Comparison of CBS-QB3, CBS-APNO, G2, and G3 thermochemical predictions with experiment for formation of ionic clusters of hydronium and hydroxide ions complexed with water

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The GAUSSIAN 2, GAUSSIAN 3, complete basis set-QB3, and complete basis set-APNO methods have been used to calculate $\Delta H^\circ$ and $\Delta G^\circ$ values for ionic clusters of hydronium and hydroxide ions complexed with water. Results for the clusters $\text{H}_2\text{O}^+(\text{H}_2\text{O})_n$ and $\text{OH}^-(\text{H}_2\text{O})_n$, where $n = 1$–$4$, are reported in this paper, and compared against experimental values contained in the National Institutes of Standards and Technology (NIST) database. Agreement with experiment is excellent for the three \textit{ab initio} methods for formation of these clusters. The high accuracy of these methods makes them reliable for calculating energetics for the formation of ionic clusters containing water. In addition, this allows them to serve as a valuable check on the accuracy of experimental data reported in the NIST database, and makes them useful tools for addressing unresolved issues in atmospheric chemistry. © 2005 American Institute of Physics. [DOI: 10.1063/1.1811611]

I. INTRODUCTION

The Gaussian-$n$(Gn) (Refs. 1 and 2) and complete basis set (CBS) (Refs. 3–5) model chemistries have been developed for the calculation of accurate gas phase thermochemical quantities. To achieve chemical accuracy, computed values of $\Delta G^\circ$ must be correct to within 1 kcal/mol. A serious challenge to these methods is the accurate calculation of the energetics of formation of ionic clusters. Calculation of the enthalpy and free energy changes of ionic clusters is difficult, as the basis set superposition error (BSSE) and fragment relaxation energies for these complexes have large effects. In principle the $\text{Gn}$ and CBS model chemistries, which extrapolate the energies to the complete basis set limit, should provide energies that do not need to be corrected for limitations in the basis set used for the different geometries in an ionic cluster calculation. To better evaluate the ability of the GAUSSIAN and complete basis set model chemistries to accurately model gas phase ionic cluster formation, we have evaluated their performance for cluster reactions of water binding to the hydroxide and hydronium ions. In this paper, we report on the predictive ability of the GAUSSIAN 2 (G2), GAUSSIAN 3 (G3), CBS-QB3, and CBS-APNO methods against the National Institutes of Standards and Technology (NIST) data set.

The study of hydrates of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ in the gas phase extends back over 40 years. The $\text{OH}^-(\text{H}_2\text{O})_2$ cluster was identified by a mass spectrometric examination of negative ions in flame gases in 1962. $^8$ The $\text{H}_3\text{O}^+$ ion was observed in the $D$ region ($62$–$82$ km) of the atmosphere, disappearing at $82.5$ km, in 1965. $^7$ In 1977 proton hydrates were identified in the stratosphere, at altitudes of $24$–$60$ km. $^{10}$ Initial experiments to determine $\Delta H^\circ$ and $\Delta G^\circ$ for ion-hydrate formation were difficult, $^{11}$ but improvements in experimental design led to reliable experimental values. $^{13,15}$ The solvation shell effects present in the mass spectrometry experiments for $\text{OH}^-(\text{H}_2\text{O})_n$, after $n = 3$, $^{17}$ were confirmed by high resolution vibrational spectroscopy, $^{19}$ leading to enhanced confidence in the mass spectrometric results. $^{15,17}$

Gas phase spectroscopic experiments have also shown that the $\text{H}_3\text{O}^+$ cation has $C_{3v}$ symmetry, that $\text{H}_2\text{O}_2^+$ is a symmetric $C_2$ dimer, that $\text{H}_2\text{O}_3^+$ has $C_{2v}$ symmetry, and that $\text{OH}^-(\text{H}_2\text{O})$ is an asymmetrical hydrogen-bonded equilibrium structure. $^{20}$–$^{25}$ \textit{Ab initio} and density functional theory (DFT) calculations have predicted much of the spectroscopic results, have reinforced the idea of a shell structure inferred from mass spectrometry, and have shed light on the flatness of the $\text{H}_2\text{O}_2^+$ potential energy surface. $^{6,22,26}$–$^{45}$ Classical and quantum molecular dynamics simulations have shown that $\text{H}_2\text{O}_3^+$ and $\text{H}_2\text{O}_4^-$ are limiting structures in aqueous solution and shed insight into the proton diffusion process, $^{36}$–$^{33}$ and that the number of water molecules around $\text{OH}^-$ is $4$–$4.5$ in aqueous solution. $^{54,55}$ By contrast, in the gas phase $\text{OH}^-$ is hydrated by three water molecules in the first solvation shell. $^{19,56}$

