy, C. *J. Mol. Struct.* **2002**, *614*, 365.

(21) Alparone, A.; Millefiori, S. *Chem. Phys.* **2003**, *290*, 15.

(22) Belhayara, K.; Chamma, D.; Henri-Rousseau, O. *J. Mol. Struct.* **2003**, *648*, 93.

(23) Florio, G. M.; Zwier, T. S.; Myshakin, E. M.; Jordan, K. D.; Sibert, E. L., III. *J. Chem. Phys.* **2003**, *118*, 1735.

(24) Rai, V. K.; Rai, S. B.; Rai, D. K. *Spectrochim. Acta, Part A* **2003**, *59*, 1299.

(25) Stefov, V.; Pejov, L.; Soptrajanov, B. *J. Mol. Struct.* **2003**, *651−653*, 793.

(26) Yamamoto, N.; Shida, N.; Miyoshi, E. *Chem. Phys. Lett.* **2003**, *371*, 724.

(27) Heyne, K.; Huse, N.; Dreyer, J.; Nibbering, E. T. J.; Elsaesser, T. *J. Chem. Phys.* **2004**, *121*, 902.

(28) Smedarchina, Z.; Fernandez-Ramos, A.; Siebrand, W. *Chem. Phys. Lett.* **2004**, *395*, 339.

(29) Perchard, J. P. *Chem. Phys.* **2001**, *273*, 217.

(30) Keutsch, F. N.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533.

(31) Diken, E. G.; Robertson, W. H.; Johnson, M. A. *J. Phys. Chem. A* **2004**, *108*, 64.

(32) Myshakin, E. M.; Diri, K.; Jordan, K. D. *J. Phys. Chem. A* **2004**, *108*, 6758.

(33) Wales, D. J. *Energy Landscapes: With Applications to Clusters, Biomolecules and Glasses*; Cambridge University Press: Cambridge, U.K., 2003.

(34) Losada, M.; Leutwyler, S. *J. Chem. Phys.* **2002**, *117*, 2003.

(35) Pedulla, J. M.; Kim, K.; Jordan, K. D. *Chem. Phys. Lett.* **1998**, *291*, 78.

(36) Clary, D. C.; Gregory, J. K. In *Recent Theoretical and Experimental Advances in Hydrogen Bonded Clusters*; Xantheas, S. S., Ed.; Kluwer Academic Publishers: Norwell, MA, 2000; Vol. 561; p 187.

(37) Millot, C.; Stone, A. J. *Mol. Phys.* **1992**, *77*, 439.

(38) Bowman, J. M. *J. Chem. Phys.* **1978**, *68*, 608.

(39) Gerber, R. B.; Ratner, M. A. **1979**, *68*, 195.

(40) Bowman, J. M. *Acc. Chem. Res.* **1986**, *19*, 202.

(41) Wierzbicki, A.; Bowman, J. M. *Comput. Phys. Commun.* **1988**, *51*, 225.

(42) Chaban, G. M.; Jung, J. O.; Gerber, R. B. *J. Chem. Phys.* **1999**, *111*, 1823.

(43) Mills, I. M. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Mathews, C. W., Eds.; Academic Press: New York, 1972; Vol. 1, p 115.

(44) Martin, J. M. L.; Francois, J. P.; Gijbels, R. *J. Chem. Phys.* **1992**, *96*, 7633.

(45) Lee, T. J.; Martin, J. M. L.; Taylor, P. R. *J. Chem. Phys.* **1995**, *102*, 254.

(46) Csaszar, A. G.; Mills, I. M. *Spectrochim. Acta, Part A* **1997**, *53*, 1101.

(47) Bludsky, O.; Chocholousova, J.; Vacek, J.; Huisken, F.; Hobza, P. *J. Chem. Phys.* **2000**, *113*, 4629.

(48) Neugebauer, J.; Hess, B. A. *J. Chem. Phys.* **2003**, *118*, 7215.

(49) Yagi, K.; Hirao, K.; Taketsugu, T.; Schmidt, M. W.; Gordon, M. S. *J. Chem. Phys.* **2004**, *121*, 1383.

(50) Bouteiller, Y.; Perchard, J. P. *Chem. Phys.* **2004**, *305*, 1.

(51) Barone, V. *J. Chem. Phys.* **2005**, *122*, 014108.

(52) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.01; Gaussian, Inc.: Pittsburgh, PA, 2003.

(53) Mhin, B. J.; Kim, H. S.; Kim, H. S.; Yoon, C. W.; Kim, K. S. *Chem. Phys. Lett.* **1991**, *176*, 41.

(54) Tsai, C. J.; Jordan, K. D. *Chem. Phys. Lett.* **1993**, *213*, 181.

(55) Kim, K.; Jordan, K. D.; Zwier, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 11568.

(56) Xantheas, S. S.; Burnham, C. J.; Harrison, R. J. *J. Chem. Phys.* **2002**, *116*, 1493.

(57) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(58) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(59) Diri, K.; Myshakin, E. M.; Jordan, K. D., unpublished work.

(60) Martin, J. M. L.; Lee, T. J.; Taylor, P. R.; François, J. *J. Chem. Phys.* **1995**, *103*, 2589.

(61) Losada, M.; Leutwyler, S. *J. Chem. Phys.* **2003**, *119*, 304.

(62) Huang, Z. S.; Miller, R. E. *J. Chem. Phys.* **1989**, *91*, 6613.

(63) Bentwood, R. M.; Barnes, A. J.; Orville-Thomas, W. J. *J. Mol. Spectrosc.* **1980**, *84*, 391.

(64) Braly, L. B.; Liu, K.; Brown, M. G.; Keutsch, F. N.; Fellers, R. S.; Saykally, R. J. *J. Chem. Phys.* **2000**, *112*, 10314.

(65) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128.

(66) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(67) Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501.

(68) Liu, K.; Brown, M. G.; Saykally, R. J. *J. Phys. Chem. A* **1997**, *101*, 8995.

(69) Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293.

(70) Steinbach, C.; Andersson, P.; Melzer, M.; Kazimirski, J. K.; Buck, U.; Buch, V. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3320.