Theoretical Investigation of the Neutral Precursor of $(H_2O)_6^-$ †

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In a recent ingenious experiment Diken et al. (Diken, E. G.; Robertson, W. H.; Johnson, M. A. *J. Phys. Chem. A* **2004**, *108*, 64) obtained the vibrational spectrum in the OH stretch region of the neutral $(H_2O)_6$ precursor to the $(H_2O)_6^-$ ion. Comparison of the measured spectrum with the calculated harmonic vibrational spectra of various low-energy isomers of $(H_2O)_6$ led these authors to conclude that the observed spectrum is due to the book isomer, although agreement between theory and experiment is only qualitative. In the present study a hybrid MP2/QCISD method is used to overcome a shortcoming of earlier theoretical calculations of the harmonic spectra of low-energy $(H_2O)_6$ isomers, and the coupling of the fundamentals with overtones and combination states is accounted for by means of a cubic force-field approximation. The results of these calculations provide further support for the assignment of the book form of $(H_2O)_6$ as the precursor of the dominant observed $(H_2O)_6^-$ isomer.

Introduction

Negatively charged water clusters were first observed by Haberland and co-workers in 1984.[1] Since that time there have been numerous experimental[2−15] and theoretical studies[15−26] of these fascinating species. $(H_2O)_6^-$, in particular, has attracted considerable attention, in part because it is the smallest water cluster displaying a well-defined vibrational spectrum in the OH stretch region.[11−13,15] Several different structures have been proposed for $(H_2O)_6^-$.[11,15−20] To date, comparison of the vibrational spectra calculated for various $(H_2O)_6^-$ isomers with the experimentally determined spectrum has not permitted a definitive assignment of the isomer responsible for the spectrum. What is clear from the theoretical studies is that the anion has a geometry appreciably different from that of any of the low-energy forms of the neutral cluster.[15,19−21] Thus, either the electron-capture process is accompanied by a substantial rearrangement of the H-bonding network or it involves a high-energy isomer of the neutral cluster.

Recently, Johnson and co-workers have carried out a novel experiment allowing them to obtain the vibrational spectrum of the neutral $(H_2O)_6$ cluster that is responsible for the observed $(H_2O)_6^-$ spectrum.[27] This was accomplished by monitoring the formation of $(H_2O)_6^-$ upon IR absorption by $(H_2O)_6Ar_{10-12}$ followed by electron capture. Comparison of the calculated harmonic spectra for various low-energy isomers of the neutral $(H_2O)_6$ cluster with the measured spectrum revealed that the best agreement was with the spectrum calculated for the book form of $(H_2O)_6$. However, there are significant differences between the calculated and measured spectra, even after scaling the calculated harmonic frequencies to account approximately for anharmonicity effects. There are two major sources of error in calculations of the vibrational frequencies of various isomers of $(H_2O)_6$ carried out to date, namely, the use of the normal-mode approximation and the neglect of high-order electron correlation effects. With regards to the latter, both the MP2 and density functional methods, e.g., Becke3LYP,[28,29] that have been used in earlier theoretical studies of $(H_2O)_6$, tend to overestimate the elongation of OH bonds engaged in H-bonding, causing too large a red shift in the associated vibrational frequencies.[15,30,31] The remedy to this problem is well-understood, namely, to optimize the geometries and to calculate the vibrational frequencies using a method such as coupled-cluster theory that recovers high-order correlation effects.[31] However, such calculations with suitably flexible basis sets would be computationally prohibitive for a cluster of the size of $(H_2O)_6$.

In the present study, we use a hybrid MP2/QCISD[32] approach to calculate the harmonic vibrational spectra of the lowest energy ring, cage, prism, and book isomers of $(H_2O)_6$. These isomers, which are depicted in Figure 1, are known from prior theoretical studies[33−36] to be close in energy. The hybrid MP2/QCISD approach is used to overcome the problems associated with the use of MP2 or DFT geometries for calculating frequencies. In addition, the effects of vibrational anharmonicity, specifically the coupling of the fundamentals with overtones and combination states, are calculated using a cubic force field. Comparison of the calculated and measured[27] spectra allows us to conclude unambiguously that the book isomer of $(H_2O)_6$ is the precursor of the dominant form of $(H_2O)_6^-$. We conclude by discussing the implications of these results for the formation of $(H_2O)_6^-$.

