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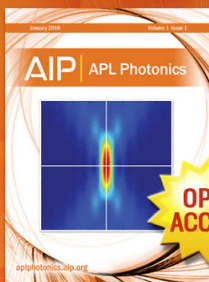
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Hydrated copper and gold monovalent cations: *Ab initio* study

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To understand the hydration phenomena of noble transition metals, we investigated the structures, hydration energies, electronic properties, and spectra of the $\text{Cu}^+(\text{H}_2\text{O})_{1-6}$ and $\text{Au}^+(\text{H}_2\text{O})_{1-6}$ clusters using *ab initio* calculations. The coordination numbers of these clusters are found to be only two, which is highly contrasted to those of $\text{Ag}^+(\text{H}_2\text{O})_n$ (which have the coordination numbers of 3–4) as well as the hydrated alkali metal ions (which have the coordination numbers of ~ 6). For the possible identification of their interesting hydration structures, we predict their IR spectra for the OH stretch modes. © 2005 American Institute of Physics. [DOI: 10.1063/1.1849134]

I. INTRODUCTION

The hydration phenomena are very interesting subjects in solvation chemistry and bio-inorganic chemistry.^{1–3} Hydration chemistry of monovalent systems including alkali metal ions has been intensively studied experimentally^{4–12} and theoretically.^{13–22} Their characteristic coordination reflects the intrinsic properties of ions. It is of importance to investigate the hydration structure of transition metal ions which can be self-synthesized into self-assembled nanostructures upon reduction.²³ Despite very few studies on hydrated heavy metal ions, there are some interesting studies on the hydration energies of transition metal ions.^{19–22} In particular, experimental hydration and solvation energies and coordination numbers (CN) of hydrated copper and silver cation clusters have been reported.^{5–8} The noble monovalent cations (Cu, Ag, and Au) have characteristic electronic properties with high electron affinity (EA). These noble metal monovalent cations have much smaller energy gaps E_{gap} between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in comparison with alkali metal monovalent cations. Their LUMOs are composed of *s* orbitals. The energies of occupied *d* orbitals are close to the *s* orbitals, while those of virtual *p* orbitals are high. The noble metal atoms show considerable solvation energies,²⁴ which would provide important information of the interface between metal (*d* block) and organic materials (*p* block).²⁵

There are a few theoretical studies of small hydrated noble metal ions.^{20–22} In particular, Feller *et al.* reported high level theoretical values for accurate prediction of the binding energy of novel metal clusters with a few water molecules.²⁰ Then, they conjectured that the structure of pentahydrated copper cation would have tricoordination. On the other hand, we have studied monohydrated to hexahydrated silver cations, focusing on the changes of various thermodynamic

quantities, spectra, and structural and coordination chemistry of multiply hydrated systems with respect to the hydration number.¹⁹ This will provide the right answer for the coordination numbers of copper and gold cations by hydration. Thus, for the comparison of these hydrated clusters with the hydrated silver cation clusters, we here investigate monohydrated to hexahydrated copper and gold cations, focusing on the same subjects. We have employed density functional theory (DFT) calculations using the hybrid Becke three-parameter with Lee–Yang–Parr correlation functionals (B3LYP), Møller–Plesset second-order perturbation method (MP2), and coupled cluster method including single, double, and perturbative triple excitations [CCSD(T)]. The coordination structures, binding energies, and IR spectroscopic features are discussed, and compared to those of hydrated silver monocations. The distinctive differences in hydration features between Cu^+/Au^+ and Ag^+ are discussed.

II. CALCULATION METHODS

To obtain the low-lying energy structures, we searched for various hydration structures of $\text{Cu}^+(\text{H}_2\text{O})_{1-6}$ and $\text{Au}^+(\text{H}_2\text{O})_{1-6}$ and calculated their binding energies at the B3LYP/6-31+G* and MP2/6-31+G* levels of theory, as in our previous study of $\text{Ag}^+(\text{H}_2\text{O})_{1-6}$.¹⁹ The relativistic effective core potentials (RECP) including contracted [6*s*5*p*3*d*1*f*] and [7*s*5*p*4*d*1*f*] basis sets were used for Cu^+ and Au^+ ions.^{20,24,26} The relativistic effect is known to be very large in gold.²⁷ The interaction energies for the low-lying energy structures were further investigated using MP2 and CCSD(T)//MP2 calculations with the aug-cc-pVDZ basis set (which will be shortened as aVDZ) for water, the Wachters contracted basis set [8*s*4*p*3*d*] with Hay's diffuse functions [2*p**d*] and one *f* function for Cu^+ ,²⁸ and the RECP potential and the [7*s*5*p*4*d**f*] basis set for Au^+ . This whole basis set will be simply denoted as aVDZ for brevity. The experimental IP/EA of Cu and Au are 7.73/1.23 and 9.23/2.31 eV, respectively.²⁹ The calculated IP/EA of Cu and Au are 8.26/1.31 and 9.23/2.20 eV at the B3LYP/6-31+G* level,

