Structures, energetics, and spectra of hydrated hydroxide anion clusters
Han Myoung Lee, P. Tarkeshwar, and Kwang S. Kim

Citation: The Journal of Chemical Physics 121, 4657 (2004); doi: 10.1063/1.1779566
View online: http://dx.doi.org/10.1063/1.1779566
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/121/10?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Communication: Solute anisotropy effects in hydrated anion and neutral clusters

A theoretical study on structures, energetics, and spectra of Br––nCO2 clusters: Towards bridging the gap between micro-domain and macro-domain

Electron binding motifs in the ( CS 2 ) n – ( n > 4 ) cluster anions

Hydrated hydride anion clusters

Structures, energetics, and spectra of fluoride–water clusters F – (H 2 O) n , n=1–6: Ab initio study
J. Chem. Phys. 110, 9116 (1999); 10.1063/1.478833
Structures, energetics, and spectra of hydrated hydroxide anion clusters

Han Myoung Lee,a) P. Tarkeshwar,b) and Kwang S. Kimc)

National Creative Research Initiative Center for Superfunctional Materials, Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea

(Received 21 May 2004; accepted 15 June 2004)

The structures, energetics, electronic properties, and spectra of hydrated hydroxide anions are studied using density functional and high level ab initio calculations. The overall structures and binding energies are similar to the hydrated anion clusters, in particular, to the hydrated fluoride anion clusters except for the tetrahydrated clusters and hexahydrated clusters. In tetrahydrated system, tricoordinated structures and tetracoordinated structures are compatible, while in pentahydrated systems and hexahydrated systems, tetracoordinated structures are stable. The hexahydrated system is similar in structure to the hydrated chloride cluster. The thermodynamic quantities (enthalpies and free energies) of the clusters are in good agreement with the experimental values. The electronic properties induced by hydration are similar to hydrated chloride anions. The charge-transfer-to-solvent energies of these hydrated-hydroxide anions are discussed, and the predicted ir spectra are used to explain the experimental data in terms of the cluster structures. The low-energy barriers between the conformations along potential energy surfaces are reported.

© 2004 American Institute of Physics. [DOI: 10.1063/1.1779566]

I. INTRODUCTION

A hydroxide anion OH− is one of the most important species as the source of base in chemistry. In particular, the hydroxide anion is an autoionized species in water and a key species in hydrolysis. In this regard, understanding the hydration phenomena of OH− is an important and intriguing subject in various fields including solvation chemistry, electrochemistry, biochemistry, and environmental chemistry.1 Hydrated anion species are biologically very important. Thus, there have been various experimental and theoretical studies on water anion clusters and halide-water clusters, and hydrated molecular anion clusters.2–4 Owing to the complementary nature of experimental and theoretical studies, both approaches have improved our understanding of these hydration structures of anionic species. In this regard, we believe that more accurate theoretical understanding of OH−, which is the most important species among anions, is essential.

Several spectroscopic experiments and ab initio studies of pure OH− ion were carried out,5,6 and experimental hydration energies of the hydroxide anion depending on the number of water molecules are available in terms of enthalpy changes and free energy changes according to the increase of water molecules.7,8 In particular, experimental ir spectra of small hydrated hydroxide anions were recently reported along with interesting theoretical analyses.6 Their spectra have provided the characteristic signatures of H-bonding structures of the clusters. Theoretical studies of small hydrated hydroxide anions were previously investigated using density functional theory (DFT),9 ab initio calculations,10–12 and simulations.13

Hydroxide anion would be considered to be similar to halide anions as a negatively charged species, but the existence of a dangling H atom in OH− distinguishes it from halides. Detailed conformational studies and analyses of the hydroxide anion in comparison with those of halide-water clusters are useful for understanding the hydration chemistry of hydroxide anion. Since the conformational structures corresponding to experimental results are still not clear, we here investigate various structures of hydrated hydroxide anions using DFT and high level ab initio calculations, and analyze their energies, electronic properties, and ir spectra.