II. METHODS

We used the G2, $^1$ G3, $^2$ CBS-QB3, $^3$ and CBS-APNO $^{4,5}$ methods implemented within GAUSSIAN 98. $^{57}$ The absence of imaginary frequencies verified that all structures were true minima at their respective levels of theory. For the reaction of a proton and a water to form the hydronium ion, we used the translational energy of $1.5RT$ combined with $PV = RT(H = E + PV)$ to get a value of $H(H^+) = 5/2(RT)$, or $1.48\text{ kcal/mol}$. The Sackur-Tetrode equation $^{58}$ was used to evaluate the entropy, $TS(H^+) = 7.76\text{ kcal/mol}$ at $298.15\text{ K}$ and $1\text{ atm}$ pressure, which gives a value $(G = H - TS)$ for $G(H^+) \approx -6.28\text{ kcal/mol}$. $^{59,60}$ The geometries of all the stationary points and absolute energies in hartrees of each stationary point at each level of theory are available as...
The five-step CBS-QB3 series of calculations starts with a geometry optimization at the B3LYP level, followed by a frequency calculation to obtain thermal corrections, zero-point vibrational energy, and entropic information. The next three computations are single-point calculations (SPCs) at the CCSD(T), MP4SDQ, and MP2 levels. The CBS extrapolation then computes the final energies. By contrast the CBS-APNO method is a more expensive procedure. The acronym APNO stands for atomic pair natural orbital, and Petersson and co-workers have demonstrated that using APNO basis sets allows for accurate extrapolations to the complete basis set limit. The CBS-APNO procedure starts with a (U)HF/6-31G(d,p) geometry optimization and frequency calculation, to obtain the enthalpic and free energy corrections, followed by a second geometry optimization at the QCISD/6-311G(d,p) level. This correlated geometry is then used in a series of four SPCs at the QCISD(T), MP2(full), HF, and MP2 levels, each with different basis sets. The CBS extrapolation included in the last step computes the final energies. The GAUSSIAN-n model chemistries, which were the first systematic model chemistries to be developed with broad applicability to a wide range of chemical problems, have a similar philosophy and implementation. The G2 and G3 methods fall between the two CBS methods in terms of computational cost. They both begin with a HF/6-31G(d) geometry optimization and a frequency calculation, with the frequencies scaled by 0.8929. The third step is an MP2(full)/6-311G(d) geometry optimization, using all electrons for the calculation of correlation energies. For the G3 model the MP2 geometry is then used for a series of four SPCs, at the QCISD(T,E4T)/6-31G(d), MP4/6-31+G(d), MP4/6-311G(2df,p), and MP2(full)/GT large levels. These calculated values are then used to arrive at the final G3 energies, which include corrections for diffuse functions and higher polarization functions at the MP4 level, and a correction for correlation effects beyond MP4 using quadratic configuration interaction. The G3 method also contains an empirical correction step to account for core-valence correlation, and for unpaired valence electrons. The G2 method is similar, but with different basis sets used for the four SPCs, a different formulation of the higher level correction, and without spin-orbit correction for atoms and core-related correlation correction. The details of the basis sets and formulas used to obtain the final energies can be found in the original publications and a recent text. These methods have been used to calculate accurate values for enthalpies of formation, atomization energies, ionization potentials, electron affinities, proton affinities, isodesmic reactions, cation-atom reactions, molecule-atom reactions, deprotonation reactions, accurate thermodynamic cycles for pK_a calculations, free energies of water cluster formation at different energies, and to explore activation energy barriers and potential intermediates in chemical reactions.