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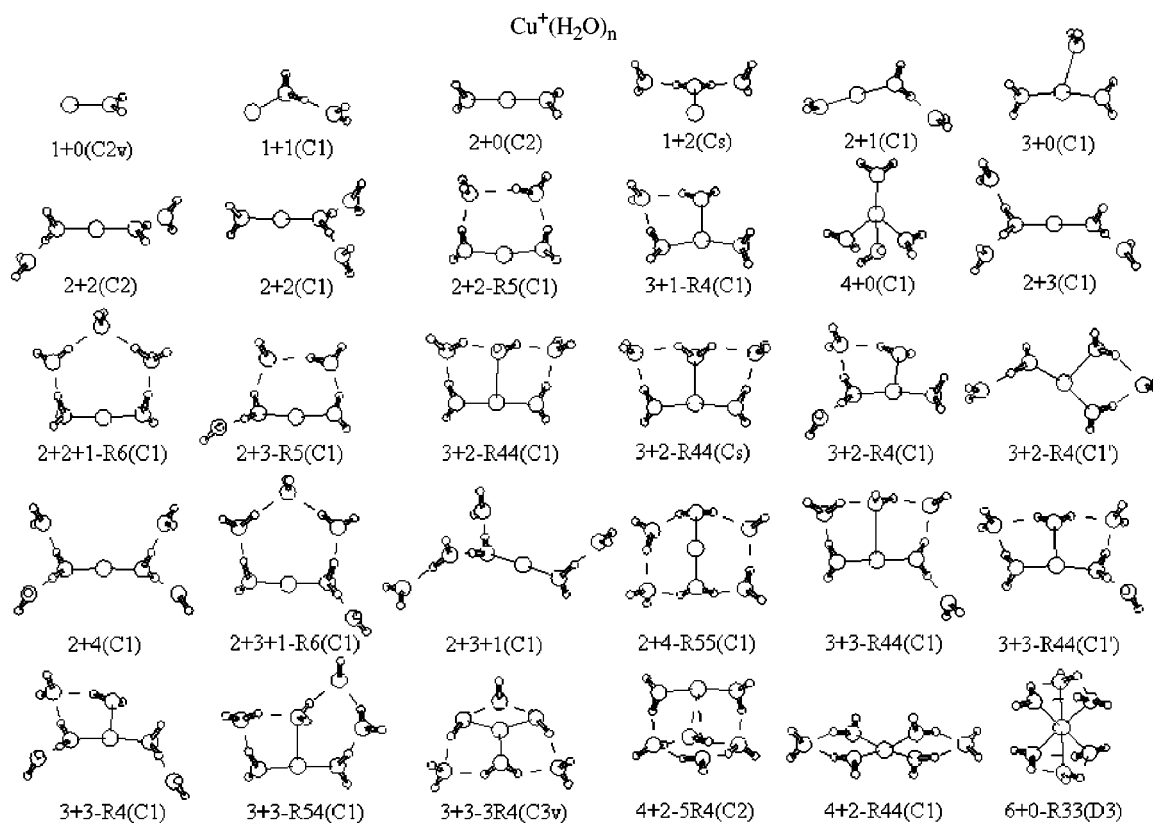


FIG. 1. Structures of monohydrated to hexahydrated copper monocations, $\text{Cu}^+(\text{H}_2\text{O})_n$.

7.47/0.77 and 8.69/1.81 eV at MP2/6-31+G*, 7.15/0.52 and 8.69/1.81 eV at MP2/aVDZ, and 7.16/0.83 and 8.59/1.88 eV at CCSD(T)/aVDZ. The HOMO-LUMO energy gaps of Cu^+ and Au^+ are 4.64 and 4.69 eV at B3LYP/6-31+G*. These energy gaps (i.e., between the splitting the d and s orbitals) are smaller than that of Ag^+ ion (6.49 eV).

The vibrational frequencies were calculated at the B3LYP/6-31+G*, MP2/6-31+G*, and MP2/aVDZ levels. These frequencies were used to obtain the zero point energies (ZPE) and thermal energies (enthalpy change: ΔH , free energy change: ΔG at 298 K and 1 atm). Their infrared (IR) spectra were analyzed using the MP2/aVDZ calculation results. The CCSD(T) thermodynamic quantities were obtained using the MP2/aVDZ thermal energies. The interaction energies (ΔE ; $\Delta E_c/\Delta E_0$: ZPE-uncorrected/corrected energy) are reported with full/half basis set superposition error (BSSE) correction ($\Delta E^B/\Delta E^H$) or without BSSE correction (ΔE^N).³⁰ For the calculations using small basis sets (6-31+G*) the BSSE correction was made using the counterpoise method³¹ since otherwise the binding energy is overestimated, while for the calculations obtained with large basis sets (aVDZ), we did not employ the BSSE correction with which the binding energies are seriously underestimated. For the aVDZ basis set, the MP2 energies without BSSE correction are close to the experimental value. All the calculations were performed using the GAUSSIAN 03 suite of programs.³² Pohang Sci-Tech Molecular Modeling (POSMOL) package was used to draw figures.³³