Methodology

In the present approach the QCISD procedure,[32] which is closely related to the coupled-cluster singles-plus-doubles (CCSD) method, was used to optimize the geometries of the lowest energy ring, cage, book, and prism isomers of $(H_2O)_6$. The resulting geometries were then used to calculate the harmonic vibrational frequencies using the MP2 method. Hereafter, this will be referred to as the MP2/QCISD method. A detailed study of the $(H_2O)_n$, $n = 2-4$, clusters has shown that this approach gives vibrational frequencies and intensities for the OH stretch vibrations very close to those obtained from calculations in which the QCISD method is used for both the geometry optimizations and the vibrational frequency calcula-

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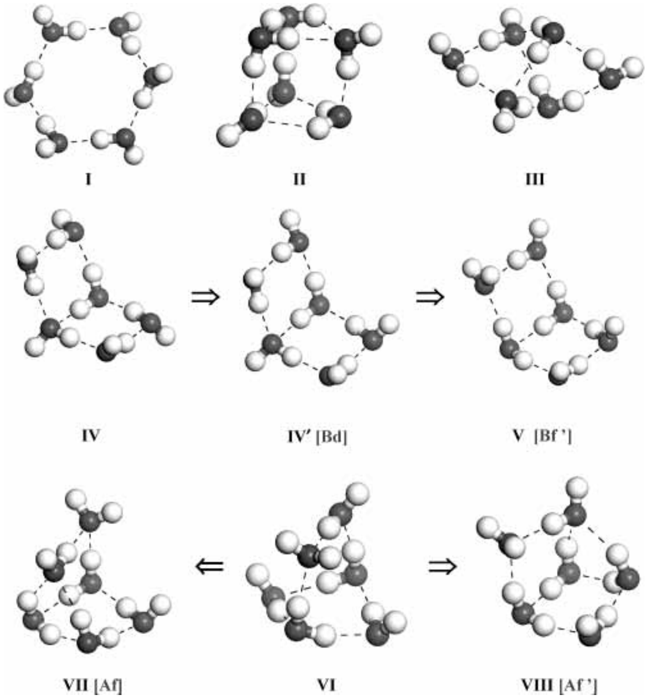

Figure 1. Low-energy isomers of $(H_2O)_6$ and $(H_2O)_6^-$ considered in this study. Structures **I**−**IV** correspond, respectively, to the lowest energy ring, prism, cage, and book forms of neutral $(H_2O)_6$. **IV′** and **V**−**VIII** are local minima of the anion. The arrows indicate a possible pathway for proceeding from the neutral book to the most stable forms of the anion (**VII** and **VIII**). **V** can rearrange to **VIII** either by direct means or via intermediate **VI**. **IV′** differs from **IV** only with respect to the flip of one of the free OH groups. This flip is accompanied by an increase in the dipole moment and, hence, by increased electron binding.

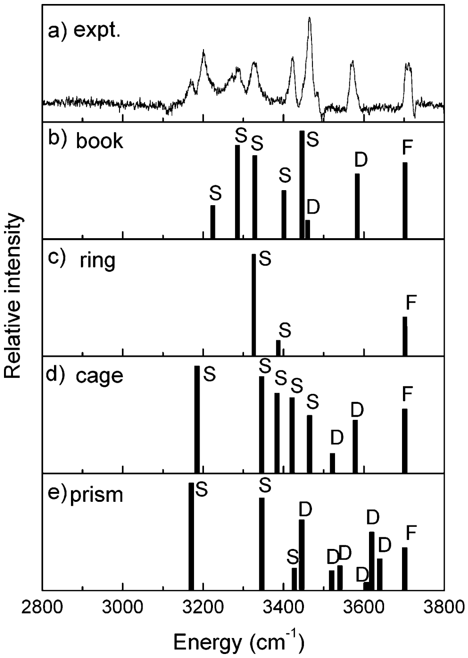

Figure 2. Vibrational spectra of the $(H_2O)_6$ cluster in the OH stretch region. The experimental spectrum (a) results from $(H_2O)_6Ar_{10-12}$ clusters that are precursors of $(H_2O)_6^-$ (reproduced from ref 27). The theoretical spectra for the book (b), ring (c), cage (d), and prism (e) isomers were obtained in the harmonic approximation from MP2 calculations using QCISD geometries. The calculated frequencies have been scaled by 0.942. F and S denote, respectively, transitions associated, with free and donor OH groups of single-donor water molecules, and D denotes transitions associated with double-donor water molecules.