II. CALCULATION METHODS

Based on previous studies of water clusters,14,15 anionic water clusters,16,17 and hydrated halides,18,19 we investigated various conformers. These conformers were optimized using DFT calculations employing Lee-Yang-Parr functional (B3LYP) using the 6-311 + + G** (sp) basis set. The B3LYP/6-311++G** (sp) low-energy conformers were further optimized at the Möller-Plesset second order perturbation (MP2) level using the aug-cc-pVDZ+(2s2p2s) and TZ(2df2pd)++ basis sets. Here, (s) and (2s2p2s) are the highly diffuse basis sets.16–19 The TZ(2df2pd)+ + was used to investigate the small halide-water clusters (n = 1–4) and the aug-cc-pVDZ+(2s2p2s) was used to study the halide-water pentamers and hexamers.18,19 For better reliability, coupled cluster calculations with singles and doubles excitations (CCSD) at the MP2 optimized geometries [CCSD//MP2/aug-cc-pVDZ+(2s2p2s) and CCSD//MP2/ TZ(2df2pd)+ + ] were performed with the same basis sets.

a)Electronic mail: abcd@hm@postech.ac.kr
b)Present address: Department of Computational Science, Korea Institute of Advanced Science, 207-43 Cheongnyangni 2-dong, Dongdaemun-gu, Seoul 130-722, Korea. Electronic mail: tara@kias.re.kr
c)Electronic mail: kim@postech.ac.kr

© 2004 American Institute of Physics.
III. RESULTS AND DISCUSSION

A. Structures, energetics, and thermodynamic quantities of hydrated hydroxide ions

Low energy structures of hydrated hydroxide anions are shown in Fig. 1, and the calculated energies at the B3LYP and MP2 levels are listed in Table I. The cluster structures are described based on the shapes of only water clusters excluding the OH\(^-\) group in order to compare with the structures of neutral water clusters, anionic water clusters, and hydrated halide clusters. For the notation of cluster shape, \(R_n\) and \(B\) denotes an \(n\)-membered ring structure; “\(A/D\)” means the role of proton acceptor/donor of the water molecules adjacent to OH\(^-\), “\(B\)” represents the “Booklike” structure, “\(O\)” in 4CsO denotes the “open” structure, “\(d\)” means the dipole-oriented structure, and “\(f\)” means the case with the water having double free hydrogen atoms.

The interaction energies (ZPE-uncorrected binding energies \(-\Delta E_r\)) are reported with the median value of the energies with and without basis set superposition error (BSSE) correction, while half a BSSE is reported as an error bar in Table I. ZPEs and thermal energies based on B3LYP/6-311 + + \(G^{**}(sp)\) frequencies were used at other levels of calculation to obtain ZPE-corrected binding energies \((\Delta E_0)\) from \(\Delta E_r\), and the values of enthalpy \((\Delta H)\) and free energies \((\Delta G)\) at 298 K and 1 atm.

The random phase approximation (RPA) (Ref. 20) calculations at the B3LYP/6-311 + + \(G^{**}\) level and the configuration interaction with single excitation (CIS) calculations at the MP2/TZ(2df/2pd) + + level were carried out to obtain the vertical excitation energies as charge-transfer-to-solvent (CTTS) energies. The RPA-B3LYP calculations using the 6-311 + + \(G^{**}(sp)\) basis set generally give the CTTS energies close to the experimental values.\(^{18,19}\) The OH stretch frequencies were calculated at the B3LYP/6-311 + + \(G^{**}(sp)\) level. The frequency calculations of small clusters were carried out at MP2/aug-cc-pVDZ + + (2s2p2d), MP2/TZ(2df/2pd) + +, and CCSD(T)/TZ (2df/2pd) + + levels. All calculations were carried out using a GAUSSIAN 98 suite of programs and an ACES II code. Most figures were drawn using the Postech Molecular Modeling package.

### Table I. Interaction energies of OH\(^-\)(H\(_2\)O)\(_{1-6}\) a

<table>
<thead>
<tr>
<th>n</th>
<th>Conf.</th>
<th>(-\Delta E_r) BSSE/2</th>
<th>(-\Delta E_0)</th>
<th>(-\Delta H)</th>
<th>(-\Delta G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1+0</td>
<td>27.42±0.43</td>
<td>26.65</td>
<td>27.82</td>
<td>20.87</td>
</tr>
<tr>
<td>2</td>
<td>2+0</td>
<td>50.14±0.94</td>
<td>46.31</td>
<td>47.80</td>
<td>33.60</td>
</tr>
<tr>
<td>3</td>
<td>3+0</td>
<td>60.30±1.26</td>
<td>56.75</td>
<td>57.15</td>
<td>41.88</td>
</tr>
<tr>
<td>4</td>
<td>4+0</td>
<td>73.13±1.58</td>
<td>69.13</td>
<td>70.31</td>
<td>37.55</td>
</tr>
<tr>
<td>5</td>
<td>5+0</td>
<td>82.57±2.14</td>
<td>78.24</td>
<td>79.51</td>
<td>40.56</td>
</tr>
<tr>
<td>6</td>
<td>6+0</td>
<td>91.96±2.82</td>
<td>87.34</td>
<td>88.75</td>
<td>44.00</td>
</tr>
<tr>
<td>7</td>
<td>7+0</td>
<td>101.36±3.58</td>
<td>96.71</td>
<td>98.12</td>
<td>47.53</td>
</tr>
<tr>
<td>8</td>
<td>8+0</td>
<td>110.76±4.31</td>
<td>105.98</td>
<td>107.43</td>
<td>51.06</td>
</tr>
<tr>
<td>9</td>
<td>9+0</td>
<td>120.16±5.11</td>
<td>115.26</td>
<td>116.70</td>
<td>54.63</td>
</tr>
</tbody>
</table>