III. RESULTS AND DISCUSSION

A. Hydration structures

Figure 1 shows monohydrated to hexahydrated structures of copper monocations [$\text{Cu}^+(\text{H}_2\text{O})_{n=1-6}$]. Table I lists the MP2/6-31+G* predicted interaction energies ($\Delta E_e^B/\Delta E_0^B$), enthalpies, and free energies. These energies are reported with full BSSE correction, since these BSSE-corrected energies are close to the experimental energies and the BSSE-uncorrected energies at the MP2/aVDZ and CCSD(T)/aVDZ levels which will be discussed later. Here, n_1 , n_2 and n_3 in cluster $n_1+n_2+n_3$ indicate the numbers of water molecules in the primary, secondary, and tertiary hydration shells, respectively. The symmetry of each cluster is given in parentheses. If the structure is composed of ring(s), it is denoted as $n_1+n_2+n_3-mRn_r$, where mRn_r is m n_r -membered rings. A structure with two n_r -membered and one n'_r -membered rings is simply denoted as $2Rn_rRn'_r$. $Rn_rn_rn_r$ and $Rn_rn_rn_rn_rn_r$ are simply denoted as $3Rn_r$ and $5Rn_r$, respectively. If the structures have the same coordination numbers with same notations, the additional structure is distinguished by a prime. In the cases of $\text{Cu}^+(\text{H}_2\text{O})_n$, the lowest-energy structures in ΔE_0 for $n=1-6$ are 1+0(C_{2v}), 2+0(C_2), 2+1(C_1), 2+2(C_2), 2+3(C_1), and 2+4(C_1), respectively. The second lowest-energy structures for $n=3-6$ are 3+0(C_1), 2+2(C_1), 2+3-R5(C_1) [3+2-R4(C_1')], and 2+3+1(C_1), which are 4.1 [3.7], 1.9 [2.2], 5.1 [4.5], and 2.9[1.1] kcal/mol higher than the lowest ones at the MP2/6-31+G* [B3LYP/6-31+G*] level. The coordination numbers for Cu^+ are 2 for $n \geq 2$. The lowest-energy struc-

TABLE I. MP2/6-31+G* interaction energies, enthalpies, and free energies of $\text{Cu}^+(\text{H}_2\text{O})_n$ ($n=1-6$). IF is the number of imaginary frequencies. CN/HB is the number of coordination/the number of water-water H bonds. Superscripts “N” and “B” denote non-BSSE and full-BSSE corrections, respectively. The free energy changes for low frequencies less than 26 cm^{-1} were corrected using the smallest rotational free energy of the water monomer.