tions.[31] The 6-31+G[2d,p][37,38] basis set was used for the majority of the calculations on the neutral clusters. To establish that this basis set is suitable for calculating the structures and the harmonic vibrational spectra, in the case of the cage isomer the calculations were also carried out with the more flexible aug-cc-pVDZ[39,40] basis set. The Gaussian 03[41] program suite was used for the calculations.

To account for "near-degeneracy" mixing of the OH stretch with combination and overtone bands, the cubic force constants were calculated at the Becke3LYP level. (Studies of smaller water clusters have shown that there is fairly good agreement between the cubic couplings calculated in the Becke3LYP and MP2 approximations.[31]) The Hamiltonian allowing for cubic couplings was constructed by combining the MP2/QCISD fundamental frequencies and Becke3LYP cubic force constants, with the former being scaled to allow for "diagonal" anharmonicities and the latter to compensate for the tendency of the cubic-force field method to overestimate the couplings.[42−44] The vibrational spectra were calculated variationally using this Hamiltonian and bases consisting of the OH stretch fundamentals and all combination and overtones states that fall within 600 cm^{-1} of the OH stretch fundamentals.[42,43] The intensities of the various transitions were assumed to derive from the OH stretch normal modes, and the dipole moments were assumed to vary linearly with the OH stretch coordinates. All calculated vibrational lines were given Gaussian line shapes with 7 cm^{-1} half-widths to facilitate comparison with experiment.

In addition to presenting new theoretical results for the vibrational spectra of various isomers of the neutral $(H_2O)_6$ cluster, we also examine pathways for rearrangement of the neutral book isomer to the most stable form of the anion. These calculations were carried out at the Becke3LYP level using the 6-311++G**(sp) basis set, formed by adding on the O atoms extra diffuse sp Gaussian functions[45] to the 6-311++G** basis set.[46,47]

Results

Rotational constants have been determined experimentally for the cage isomer of $(H_2O)_6$,[48,49] making this a valuable system for judging the reliability of various theoretical methods for predicting the geometries of H-bonded clusters. Our QCISD/6-31+G[2d,p] and QCISD/aug-cc-pVDZ calculations for this isomer give rotational constants of 2183, 1139, and 1065 MHz, and 2186, 1123, and 1077 MHz, respectively. These two sets of rotational constants are in close agreement with one another and with experiment (2162, 1129, and 1067 MHz), thereby establishing the suitability of the 6-31+G[2d,p] basis set for calculating the geometries of the clusters. In contrast, the rotational constants associated with the MP2/aug-cc-pVDZ-optimized geometry, 2240, 1151, and 1104 MHz, are in much poorer agreement with experiment.[50]

The calculated harmonic spectra in the OH stretch region for the book, ring, cage, and prism isomers of $(H_2O)_6$ are reproduced in Figure 2 together with the experimental spectrum measured by Diken et al.[27] The calculated OH stretch frequencies have been reduced by a factor of 0.942 to correct in an approximate manner for vibrational anharmonicity. Overall, the calculated harmonic spectrum for the book isomer is in the best agreement with the measured spectrum, as was concluded previously by Diken et al.[27] Moreover, the agreement between theory and experiment is significantly better than when using the harmonic spectrum calculated using the MP2 method (in which the same approach is used to optimize the geometry and to calculate the frequencies).