\(^a\)All the structures have no symmetry except for the cases 4R4(C\(_4\)), 4Cs(C\(_4\)), 4Cs' (C\(_4\)), and 4CsO(C\(_4\)). Interaction energies are reported with the median value of the energies with and without BSSE correction (50% BSSE). The error range (50% BSSE) is given in the values of \(\Delta E_r\). The thermal energies were used with the B3LYP/6-311 + + \(G^{**}(sp)\) values at 298 K and 1 atm. The free energy changes of chiral complexes were corrected for chirality by \(-RT\ln2\) (\(R\), gas constant; \(T\), temperature). \([2+0]\) is fixed structure with 80.9° of O-O-O angle.
most reliable CCSD//MP2/aug-cc-pVDZ+ (2s2p/2s) and CCSD//MP2/TZ(2df/2pd)++ calculations predict that 4R4 is the most stable, while it is almost isoenergetic to 4Cs (Table II). However, at room temperature, the calculations predict that 4CsO is more stable than 4Cs and 4R4, due to the entropy effect (Table I).

As shown in Table II the enthalpy changes for $n = 1–6$ at 298 K and 1 atm are in good agreement with the experimental values. For large clusters the isomeric effect on entropy is significant. Therefore, the free energy changes should take into account the distribution probability according to the relative stability of each configuration. More importantly, the anharmonic correction is critical for large size clusters, and so the free energy values based on harmonic frequency approximation would not be reliable. Therefore, these values above $n = 4$ are not reported. Indeed, $\Delta G$ for $n = 1–3$ are in good agreement with the experimental values, while $\Delta G$ for $n = 4$ is underestimated by more than 3 kcal/mol.

Conformers 1(1+0), 2(2+0), 3(3+0), and 5R4A(4 + 1) of OH$^-$($H_2O)_n$ are very similar to the fluoride-water clusters.\textsuperscript{18,19} The most stable fluoride-water hexamer is $6R4AA(4 + 2)$, while the most stable hydroxide-water hexamer is $Bf$. In tetra-hydrated system, tricoordinated structures and tetracoordinated structures [4Cs(3+1) and 4R4(4 + 1)] are compatible in energy. In penta-hydrated clusters and hexahydrated clusters [4R4A(4 + 1),6Bf(4 + 2)], tetracoordinated conformers are more stable than tricoordinated clusters.

The monohydrated hydroxide has very strong ion-water interaction showing very low energy barrier for proton transfer, while the dihydrated OH$^-$ ion has very small energy difference between linear and near-cyclic structures. The proton transfer process in OH$^-$($H_2O)_1$ has very low potential-energy barrier (1.8 kcal/mol at CCSD(T)/TZ(2df/2pd) + +, 0.05 kcal/mol at MP2/TZ(2df/2pd) + +, and 0.1 kcal/mol at B3LYP/6-311++G** (sp) as in short-strong H-bond.\textsuperscript{24} The potential energy surface of OH$^-$($H_2O)_2$ is

\begin{table}[h]
\centering
\begin{tabular}{cccccc}
\hline
$n$ & Conf. & $-\Delta E_p$ & $-\Delta E_0$ & $-\Delta H$ & $-\Delta G$ & Experiments (298 K) \\
\hline
2 & 2+0 & 45.93\,[46.79] & 42.10\,[42.96] & 43.84\,[44.70] & 29.39\,[30.25] & 44.1\,[42.9] \\
3 & 3+0 & 64.26\,[64.97] & 57.71\,[58.43] & 60.12\,[60.83] & 37.55\,[38.26] & 60.3\,[58.0] \\
4 & 4R4 & 80.74\,[80.99] & 69.88\,[70.12] & 73.52\,[73.76] & 72.3\,[72.2] & 46.0\,[43.5] \\
& 4Cs & 80.04\,[80.55] & 69.29\,[69.80] & 73.26\,[73.77] & 83.8\,[86.3] & 50.3\,[48.7] \\
5 & 5R4A & 94.99 & 80.62 & 85.52 & 95.0\,⋯ & 95.0\,⋯ \\
6 & 6Bf & 108.77 & 91.12 & 97.09 & & \\
\hline
\end{tabular}
\caption{CCSD//MP2/aug-cc-pVDZ+ (2s2p/2s) [CCSD//MP2/TZ(2df/2pd) + +] predicted and experimental interaction energies of OH$^-$($H_2O)_n$.\textsuperscript{a}}
\end{table}