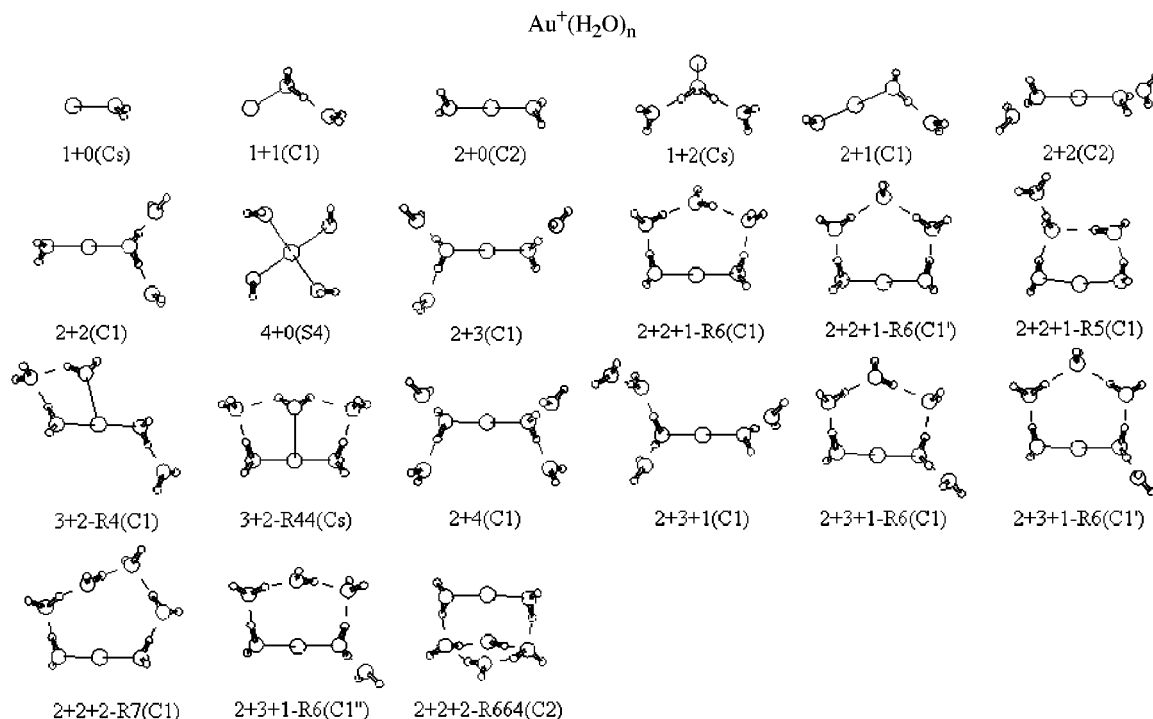
| n | $\text{Cu}^+(\text{H}_2\text{O})_n$ | CN/HB | IF | $-\Delta E_e^N$ | $-\Delta E_e^B$ | $-\Delta E_0^B$ | $-\Delta H_{298}^B$ | $-\Delta G_{298}^B$ |
|-----|-------------------------------------|-------|-----|-----------------|-----------------|-----------------|---------------------|---------------------|
| 1 | 1+0(C_{2v}) | 1/0 | 0 | 43.54 | 38.21 | 36.75 | 37.48 | 31.24 |
| 2 | 1+1(C_1) | 1/1 | 0 | 65.23 | 56.75 | 52.82 | 54.30 | 40.07 |
| | 2+0(C_2) | 2/0 | 0 | 91.89 | 79.06 | 74.70 | 76.26 | 60.13 |
| | 2+0(D_{2d}) | 2/0 | 2 | 91.77 | 78.94 | ... | ... | ... |
| 3 | 1+2(C_s) | 1/2 | 0 | 83.79 | 72.41 | 66.23 | 68.12 | 45.89 |
| | 2+1(C_1) | 2/1 | 0 | 112.32 | 96.40 | 89.74 | 91.88 | 68.08 |
| | 3+0(C_1) | 3/0 | 1 | 107.79 | 91.86 | 85.63 | 88.10 | 62.60 |
| 4 | 2+2(C_2) | 2/2 | 0 | 131.62 | 112.74 | 103.96 | 106.50 | 74.24 |
| | 2+2(C_1) | 2/2 | 0 | 129.62 | 110.81 | 102.11 | 104.48 | 73.17 |
| | 2+2-R5(C_1) | 2/3 | 0 | 127.34 | 108.18 | 97.90 | 101.28 | 66.73 |
| | 3+1-R4(C_1) | 3/2 | 0 | 127.30 | 107.30 | 97.76 | 100.71 | 67.00 |
| | 4+0(C_1) | 4/0 | ... | 120.46 | 100.74 | ... | ... | ... |
| 5 | 2+3(C_1) | 2/3 | 0 | 148.24 | 126.55 | 115.86 | 118.49 | 79.33 |
| | 2+2+1-R6(C_1) | 2/4 | 0 | 146.46 | 123.59 | 110.55 | 114.71 | 70.79 |
| | 2+3-R5(C_1) | 2/4 | 0 | 145.34 | 123.14 | 110.79 | 114.46 | 71.83 |
| | 3+2-R44(C_1) | 3/4 | 0 | 145.73 | 122.24 | 110.10 | 113.72 | 70.77 |
| | 3+2-R44(C_s) | 3/4 | 0 | 145.39 | 122.25 | 109.42 | 113.52 | 69.42 |
| | 3+2-R4(C_1) | 3/3 | 0 | 145.11 | 123.00 | 110.73 | 114.37 | 71.88 |
| | 3+2-R4(C_1') | 3/3 | 0 | 144.56 | 121.83 | 110.40 | 113.56 | 71.97 |
| 6 | 2+4(C_1) | 2/4 | 0 | 163.90 | 139.43 | 126.81 | 129.56 | 82.81 |
| | 2+3+1-R6(C_1) | 2/5 | 0 | 162.67 | 137.07 | 122.29 | 126.44 | 75.35 |
| | 2+3+1(C_1) | 2/4 | 0 | 160.91 | 136.65 | 123.94 | 126.87 | 80.04 |
| | 2+4-R55(C_1) | 2/6 | 0 | 157.62 | 131.93 | 116.48 | 120.99 | 68.26 |
| | 3+3-R44(C_1) | 3/5 | 0 | 162.21 | 136.07 | 121.26 | 125.57 | 73.56 |
| | 3+3-R44(C_1') | 3/5 | 0 | 161.34 | 135.01 | 120.75 | 124.63 | 73.51 |
| | 3+3-R4(C_1) | 3/4 | 0 | 160.13 | 134.78 | 121.33 | 124.69 | 75.42 |
| | 3+3-R54(C_1) | 3/5 | 0 | 161.09 | 134.29 | 118.82 | 123.63 | 70.40 |
| | 3+3-3R4(C_{3v}) | 3/6 | 0 | 154.72 | 128.72 | 114.10 | 118.22 | 66.98 |
| | 4+2-5R4(C_2) | 4/6 | 0 | 163.90 | 136.27 | 119.83 | 125.25 | 69.42 |
| | 4+2-R44(C_1) | 4/4 | 1 | 154.98 | 128.97 | ... | ... | ... |
| | 6+0-R33(D_3) | 6/6 | ... | 147.11 | 121.10 | ... | ... | ... |

tures with coordination number 3 for clusters $n=3-6$ are 3+0(C_1), 3+1-R4(C_1), 3+2-R4(C_1)[3+2-R4(C_1')], and 3+3-R4(C_1), which are 4.1 [3.7], 5.6 [4.9], 5.1 [4.5], and 5.5 [3.6] kcal/mol higher in energy than the lowest-energy structures with the coordination number 2. The structures with the coordination numbers 3, 4, and 6 are higher in energy than that with the coordination number 2 by 4–6, 7–12, and ~ 18 kcal/mol, respectively. Thus, multicoordination of Cu^+ by water molecules is practically difficult.