III. RESULTS

Figure 1 shows the computed structures for H_3O^+ (H_2O)_n, where n = 0–3, and Fig. 2 displays the structures for OH^- (H_2O)_n, where n = 1–4. The figures show the values for key atom-atom separation distances and bond angles, for the QCISD/6-311G(d,p) structure computed with the CBS-APNO model chemistry, along with results from the literature. Table I includes calculated values for ΔE_z, ΔH_z, and ΔG for reactions of the hydronium cation with successive additions of water, along with results from the literature. Table II contains calculated values for ΔE_z, ΔH_z, and ΔG for reactions of the hydroxide anion with successive additions of water, along with results from the literature.
tain the absolute values for G2, G3, CBS-QB3, and CBS-APNO energies for each molecule and cluster reported in this paper, as well as all of the geometries computed with these methods. 82

IV. DISCUSSION
A. Structures

The G2, G3, CBS-QB3, and CBS-APNO methods yield similar structures compared to each other, and are quite similar to previous high level ab initio results. 6,22,26–45 Comparison of the clusters reveals no significant changes in the basic geometry, other than the well-established effect of strengthening the hydrogen bonds upon inclusion of electron correlation. 83,84 For instance, the H9O4+ species has hydrogen-bond distances of 1.610 and 1.633 Å for the Hartree-Fock structures that are used by the CBS-APNO and G2/G3 methods for the frequency calculation in these methods. These hydrogen-bond distances decrease to 1.553 and 1.579 Å for the electron correlated structures that are used for the energy calculations. Similarly, the H7O3+ cluster has Hartree-Fock hydrogen-bond distances of 1.524 and 1.557 Å, which decrease to 1.462 and 1.494 Å at the correlated level of theory. The CBS-QB3 B3LYP structures have hydrogen-bond distances of 1.538 and 1.441 Å for the H9O4+ and H7O3+ clusters, values that are quite close to the CBS-APNO QCISD and G2/G3 MP2 structures. It is well known

TABLE I. Changes in electronic energies, standard enthalpies, and free energies for the successive reactions H+(H2O)n+H2O→H+(H2O)n+1 using model chemistries.

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aMCCM-UT-CCSD//MP2/TZ2P (Ref. 36).
bMCCM-UT-CCSD//MP2/cc-pVTZ (Ref. 36).
cReference 27.
dMP2/6-311+ + G(d,p) (Ref. 29).
eSCF/DZ + p with SAC correction (Ref. 80).
that the H$_5$O$_3^-$ potential energy surface is quite flat, with an asymmetric C$_2$ dimer found at lower levels of theory, but with the C$_2$ structure occurring as the global minima at higher levels of electron correlation.\cite{14,22,24,27,28,30,32,33,46,80,85}

Our results mirror these previously reported results, as the HF results produce an asymmetric H$_2$O$_2^-$ structure while the electron correlated structures from the G2/G3/CBS-APNO calculations, and the B3LYP structure from the CBS-QB3 calculation, produce the C$_2$ geometry. The electron correlated structures agree with prior reports, such as the MP2/cc-pVTZ structures of Kim and Kim, which are quite similar to our QCISD geometries.\cite{36}

The OH$^-$ (H$_2$O)$_n$ structures display a similar pattern of consistency. For instance, the H$_3$O$_2^-$ cluster has hydrogen bond lengths of 1.735 and 1.721 Å for the HF structures, 1.668 and 1.678 Å for the electron correlated structures, and 1.678 Å for the CBS-QB3 structure. The same pattern of shorter hydrogen bonds with electron correlation is found for all of the OH$^-$ (H$_2$O)$_n$ clusters. Previous results at the MP2 level with augmented basis sets display similar geometries, with the covalent O–H bond distances generally slightly longer and the O–H hydrogen bond lengths slightly shorter, than the QCISD and B3LYP structures. This can be attributed to the use of diffuse functions, which should be better for modeling the geometries of anions. The slight changes in geometries appear not to significantly alter the accuracy of the thermochemical results described below. Masamura has shown that the minimum on the OH$^-$ (H$_2$O)$_3$ surface is the H$_2$O$_4^-$ C$_3$ structure displayed in Fig. 2.\cite{42} He has found four low lying minima on the OH$^-$ (H$_2$O)$_4$ potential energy hypersurface. Our structure in Fig. 2 is equivalent to his 3-1(3) structure, which has an $\Delta E$ of 1.8 kcal/mol relative to the symmetric C$_4$ isomer at the MP4 SPC level.