\textsuperscript{a}All estimated interaction energies were corrected with the MP2 half-BSSE correction, since the CCSD and MP2 BSSEs are very similar in the case of small clusters. The experimental data are from Refs. 7 and 8. The thermodynamic interaction energies were estimated using the B3LYP/6-311++G** (sp) thermodynamic quantities at 298.15 K. For $n > 4$, the Gibbs free energies of the experimental structures at 298 K and 1 atm would not correspond to those of the calculated lowest-energy structures. Furthermore, the anharmonic correction in calculating free energies is significant, and so the free energies based on harmonic approximation are not reported here.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{low_energy_structures.png}
\caption{Low-energy structures of OH$^-$($H_2O)_{1–6}$ clusters. Here, the structure in braces [4CsO] was obtained only at the B3LYP level.}
\end{figure}
very flat toward very weak water-water H-bonded conformation (from linear to near-cyclic structure) at the MP2 and CCSD(T) levels of theory. The near-cyclic structure (constrained with the B3LYP bending angle) was obtained to have no imaginary frequency and to be higher in energy by 0.08 and 0.28 kcal/mol at the MP2/aug-cc-pVDZ + (2s2p/2s) and MP2/TZ(2df/2pd) + + levels and by 0.24 kcal/mol at the CCSD(T)/MP2/TZ(2df/2pd) + + level than the minimal-energy linear structure. In the ZPE-corrected energies the near-cyclic structure is higher in energy by 0.45, 0.68, and 0.64 kcal/mol at the above three levels. The calculated and experimental ir spectra for n = 2 – 4 are compared in Fig. 2.

Table II lists the geometrical characteristics (coordinates, H-bond interactions, H-bonding distances, bond angles, and rotational constants). In small hydrated hydroxide anion clusters, even tetracoordination is found to be favorable in spite of its three lone pairs of hydroxide ion. The oxygen-oxygen distances tend to increase with the increase of water molecules, expectedly. The O-H distance of hydroxide ion increases slightly with the increase of water molecules due to the hydration effect.

The conformational changes of OH⁻(H₂O)₃ and OH⁻(H₂O)₄ are interesting at each calculation level. The B3LYP calculation of OH⁻(H₂O)₃ gives no water-water H-bond interaction, while the MP2 calculation has very weak water-water H-bond interactions between water molecules. These conformational changes by very small energy difference result in significant changes in ir frequency shift for the OH stretch modes. The potential energy surfaces and frequency changes of OH stretches according to the conformational change from 4Cs and 4CsO are shown in Fig. 2. At the B3LYP/6-311 + +G** (sp) level, 4CsO is the lower energy conformer. At the MP2/aug-cc-pVDZ + (2s2p/2s) level, 4Cs is the lower-energy conformer based on half-BSSE-corrected ΔE₀(ΔE₀(sp)). With full BSSE correction, both 4Cs and 4CsO are isoenergetic with no potential barrier between the two conformers. However, the MP2 binding energy based on full BSSE correction is underestimated. Therefore, we are inclined to believe that the half-BSSE-corrected MP2 energies are more reliable in this case. The possible conformational change due to the shallow potential surface reveals the ir spectral change due to the water-water H-bond interaction depending on the bending angle. As the temperature increases, the structure would become 4CsO due to the entropy effect. Indeed, the ir spectra of the configurations ranging from 4Cs to 4CsO are similar to the experimental spectra. Unless the temperature of the cluster is near 0 K, the cluster would exist as 4CsO.