The structures and energies for $\text{Au}^+(\text{H}_2\text{O})_{n=1-6}$ at the MP2/6-31+G* level are reported in Fig. 2 and Table II. In this case, the energies are reported with 50% BSSE correction because the MP2/6-31G* binding energies with full BSSE correction are much smaller than the MP2/aVDZ and CCSD(T)/aVDZ binding energies, while those with 50% BSSE correction are very close to them. The reason why different levels of BSSE correction were employed for $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Au}^+(\text{H}_2\text{O})_n$ is that the former used full atomic basis sets and the latter used effective core potentials, while the 6-31+G* basis set is somewhat incomplete to describe the systems. However, regardless of the level of BSSE correction, the relative energies between clusters hardly

change, while the absolute binding energies seriously depend on it. Since these low level calculations focus on the relative energies to find the lowest-energy structures, the level of BSSE correction is not an issue here. The lowest-energy structures in ΔE_0 for $\text{Au}^+(\text{H}_2\text{O})_{n=1-6}$ are the same with those of $\text{Cu}^+(\text{H}_2\text{O})_{n=1-6}$, except that $\text{Cu}^+(\text{H}_2\text{O})$ has the C_{2v} symmetry while $\text{Au}^+(\text{H}_2\text{O})$ has C_s symmetry. The lowest-energy structures of $\text{Au}^+(\text{H}_2\text{O})_n$ for $n \geq 2$ have coordination number 2. The most lowest-energy structures for $n=4-6$ {2+2(C_2), 2+3(C_1), and 2+4(C_1)} are lower than the second lowest-energy structures {2+2(C_1), 2+2+1+R6(C_1), and 2+3+1(C_1)} by 1.6 [1.7], 4.9 [4.5], and 3.4 [1.1] kcal/mol (in ΔE_0) at the MP2/6-31+G* [B3LYP/6-31+G*] level. For $\text{Au}^+(\text{H}_2\text{O})_5$, the case with coordination number 2 is 7.4 kcal/mol lower than that with coordination number 3. This energy difference is much greater than that for $\text{Cu}^+(\text{H}_2\text{O})_5$ (5.1 kcal/mol). Thus, in the case of $\text{Au}^+(\text{H}_2\text{O})_n$, the tricoordination is hardly possible.

The LUMO of Cu^+ , Ag^+ , and Au^+ are s orbitals, while their HOMO are fivefold degenerate d orbitals. The LUMO energies of Cu^+ (–11.09 eV) and Au^+ (–12.11 eV) ions are

FIG. 2. Structures of monohydrated to hexahydrated gold monocations, $\text{Au}^+(\text{H}_2\text{O})_n$.

lower than that of Ag^+ ion (-10.68 eV). The HOMO energies of Cu^+ (-15.73 eV) and Au^+ (-16.80 eV) are higher than that of Ag^+ (-17.17 eV). Therefore, the s - d or LUMO-HOMO energy gaps E_{gap} of Cu^+ (4.64 eV) and Au^+ (4.69 eV) are much smaller than that of Ag^+ (6.49 eV). Then, the s -orbital characteristics of Cu^+ and Au^+ ions are more included in the hydrated structure in comparison with Ag^+ -water complexes.¹⁹ Therefore, in the copper and gold-

water cations the dihydrated structures show better stabilities, while in the cases of silver-water cations, the trihydrated and tetrahydrated systems have better stabilities than the dihydrated systems at high *ab initio* calculation levels. Namely, all the coordination numbers for hydrated Cu^+ and Au^+ are 2, while the coordination numbers for hydrated Ag^+ are 3–4.³⁴ The lowest-energy structures of $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Au}^+(\text{H}_2\text{O})_n$ at 0 K are the same with those at room temperature.

TABLE II. MP2/6-31+G* interaction energies, enthalpies, and free energies of $\text{Au}^+(\text{H}_2\text{O})_n$ ($n=1-6$). See the caption of Table I. Superscript "H" denotes 50%-BSSE correction.

| N | $\text{Au}^+(\text{H}_2\text{O})_n$ | CN/HB | IF | $-\Delta E_c^N$ | $-\Delta E_c^H$ | $-\Delta E_0^H$ | $-\Delta H_{298}^H$ | $-\Delta G_{298}^H$ |
|-----|-------------------------------------|-------|----|-----------------|-----------------|-----------------|---------------------|---------------------|
| 1 | 1+0(C_s) | 1/0 | 0 | 38.96 | 35.73 | 34.04 | 34.98 | 28.59 |
| 2 | 1+1(C_1) | 1/1 | 0 | 61.06 | 56.05 | 51.93 | 53.59 | 38.83 |
| | 2+0(C_2) | 2/0 | 0 | 85.68 | 78.92 | 74.14 | 75.92 | 59.37 |
| | 2+0(D_{2d}) | 2/0 | 2 | 84.39 | 77.68 | ... | ... | ... |
| 3 | 1+2(C_s) | 1/2 | 0 | 80.45 | 73.80 | 67.61 | 69.55 | 46.98 |
| | 2+1(C_1) | 2/1 | 0 | 106.85 | 98.44 | 91.55 | 93.80 | 69.76 |
| 4 | 2+2(C_2) | 2/2 | 0 | 126.74 | 116.73 | 107.67 | 110.36 | 78.12 |
| | 2+2(C_1) | 2/2 | 0 | 125.04 | 115.03 | 106.10 | 108.56 | 76.83 |
| | 4+0(S_4) | 4/0 | 4 | 104.98 | 95.15 | ... | ... | ... |
| 5 | 2+3(C_1) | 2/3 | 0 | 144.27 | 132.71 | 121.74 | 124.52 | 84.52 |
| | 2+2+1-R6(C_1) | 2/4 | 0 | 142.06 | 130.02 | 116.87 | 121.08 | 76.89 |
| | 2+2+1-R6(C_1') | 2/4 | 0 | 140.45 | 128.33 | 115.58 | 119.64 | 75.60 |
| | 2+2+1-R5(C_1) | 2/4 | 0 | 137.95 | 126.05 | 113.35 | 117.28 | 73.89 |
| | 3+2-R4(C_1) | 3/3 | 0 | 137.19 | 125.48 | 114.32 | 117.33 | 76.27 |
| 6 | 3+2-R44(C_s) | 3/4 | 0 | 137.25 | 125.18 | 113.17 | 116.70 | 74.20 |
| | 2+4(C_1) | 2/4 | 0 | 160.64 | 147.58 | 134.60 | 137.64 | 89.31 |
| | 2+3+1(C_1) | 2/4 | 0 | 157.30 | 144.38 | 131.21 | 134.41 | 86.29 |
| | 2+3+1-R6(C_1) | 2/5 | 0 | 159.08 | 145.54 | 130.64 | 134.84 | 83.29 |
| | 2+3+1-R6(C_1') | 2/5 | 0 | 158.53 | 144.85 | 129.94 | 134.29 | 82.21 |
| | 2+2+2-R7(C_1) | 2/5 | 0 | 157.31 | 143.51 | 128.11 | 132.90 | 79.93 |
| | 2+3+1-R6(C_1'') | 2/5 | 0 | 158.34 | 144.57 | 129.71 | 134.06 | 81.72 |
| | 2+2+2-R644(C_2) | 2/6 | 0 | 159.84 | 145.23 | 128.67 | 134.16 | 77.98 |