### B. Thermochemistry

Tables I and II were compiled using the absolute values contained in Tables S1 and S2, for the four model chemistries, for each cluster displayed in Figs. 1 and 2. The thermodynamics of cluster formation for each reaction in Tables I and II, for a standard state of 1 atm, are given for each model along with the experimental values.\cite{7,15,17,27,29,36,80}

As Table I reveals, the free energy and enthalpic values (and thus the entropic values as well), are in excellent agreement for reactions of clusters of H$_3$O$^+$ (H$_2$O)$_n$ with an additional water to make each successive H$_3$O$^+$ (H$_2$O)$_n$ cluster. All four model chemistries predict $\Delta G^0$ and $\Delta H^0$ values that are consistent with each other, and with the MCCM-UT-CCSD//MP2/6-31+G(d,p) results of Kim and Kim.\cite{30} The CBS-APNO, G2, and G3 $\Delta G^0$ values for formation of the clusters are consistent with each other and with the MP2/6-311+G(2df,2p)//MP2/6-31+G(d,p) results of Pudzianowski,\cite{29} and the single and double configuration interaction (CI) and symmetry-adapted-cluster (SAC) calculations of Yamabe, Minato, and Hirao\cite{31} for the formation of H$_3$O$^+$ (H$_2$O). The CBS-APNO, G2, and G3 results for $\Delta G^0$ are also within 1–1.5 kcal/mol of the experimental results.\cite{15,17} The CBS-QB3 method predicts $\Delta G^0$ values that

### Table II. Changes in electronic energies, standard enthalpies, and free energies for the successive reactions OH$^-$ (H$_2$O)$_{n-1}$ + H$_2$O $\rightarrow$ OH$^-$ (H$_2$O)$_n$ using model chemistries.

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<th>G3</th>
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<td>−17.9</td>
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$^a$CCSD(T)/aug-cc-pVDZ (Ref. 41).

$^b$MP4/aug-cc-pVDZ (Ref. 41).

$^c$MP2/cc-pVTZ (Ref. 37).
are about 1 kcal/mol higher than the other three methods for the reaction of \( \text{H}_2\text{O}^+(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+(\text{H}_2\text{O})_2 \), and about 1 kcal/mol lower than the other three methods for the reaction of \( \text{H}_2\text{O}^+(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+(\text{H}_2\text{O})_3 \).

Table II shows the thermodynamic values for formation of successive clusters of \( \text{OH}^-(\text{H}_2\text{O})_n \). The computed values for \( \Delta E_c \) are in excellent agreement with the values obtained at the CCSD(T)/aug-cc-pVQZ/MP2/aug-cc-pVDZ level, without corrections for BSSE, as well as with previous results at the MP4/aug-cc-pVQZ and MP2/aug-cc-pVQZ levels of theory. The computed values for \( \Delta H^0 \) are within 2 kcal/mol of the most recent experimental values for the first three reactions, but are 3 kcal/mol more negative for the reaction \( \text{OH}^- (\text{H}_2\text{O})_3 + \text{H}_2\text{O} \rightarrow \text{OH}^- (\text{H}_2\text{O})_4 \). The values computed by CBS-APNO, G2, and G3 are more consistent with experiment, and with each other, relative to the CBS-QB3 values. There is more error between the model chemistry methods and experiment for the \( \text{OH}^- (\text{H}_2\text{O})_n \) system than for the \( \text{H}^+ (\text{H}_2\text{O})_n \) system, which is probably a consequence of the lack of diffuse functions in the basis sets used for the geometry optimizations in these compound methods. In particular, the free energy for the fourth reaction, to form \( \text{H}_2\text{O}_5^- \) from \( \text{H}_2\text{O}_4^- \) (Fig. 2, Table II) and a water, is noticeably out of line with the preceding reaction for the CBS methods. This could be because of an incorrect geometry for \( \text{H}_2\text{O}_5^- \). Pliego and Riveros have determined that the symmetric \( C_4 \) isomer of \( \text{H}_2\text{O}_4^- \) is the lowest free energy structure using MP4/6-311 G(2df,2p)//MP2/6-31 + G(d,p) calculations. The recent spectroscopic determination of the \( \text{OH}^- (\text{H}_2\text{O})_4 \) structure reveals that the \( \text{H}_2\text{O}_5^- \) ion observed in a cold ion beam represents the beginning of the second solvation shell, and is identical to the \( \text{H}_2\text{O}_3^- \) structure that we used in our calculations (Fig. 2). Therefore we conclude that the G2 and G3 methods match better with experiment for calculations of \( \Delta G^0 \) compared to the CBS methods. Neither the \( E_n \) or CBS methods optimize geometries using diffuse functions. The \( G_n \) methods do include explicit correction terms for diffuse functions, so for instance the G2 method has three diffuse function correction terms: \( E[\text{MP4}/6-311 + G(d,p)] - E[\text{MP4}/6-311G(d,p)] \), \( E[\text{MP2}/6-311 + G(2df,p)] - E[\text{MP2}/6-311G(d,p)] \), and \( E[\text{MP2}/6-311 + G(d,p)] - E[\text{MP2}/6-311G(d,p)] \). These corrections for diffuse- \( sp \) functions are combined with similar corrections for higher polarization functions to get the final G2 energy. Our results show that these corrections for the G2 and G3 model chemistries are effective in yielding more accurate thermochemical predictions relative to experiment for the anionic water clusters. The CBS-QB3 method lacks the extensive diffuse function correction terms of the \( G_n \) methods. The CBS-APNO method, which also lacks diffuse function correction terms, uses larger basis sets that should do a better job spanning the relevant orbital space. It is not clear why CBS-APNO performs so poorly for the calculation of \( \Delta G^0 \) for the \( \text{OH}^- (\text{H}_2\text{O})_3 + \text{H}_2\text{O} \rightarrow \text{OH}^- (\text{H}_2\text{O})_4 \) reaction relative to the \( G_n \) methods. We have previously shown that small neutral water clusters are modeled accurately by the G2, G3, and CBS-APNO model chemistries. Deficiencies in the CBS-QB3 DFT model chemistry appear to make it less reliable for obtaining accurate thermochemical values for hydrogen bonded systems such as neutral water clusters, and cationic and anionic water clusters.