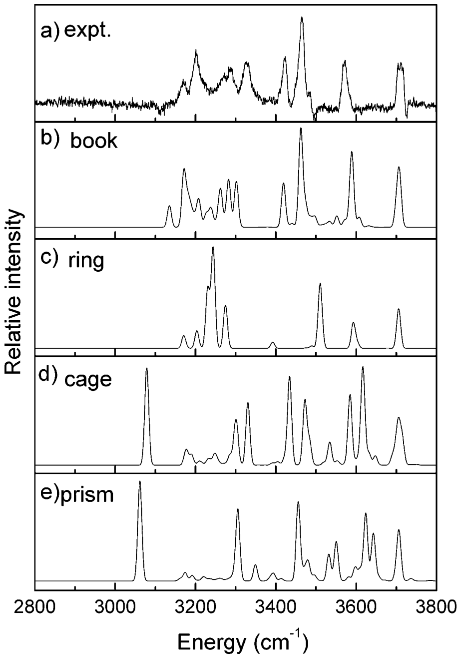

Figure 3. Vibrational spectra of the $(H_2O)_6$ cluster in the OH stretch region. The experimental spectrum (a) results from $(H_2O)_6Ar_{10-12}$ clusters that serve as the precursor to $(H_2O)_6^-$ (reproduced from ref 27). The simulated spectra for the book (b), ring (c), cage (d), and prism (e) isomers were calculated by allowing for near-degeneracy mixing of the OH stretch fundamentals with various overtones and combination states. The frequencies of the fundamentals were scaled as discussed in the text. The cubic force constants were reduced by 15%.

Comparison of the calculated and experimental spectra allows us to conclude that the line observed near 3720 cm^{-1} is due to the five free OH stretch vibrations, those near 3450 and 3470 cm^{-1} are due to the OH stretch vibrations of the double-donor water, and the two lines near 3410 cm^{-1} are due to single-donor OH stretch vibrations. Nonetheless, there remains the problem that the experimental spectrum has five peaks between 3170 and 3330 cm^{-1}, whereas the calculated harmonic spectrum has only three single-donor OH stretch transitions in this range. This is not an unexpected result, since clusters containing water molecules often display extra structure in this region as a result of mixing of H−O−H bend overtones with the OH stretch fundamentals.[51,52]

Figure 3 displays the vibrational spectra for the book, ring, cage, and prism isomers of $(H_2O)_6$ calculated by allowing for mixing of the OH stretch fundamentals with overtones and combination states. The experimental spectrum is reproduced for comparison. In calculating these spectra, the frequencies of the OH stretch fundamentals were reduced by 0.942, with this scale factor being determined by comparing the average of the OH stretch frequencies calculated in the harmonic and anharmonic approximations and using the Becke3LYP level of theory.[31] For the other classes of vibrations (H−O−H bend, OH wag, intermolecular stretch) the MP2/QCISD harmonic frequencies were scaled by the factors needed to bring their average into agreement with the average of the anharmonic frequencies from the Becke3LYP calculations. The anharmonic frequencies used for determining the scaling factors were obtained using the second-order perturbative approach[53] implemented in Gaussian 03[41] and will be reported in ref 31. In generating the theoretical spectrum reported in Figure 3, the cubic force constants were reduced by 15% to compensate for the tendency of the unscaled force constants to overestimate the couplings.[42−44] However, it should be noted that this scaling does not significantly alter the appearance of the calculated spectra.

By far the best agreement between the calculated spectra reported in Figure 3 and the experimental spectrum is for the book isomer. The four intense transitions observed between 3420 and 3720 cm^{-1} are closely reproduced by the calculations. Moreover, the calculated spectrum of the book isomer displays considerable structure due to overtones and combination bands in the 3170−3330 cm^{-1} region, in agreement with experiment. Given the sensitivity of the spectral features in this region to the energy spacings between the unmixed fundamentals and the overtones and combination states, the agreement between theory (book isomer) and experiment is quite satisfying. In light of these results, we conclude that the book form of $(H_2O)_6$ is the precursor for the dominant experimentally observed isomer of $(H_2O)_6^-$, i.e., that which has a vertical detachment energy of 0.42 eV[2,6] and for which the vibrational spectrum in the OH stretch region was measured by Ayotte et al.[15]