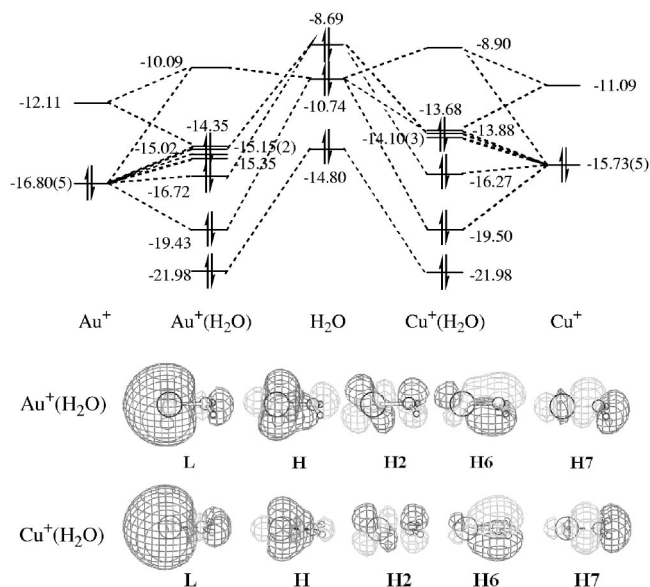


FIG. 3. B3LYP/6-31+G* orbital interaction diagram of $\text{Au}^+(\text{H}_2\text{O})_n$ and $\text{Cu}^+(\text{H}_2\text{O})_n$ complexes. Orbital energies are in eV, and their degeneracies are in parentheses. *L* and *H* denote the LUMO and HOMO, and H_n is the n th HOMO.

In Fig. 3, the stronger *s*- and *d*-orbital hybridization appears in the orbital interactions of Au^+ -water and Cu^+ -water complexes due to their smaller E_{gap} , in comparison with the Ag^+ -water complex. In the case of the monohydrated cation systems, $\text{Cu}^+(\text{H}_2\text{O})$ has charge-dipole ($q-\mu$) interaction with C_{2v} symmetry, while $\text{Au}^+(\text{H}_2\text{O})$ shows the interaction between charge and “lone-pair electrons” with C_s -bent structure. For $\text{Au}^+(\text{H}_2\text{O})$, the C_s symmetry induces more stabilized orbital interaction due to the effective orientations of *d* orbitals and lone-pair electrons. The noble gold atom has large electronegativity in comparison with copper and silver atoms. The LUMO energy of Au^+ is lower than that of Cu^+ . The gold cation is a stronger electron acceptor. Thus, the

gold cation tends to attract electron clouds from water molecules (i.e., strong charge transfer from the gold cation to water molecules), and so the charge of the gold cation tends to be much smaller than 1. The charge transfer from the gold cation to water is much stronger than that from the copper cation. The LUMO energies of copper and gold cations are lower than that of silver cation, and in the hydrated systems the charge transfers from gold and copper cations to water are much greater than that from the silver cation.