**B. Electronic properties of low-energy hydrated hydroxide ions**

The electronic properties, ionization potentials, proton affinities, and excitation energies of low-energy hydrated hydroxide anions are listed in Table III. Among frontier orbitals of hydrated OH⁻ ions, the occupied orbitals mainly comprise of sp³ lone-pair orbitals of OH⁻ ion, while the virtual orbitals, diffuse orbitals. Large proton affinities of hydrated hydroxide ions tend to become stable neutral water molecules by combining with hydronium cations. As the number of water molecules increases, the hydroxide anion is better stabilized, resulting in decreased proton affinity for larger clusters. The ionization potentials of hydrated OH⁻ ions are smaller than those of hydrated fluoride ions, but rather closer to those of chloride-water clusters.

The excitation energies of hydrated hydroxide anions are interesting in view of the charge transfer to solvent (CTTS), as in halide-water clusters.¹⁸,¹⁵ The CTTS energies are close to those of bromide-water clusters. The excited state of hydrated OH⁻ anion can form an excited electron bound to a hydrated OH radical. The CIS/aug-cc-pVDZ + (2s2p/2s)-optimized first singlet excited states are shown in Fig. 3. The OH⁻ anion and OH radical have different
hydrated structures. Hydrated hydroxyl radicals have weak interactions between hydroxyl radical and water molecules. The singlet excited states can be considered as electron-bounded hydrated hydroxyl radicals. The adiabatic electron detachments of hydrated hydroxide ions would also provide hydrated hydroxyl radicals.

C. IR spectra

The IR spectra of the hydrated hydroxide anions are given in Table IV. The ion-water interactions give significantly redshifted OH stretch frequencies for water molecules (Table IV), as in fluoride-water clusters. The shifts of water-water H-bonded OH stretch frequencies are smaller than those of neutral water clusters. The frequencies predicted by B3LYP/6-311+ +G**+(sp); MP2/aug-cc-pVDZ (2s2p2s); MP2/TZ(2df2pd)+++, and CCSD(T)/TZ(2df2pd)+ [which will be denoted simply as B3LYP, MP2/a, MP2/T, CCSD(T), respectively] are scaled by 0.957, 0.956, 0.948, and 0.952, respectively, to match the average value of asymmetric and symmetric stretch frequencies of the H2O monomer (3868, 3870, 3905, and 3888 cm⁻¹, respectively) with the corresponding experimental value (3700 cm⁻¹). Our predicted IR frequencies will be compared with the experimentally characterized IR spectra.  

The harmonic frequency for the H-bonded OH stretch mode of monohydrated hydroxide anion varies significantly, depending on the levels of theory. The values predicted by B3LYP, MP2/a, MP2/T, and CCSD(T) are 1372, 1534, 1143, and 1409 cm⁻¹. We here assume that the CCSD(T) is the most reliable because it is the highest level of theory among the methods employed with the largest basis set. According to the anharmonic correction for the H-bonded OH stretch mode of monohydrated hydroxide anion at the CCSD(T) level, the three lowest vibrational energy levels v₀, v₁, and v₂ are calculated to be 960, 2101, and 2777 cm⁻¹. These values are
smaller than those of monohydrated fluoride.\textsuperscript{4,18} The 2\textsuperscript{−} overtone band (1814 cm\textsuperscript{−1}; transition from 960 to 2777 cm\textsuperscript{−1}) is shown as a thick solid line in Fig. 4. The experimental very weak ir spectra around 3100 and 3180 cm\textsuperscript{−1} would show the overtones of bending modes (~3100 and ~3180 cm\textsuperscript{−1}) from the predicted bending frequencies 1550 and 1590 cm\textsuperscript{−1}.\textsuperscript{6} The main O-H stretch peak of water observed at 3653 cm\textsuperscript{−1} in the experiment is well reproduced for the four levels of theory (3650, 3645, 3659, and 3630 cm\textsuperscript{−1}), respectively. These 2\textsuperscript{−} overtones are much weaker than that of F\textsuperscript{−} (H\textsubscript{2}O\textsubscript{1}) which has very strong ion-water interaction.\textsuperscript{4,18}