Implications for Anion Formation

Two recent theoretical studies have identified **VII**, depicted in Figure 1, as the most stable form of $(H_2O)_6^-$.[19,21] One of these, by Kim et al.,[19] proposed that **VII** is the isomer responsible for the vibrational spectrum of $(H_2O)_6^-$ measured by Ayotte et al.,[15] although, in our opinion, the agreement between their calculated (Becke3LYP) vibrational spectrum of this isomer and that measured is not close enough for an unambiguous assignment. The inability to account for the spectrum in a quantitative manner at the Becke3LYP level is not surprising, since this approach (at least when used with a flexible basis set) considerably overbinds the excess electron[15] and also suffers from the problem (mentioned above) of exaggerating red shifts associated with the OH stretch vibration of the H-bonded OH groups. We have calculated the vibrational spectrum of **VII** using the MP2 approximation, which shares with the B3LYP method the tendency to overestimate the bond lengths of OH groups engaged in H-bonding but, in contrast to the B3LYP method, considerably underestimates the binding of the excess electron. The resulting spectrum is in poorer agreement with the experimental spectrum for the anion than is that calculated using the Becke3LYP method. It is well-established that high-level electronic structure methods such as CCSD(T) are required to accurately describe the binding of an excess electron to clusters such as $(H_2O)_6$[54−56] As a result, we believe that a definitive identification of the observed anionic isomer based on comparison of calculated and observed vibrational spectra would require optimizing the geometries and calculating the vibrational spectra of the various low-energy isomers of the anion at the CCSD(T) level, a computationally daunting task, particularly given the large basis set required.

In the absence of a definitive assignment of the structure of the $(H_2O)_6^-$ anion based on comparison of calculated and measured vibrational spectra, it is useful to consider whether there is an energetically accessible pathway leading from the book form of the neutral cluster (**IV**) to the most stable (**VII**) isomer of the anion. Pathways for interconversion of several of the relevant low-energy minima of $(H_2O)_6^-$ have been mapped out at the Becke3LYP/6-311++G**(sp) level of theory by Kim et al.[45] For our current purpose, the most important finding of ref 45 is that the overall barrier for interconversion of the anion from **IV′** (**Bd** in ref 45) to **VII** (**Af** in ref 45) lies only about 3.2 kcal/mol above **VII** and proceeds through the intermediate **V** (**Bf′** in ref 45). In this discussion all energies have been corrected for vibrational zero-point energy. The **IV′** anion is formed from the book isomer of the neutral cluster by a flip of one of the free OH groups and electron capture. The free OH flip is accompanied by an increase in the dipole moment and, hence, also by an enhanced binding of the excess electron. Our calculations indicate that this occurs without a barrier. Moreover, **VII** is calculated to lie energetically 5.3 kcal/mol below the neutral book isomer (**IV**), which implies that the barriers for rearrangement of the anion lie energetically below the neutral cluster plus a free electron. Although the relative energies from the Becke3LYP calculations are semiquantitative at best, the conclusion that there is no net barrier between the neutral precursor **IV** plus a free electron and the **VII** anion is expected to hold up in higher level calculations such as CCSD(T).

It is also interesting to note that there are two isomers of the anion closely related to **VII**, and only slightly less stable. These are **VIII** (**Af′** in ref 45) and **VI**, located in our calculations. **VI** and **VIII** are calculated to lie respectively only 0.15 and 0.21 kcal/mol above **VII**, and the barriers for rearrangement of **VI** to either **VII** or **VIII** are calculated to be only about 0.1 kcal/mol. These results suggest that the anion does not possess a well-defined rigid structure.