For more accurate results of $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Au}^+(\text{H}_2\text{O})_n$ we further optimized the MP2/6-31+G* predicted lowest-energy conformers using the MP2/aVDZ calculations, and also carried out CCSD(T)/aVDZ//MP2/aVDZ calculations. The interaction energies and their thermodynamic quantities including the corresponding experimental data are listed in Table III. In this case, the BSSE correction was not done to reproduce realistic binding energies because otherwise the binding energies are underestimated compared with the experimental data. The thermodynamic quantities were obtained using MP2/aVDZ frequency calculations. The MP2/aVDZ ZPE-corrected binding energies $-\Delta E_0$ of $\text{Cu}^+(\text{H}_2\text{O})_n$ for $n=1-6$ are 36.2, 73.5, 89.1, 103.4, 116.0, 127.5 kcal/mol, those of $\text{Au}^+(\text{H}_2\text{O})_n$ are 36.3, 79.9, 97.3, 113.3, 127.1, and 139.8 kcal/mol, and those of $\text{Ag}^+(\text{H}_2\text{O})_n$ are 29.7, 58.4, 74.5, 88.4, 100.2, and 113.3 kcal/mol.¹⁹ At room temperature and 1 atm, the MP2/aVDZ free energies $-\Delta G_{298}$ of $\text{Cu}^+(\text{H}_2\text{O})_n$ for $n=1-6$ are 30.6, 59.3, 67.8, 74.2, 79.4, and 84.0 kcal/mol, those of $\text{Au}^+(\text{H}_2\text{O})_n$ are 30.8, 65.1, 75.4, 83.7, 90.0, and 94.7 kcal/mol, and those of $\text{Ag}^+(\text{H}_2\text{O})_n$ are 24.2, 46.1, 55.4, 60.3, 64.7, and 69.7 kcal/mol. The MP2/aVDZ enthalpies $-\Delta H_{298}$ of $\text{Cu}^+(\text{H}_2\text{O})_n$ are 37.0, 74.9, 91.1, 106.3, 118.6, and 130.1 kcal/mol for $n=1-6$, in good agreement with the experimental values (35.0, 74.0, 91.0, 106.0, and 120.0 kcal/mol for $n=1-5$,^{5,6} those of $\text{Au}^+(\text{H}_2\text{O})_{n=1-6}$ are 37.3, 81.7, 99.6, 116.1, 130.0, and 142.9 kcal/mol, and those of $\text{Ag}^+(\text{H}_2\text{O})_{n=1-6}$ are 30.4, 59.3,

TABLE III. MP2[CCSD(T)]/aVDZ interaction energies of $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Au}^+(\text{H}_2\text{O})_n$ ($n=1-6$). The experimental enthalpies are evaluated from the successive enthalpies in Ref. 6 (Magneral *et al.* for $n=1-4$) and Ref. 5 (for $n=5$). To show the realistic values close to the experimental enthalpies, the energies obtained with the large aVDZ basis set are reported without BSSE corrections in contrast to the cases obtained with small basis sets for which the BSSE correction is included. The CCSD(T) complete basis set limits (Ref. 19) of $-\Delta H_{298}$ for $\text{Cu}^+(\text{H}_2\text{O})_1$ and $\text{Au}^+(\text{H}_2\text{O})_1$ are 36.5 and 39.3 kcal/mol, respectively.

| <i>n</i> | $\text{Cu}^+(\text{H}_2\text{O})_n$ | $-\Delta E_c$ | $-\Delta E_0$ | $-\Delta H_{298}$ | $-\Delta G_{298}$ | $-\Delta H_{298}^{\text{expt}}$ |
|----------|-------------------------------------|----------------|----------------|-------------------|-------------------|---------------------------------|
| 1 | 1+0(C_{2v}) | 37.69[36.90] | 36.20[35.42] | 36.95[36.17] | 30.57[29.79] | 35.0 |
| 2 | 2+0(C_2) | 77.56[74.85] | 73.54[70.82] | 74.90[72.18] | 59.31[56.59] | 74.0 |
| 3 | 2+1(C_1) | 95.36[92.05] | 89.12[85.81] | 91.09[87.78] | 67.76[64.45] | 91.0 |
| 4 | 2+2(C_2) | 112.15[108.36] | 103.79[100.00] | 106.25[102.46] | 74.19[70.40] | 106.0 |
| 5 | 2+3(C_1) | 126.14[122.07] | 115.97[111.90] | 118.55[114.48] | 79.40[75.33] | 120.0 |
| 6 | 2+4(C_1) | 139.35[134.99] | 127.53[123.17] | 130.09[125.74] | 84.04[79.69] | |
| <i>n</i> | $\text{Au}^+(\text{H}_2\text{O})_n$ | $-\Delta E_c$ | $-\Delta E_0$ | $-\Delta H_{298}$ | $-\Delta G_{298}$ | |
| 1 | 1+0(C_s) | 38.02[36.95] | 36.30[35.23] | 37.27[36.20] | 30.81[29.74] | ... |
| 2 | 2+0(C_2) | 84.64[80.85] | 79.94[76.16] | 81.72[77.94] | 65.12[61.34] | ... |
| 3 | 2+1(C_1) | 104.02[99.62] | 97.31[92.92] | 99.64[95.24] | 75.35[70.96] | ... |
| 4 | 2+2(C_2) | 122.02[117.18] | 113.26[108.41] | 116.08[111.23] | 83.72[78.60] | ... |
| 5 | 2+3(C_1) | 137.63[132.42] | 127.11[121.90] | 130.00[124.79] | 90.00[84.49] | ... |
| 6 | 2+4(C_1) | 152.21[146.78] | 139.78[134.36] | 142.86[137.44] | 94.67[88.85] | ... |