C. Implications for the study of atmospheric chemistry

In a recent perspective published in Science, Kulmala has outlined the importance, and the historical study, of particle condensation in the atmosphere. A better understanding of health and climate effects can only be achieved with better knowledge of the pathways through which particles nucleate and grow in the atmosphere. The four main atmospheric nucleation mechanisms have been proposed as (1) homogeneous binary nucleation; (2) homogeneous ternary nucleation; (3) ion-induced nucleation of binary, ternary, or organic vapors; and (4) homogeneous nucleation of iodide species. The G3 method, or other high level MP2 methods highlighted in Tables I and II, combined with experimental information on the concentrations of the key atmospheric gases, would be an excellent model for exploring the thermodynamics of these different processes. The values of \( \Delta G^0 \) for formation of \( \text{H}^+ (\text{H}_2\text{O})_n \) and \( \text{OH}^- (\text{H}_2\text{O})_n \) complexes are so negative that these clusters should form in the atmosphere, as indeed they do. Thus the presence of \( \text{H}_2\text{O}_5^- \) or \( \text{OH}^- \) in the atmosphere assures, at a minimum, ion-induced binary nucleation.

Ion-induced ternary nucleation has been observed in the atmosphere to produce cluster ions composed of \( \text{H}_2\text{O}^+, \text{H}_2\text{O}, \) and \( \text{H}_2\text{SO}_4 \). For typical concentrations of \( \text{H}_2\text{SO}_4 \) in the atmosphere, incorporation of the first \( \text{H}_2\text{SO}_4 \) molecule into a \( \text{H}^+ (\text{H}_2\text{O})_n \) cluster is thermodynamically unfavorable at 270 K. By contrast, when ternary nucleation is induced by the \( \text{H}_2\text{SO}_4 \) anion, \( \text{H}_2\text{SO}_4 \) binds more strongly to \( \text{H}_2\text{SO}_4^- \) than does water. This is one example of many that can be explored by a combination of experimental and theoretical methods. We envision that modeling the stepwise cluster ion growth over a broad range of conditions will allow us to predict the thermodynamically favored routes for ion-induced nucleation. Experimental information on atmospheric conditions, combined with Monte Carlo or molecular dynamics simulations to derive the most likely cluster arrangements, can be followed by accurate MP2-based thermochemical calculations to deduce the most likely pathways for ion-induced nucleation. These predictions, which will stimulate laboratory studies, will then lead to further insights into the nucleation and growth of atmospheric clusters.

V. CONCLUSIONS

The G2, G3, and CBS-APNO model chemistry methods predict accurate values for the changes in enthalpy and free energy of water clusters built around the \( \text{H}_2\text{O}^+ \) and \( \text{OH}^- \) ions. The high accuracy of these methods makes them reliable for calculating energetics for the formation of ionic clusters containing water. In addition these methods can serve to check the accuracy of experimental data, and makes them useful tools for investigating nucleation and growth of clusters in the atmosphere.
ACKNOWLEDGMENTS

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82 See EPAPS Document No. E-JCPSA6-121-312445 for Tables S1 and S2, which contain the geometries and absolute energies in Hartrees for all structures discussed in this paper. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage http://www.aip.org/pubservs/epaps.html or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.