Conclusion

The present study reports for the first time calculated vibrational spectra of selected low-energy isomers of $(H_2O)_6$ using geometries optimized with inclusion of high-order electron correlation effects and allowing also for coupling of the OH stretch fundamentals with overtones and combination bands. These calculations support the assignment of Diken et al.[27] of the book isomer as the precursor to the major $(H_2O)_6^-$ isomer observed experimentally. It should be stressed that this does not necessarily imply that the book structure is the dominant $(H_2O)_6$ isomer in the neutral expansion, as there could be significant population of other isomers that do not lead to the $(H_2O)_6^-$ anion upon interaction with low-energy electrons. Indeed, near complete-basis set limit MP2 calculations predict the cage, book, and prism isomers of the neutral cluster to be nearly isoenergetic (i.e., to lie within 0.25 kcal/mol).[34] Moreover, the calculations of Losada and Leutwyler[50] predict that the ring (chair conformer), book, cage, and prism structures are all very close in energy when vibrational zero-point effects are included and that the ring is the favored isomer below $T = 8$ K, the cage to be the dominant isomer between $T = 8$ and 26 K, and the book to be the dominant isomer for $T > 26$ K. The $(H_2O)_6$ clusters characterized by Diken et al.[27] have attached Ar atoms, which implies cluster temperatures near $T = 40$ K, consistent with sizable population of the book isomer. The terahertz laser vibrational−rotational tunneling spectroscopic studies of Saykally et al.[48,49] provided evidence for only the cage form of $(H_2O)_6$. Also, Pribble and Zwier have concluded on the basis of their measured OH stretch vibrational spectra that the water portion of the observed benzene·$(H_2O)_6$ cluster has a cage structure.[57] On the basis of the calculations of Losada and Leutwyler, this would seem to imply colder clusters in the experiments of Saykally et al. and Pribble and Zwier than in those of Johnson and co-workers.

Our electronic structure calculations indicate that the most stable isomer of the anion (**VII**) can be formed from the book form of the neutral cluster with no net activation energy (i.e., that the barriers for the rearrangements to give **VII** lie energetically below the book isomer). This is consistent with the experiments of Weber et al. in which $(H_2O)_6^-$ is observed upon capture by $(H_2O)_6$ of near 0 eV electrons (in Rydberg electron-transfer experiments).[14] The main structural change associated with this process is a donor−acceptor exchange of two adjacent water monomers analogous to that of the isolated water dimer (see Figure 1). Although this rearrangement is energetically uphill for the book form of the neutral cluster, it is accompanied by a large increase in the dipole moment and, as a result, is energetically favorable for the anion.

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References and Notes

(1) Haberland, H.; Langosch, H.; Schindler, H.-G.; Worsnop, D. R. *J. Phys. Chem.* **1984**, *88*, 3903.

(2) Coe, J. V.; Lee, G. H.; Eaton, J. G.; Arnold, S. T.; Sarkas, H. W.; Bowen, K. H.; Ludewigt, C.; Harberland, H.; Worsnop, D. R. *J. Chem. Phys.* **1990**, *92*, 3980.

(3) Posey, L. A.; Johnson, M. A. *J. Chem. Phys.* **1988**, *89*, 4807.

(4) Campagnola, P. J.; Cyr, D. M.; Johnson, M. A. *Chem. Phys. Lett.* **1991**, *181*, 206.

(5) Posey, L. A.; Campagnola, P. J.; Johnson, M. A.; Lee, G. H.; Eaton, J. G.; Bowen, K. H. *J. Chem. Phys.* **1989**, *91*, 6536.

(6) Lee, G. H.; Arnold, S. T.; Eaton, J. G.; Sarkas, H. W.; Bowen, K. H.; Ludewigt, C.; Haberland, H. *Z. Phys. D: At. Mol. Clusters* **1991**, *20*, 9.

(7) Desfrancois, C.; Khelifa, N.; Lisfi, A.; Schermann, J. P.; Eaton, J. G.; Bowen, K. H. *J. Chem. Phys.* **1991**, *95*, 7760.

(8) Tachikawa, D. H.; Lund, A.; Ogasawara, M. *Can. J. Chem.* **1993**, *71*, 118.

(9) Misaizu, F.; Kondow, T.; Kuchitsu, K. *Chem. Phys. Lett.* **1997**, *178*, 369.

(10) Maeyama, T.; Tsumura, T.; Fujii, A.; Mikami, N. *Chem. Phys. Lett.* **1997**, *264*, 292.

(11) Bailey, C. G.; Kim, J.; Johnson, M. A. *J. Phys. Chem.* **1996**, *100*, 16782.