The experimental ir spectra of di-hydrated OH\textsuperscript{−} ion [3694 and 3660 cm\textsuperscript{−1}], and a very broad/weak peak at 2700 cm\textsuperscript{−1} (half-width: 150 cm\textsuperscript{−1}), and a possible peak below/around 2400 cm\textsuperscript{−1} are similar to the average of the linear-like conformer and the near-cyclic conformer with constrained geometry, which is only slightly higher in energy than the non-H-bonded linearlike conformer. The B3LYP frequencies for 2\textsuperscript{+} linearlike structure are 3702, 3680, and 2539 cm\textsuperscript{−1}. MP2/a frequencies for 2\textsuperscript{+} (cyclic 2\textsuperscript{+} 0) are 3704 (3678), 3664 \{3661\}, 2519 \{2735\), and 2342 \{2290\} cm\textsuperscript{−1}, respectively; these average values are 3691±13, 3662±2, 2627±108, and 2316±26 cm\textsuperscript{−1}. The experimental ir spectra for the trihydrated hydroxide show a main peak at 3695 cm\textsuperscript{−1} and a very broad/weak band around 2600 cm\textsuperscript{−1} (half-width: 150 cm\textsuperscript{−1}). We also see a possible ambiguous peak around 2900 cm\textsuperscript{−1} (half-width: ~50 cm\textsuperscript{−1}). The conformer 3(3+0) which has weak water-water H-bond interactions at the MP2/a level shows ir spectra (3678~3706, 2987, 2767, 2679 cm\textsuperscript{−1}), while this conformer does not have water-water H-bond interactions at the B3LYP/6-311 + G*\textsuperscript{(*)} level (3704, 2892, 2735, 2733 cm\textsuperscript{−1}). The experimental ir spectra for the tetrahydrated hydroxide show peaks at 3675, 3615, 3489, 3447 cm\textsuperscript{−1} and a very broad/weak band around 2900 cm\textsuperscript{−1} (half-width: 300 cm\textsuperscript{−1}).

![FIG. 4. Scaled B3LYP/6-311 + G*\textsuperscript{(*)} ir spectra of low-energy hydrated OH\textsuperscript{−} ions (scale factor: 0.957). See the text for the overtone effect marked by + and the experimental dangling O-H stretching frequency marked by * for the case of (1+0).](image-url)
MP2/a frequencies for conformer 4Cs are 3682, 3587, 3479, 3403, 3172, 2698, and 2575 cm$^{-1}$. However, as 4Cs changes to 4CsO with minimal energy change (Fig. 2), the frequency at 3200 cm$^{-1}$ (4Cs: 60°) changes to 2800 cm$^{-1}$ (4CsO: 140°). This could give a broad band for 2600–3200 cm$^{-1}$. Although 4R4 is the lowest energy conformer at 0 K, the energy is nearly isoenergetic to 4Cs, and furthermore, as the temperature increases, 4CsO (similar to 4Cs) or more probably the configurations ranging from 4Cs to 4CsO would be favored. The experimental IR spectra for the pentahydrated hydroxide show peaks at 3700, 3648, 3621, 3572, 3532, and 3446 cm$^{-1}$, which are in reasonable agreement with the B3LYP frequencies for 4R4A (3700, 3627, 3619, 3521, 3466, and 3418 cm$^{-1}$). The B3LYP predicted IR O-H stretch frequencies for conformer 6Bf of the hexahydrated hydroxide are 3712, 3678, 3597, 3496, 3476, 3452, 3419, 3371, 3349, 3158, 3017, and 2683 cm$^{-1}$.

IV. CONCLUDING REMARKS

Small hydrated hydroxide anions were investigated for their structures, energetics, electronic properties, and spectra using DFT and ab initio calculations. At low temperatures near 0 K, the lowest-energy conformers are 1(1+0), 2(2+0), 3(3+0), 4R4, 5R4A, and 6Bf, based on the CCSD/Mp2/aug-cc-pVDZ+/(2s2p2s) and CCSD/Mp2/TZ(2df2pd)+ interaction energies. However, 4R4 and 4Cs are very compatible in stability. At high temperatures, 4CsO is more stable than 4R4. The thermodynamic quantities are in good agreement with the experimental data, in particular, ΔH for n = 1–6 and ΔG for n = 1–3 (those for n ≥ 4 would be in good agreement if the anharmonic correction is taken into account). The interactions among solvent water molecules in the primary hydration shell are very weak and flexible. The ion-water binding energy and ionic radius are similar to fluoride ion, but the electronic properties induced by hydration are similar to somewhat larger halide ions. Their CTTS energies are comparable to those of halide-water clusters. The IR spectra of dihydrated and trihydrated ions. Their CTTS energies are comparable to those of halide-water clusters. The ir spectra of dihydrated and trihydrated ions. Their CTTS energies are comparable to those of halide-water clusters. The ir spectra of dihydrated and trihydrated ions. Their CTTS energies are comparable to those of halide-water clusters. The ir spectra of dihydrated and trihydrated ions. Their CTTS energies are comparable to those of halide-water clusters. The ir spectra of dihydrated and trihydrated ions. Their CTTS energies are comparable to those of halide-water clusters.