(12) Ayotte, P.; Bailey, C. G.; Kim, J.; Johnson, M. A. *J. Chem. Phys.* **1998**, *108*, 444.

(13) Kelley, J. A.; Weddle, G. H.; Robertson, W. H.; Johnson, M. A. *J. Chem. Phys.* **2002**, *116*, 1201.

(14) Weber, J. M.; Leber, E.; Ruf, M.-W.; Hotop, H. *Eur. Phys. J. D* **1999**, *7*, 587.

(15) Ayotte, P.; Weddle, G. H.; Bailey, C. G.; Johnson, M. A.; Vila, F.; Jordan, K. D. *J. Chem. Phys.* **1999**, *110*, 6268.

(16) Lee, S.; Kim, J.; Lee, S. J.; Kim, K. S. *Phys. Rev. Lett.* **1997**, *79*, 2038.

(17) Kim, K. S.; Lee, S.; Kim, J.; Lee, J. Y. *J. Am. Chem. Soc.* **1997**, *119*, 9329.

(18) Suh, S. B.; Lee, H. M.; Kim, J.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **2000**, *113*, 5273.

(19) Lee, H. M.; Lee, S.; Kim, K. S. *J. Chem. Phys.* **2003**, *119*, 187.

(20) Tsurusawa, T.; Iwata, S. *Chem. Phys. Lett.* **1999**, *315*, 433.

(21) Wang, F.; Jordan, K. D. *J. Chem. Phys.* **2003**, *119*, 11645.

(22) Novakovskaya, Y. V.; Stepanov, N. F. *J. Phys. Chem. A* **1999**, *103*, 10975.

(23) Smith, D. M. A.; Smets, J.; Adamowicz, L. *J. Chem. Phys.* **1999**, *110*, 3804.

(24) Chen, H.-Y.; Shen, W.-S. *J. Chem. Phys.* **1999**, *110*, 9032.

(25) Barnett, R. N.; Landman, U.; Makov, G.; Nitzan, A. *J. Chem. Phys.* **1990**, *93*, 6226.

(26) Coe, J. V. *Int. Rev. Phys. Chem.* **2001**, *20*, 33.

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

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

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

(30) Huisken, F.; Kaloudis, M.; Vigasin, A. A. *Chem. Phys. Lett.* **1997**, *269*, 235.

(31) Diri, K.; Myshakin, E. M.; Jordan, K. D. In prepration.

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

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

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

(35) Pedulla, J. M.; Jordan, K. D. *Chem. Phys.* **1998**, *239*, 593.

(36) Gregory, J. K.; Clary, D. C. *J. Phys. Chem.* **1996**, *100*, 18014.

(37) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

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

(39) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

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

(41) Frisch, M. J.; Trucks G. W.; et al. *Gaussian 03*, release B.05; Gaussian Inc.: Pittsburgh, PA, 2003.

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

(43) Myshakin, E. M.; Jordan, K. D.; Sibert, E. L., III; Johnson, M. A. *J. Chem. Phys.* **2003**, *119*, 10138.

(44) Mayrhofer, R. C.; Sibert, E. L. *Theor. Chim. Acta* **1995**, *92*, 107.

(45) Lee, H. M.; Lee, S.; Kim, K. S. *J. Chem. Phys.* **2003**, *119*, 7685.

(46) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(47) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

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

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

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

(51) Ayotte, P.; Weddle, G. H.; Kim, J.; Johnson, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 12361.

(52) Robertson, W. H.; Weddle, G. H.; Kelley, J. A.; Johnson, M. A. *J. Phys. Chem. A* **2002**, *106*, 1205.

(53) Barone, V. *J. Chem. Phys.* **2004**, *120*, 3059.

(54) Peterson, K. A.; Gutowski, M. *J. Chem. Phys.* **2002**, *116*, 3297.

(55) Gutowski, M.; Jordan, K. D.; Skurski, P. *J. Phys. Chem. A* **1998**, *102*, 2624.

(56) Skurski, P.; Gutowski, M.; Simons, J. *Int. J. Quantum Chem.* **2000**, *80*, 1024.

(57) Pribble, R. N.; Zwier, T. S. *Science* **1994**, *265*, 75.