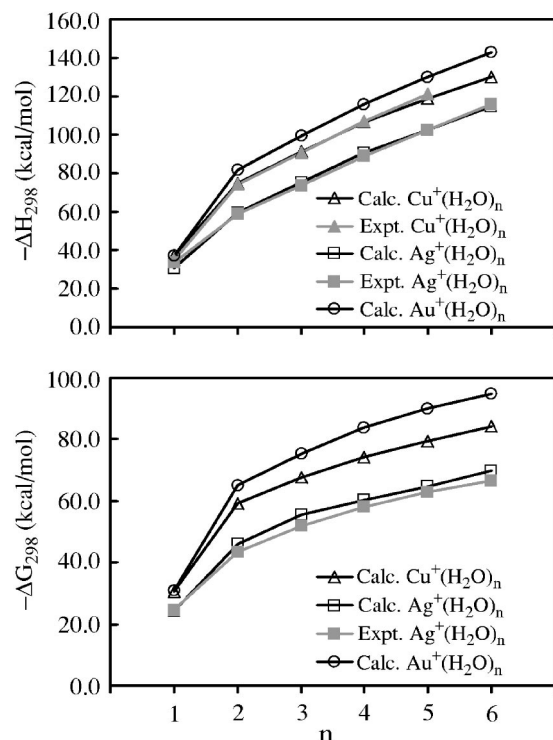


FIG. 4. MP2/aVDZ-estimated and experimental hydration enthalpy changes of $\text{Cu}^+(\text{H}_2\text{O})_n$, $\text{Ag}^+(\text{H}_2\text{O})_n$, and $\text{Au}^+(\text{H}_2\text{O})_n$.

75.5, 90.3, 102.6, and 114.9 kcal/mol, in good agreement with the experimental values (33.3, 58.7, 73.7, 88.6, 102.3, and 115.6 kcal/mol).^{5,19} Thus, $\text{Ag}^+(\text{H}_2\text{O})_n$ have smaller binding energies than $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Au}^+(\text{H}_2\text{O})_n$. The enthalpies of $\text{Cu}^+(\text{H}_2\text{O})_n$, $\text{Au}^+(\text{H}_2\text{O})_n$, and $\text{Ag}^+(\text{H}_2\text{O})_n$ are in good agreement with the experimental values, while the CCSD(T)/aVDZ//MP2/aVDZ enthalpies are underestimated due to the incompleteness of the aVDZ basis set at this level. Therefore, we discuss the energetics based on the MP2/aVDZ results.

The di-coordinated interactions in Cu^+ -water and

Au^+ -water clusters are strong due to their large charge-transfer effect. In particular, the first and second hydration energies for Cu^+ (in MP2/aVDZ ZPE-corrected binding energy) are 36.20 and 37.34 kcal/mol, respectively, and those for Au^+ are 36.30 and 43.64 kcal/mol, respectively. Thus, the second hydration energy is larger than the first hydration energy, as already demonstrated by experiments.⁶ Since the unoccupied s orbital of Au^+ is much lower than that of Cu^+ , a smaller s - d orbital energy difference for Au^+ than for Cu^+ makes this interesting phenomenon more striking. Compared with Ag^+ , the s - d orbital energy difference for Au^+ (Cu^+) is small. The LUMO of Au^+ (Cu^+) and the HOMO of water are close to each other in comparison with those of Ag^+ . Thus, the interaction energies of Au^+ -water and Cu^+ -water clusters show larger interaction energies (i.e., due to the small E_{gap} and low LUMO energies of Au^+ and Cu^+). In particular, Au^+ -water clusters have large interaction energies by strong charge transfer due to the strong electronegativity and large relativistic effect. Overall, both $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Au}^+(\text{H}_2\text{O})_n$ are similar to each other in many respects, while they behave differently from $\text{Ag}^+(\text{H}_2\text{O})_n$, as shown in Fig. 4.

B. Geometrical and electronic properties

In hydration chemistry of ions, the distances between the ion and the oxygen atoms of primary water molecules are important information. These interesting geometrical parameters including rotational constants obtained at the MP2/aVDZ level are reported in Table IV. The natural bond orbital (NBO) charges of hydrated noble metal cations are also listed in the table. The charge transfers in Au^+ and Cu^+ systems are considerably large compared with those of alkali metal cations. Especially, the gold cation is much less positive because of its strong charge-transfer effect. The gold atom has larger EA, i.e., stronger electronegativity than the Cu atom (Table IV), while the hydration effect strongly decreases the EAs of noble metal cations. Au^+ has strong electron-accepting property, as can be noted from the change

TABLE IV. MP2/aVDZ geometrical parameters and electronic properties of $\text{Cu}^+(\text{H}_2\text{O})_n$ and $\text{Au}^+(\text{H}_2\text{O})_n$ ($n=1-6$). Distances (in angstrom) and angles (in degree) are the average values. $r(\text{M}^+-\text{O})$ is the average distance between the metal cation and the oxygen atoms of the primary water molecule. $\angle(\text{HOH})$ of the water monomer is 103.9°. A , B , and C are rotational constants in GHz. $q_{\text{NBO}}^{\text{M}^+}$ is the natural bond orbital charge of noble metal cation. α is the polarizability in a.u. and EA_v is the vertical electron affinity in eV. The α 's of H_2O , Cu^+ , and Au^+ are 16.13, 8.60, and 16.46 a.u., respectively. EA_v s of Cu^+ and Au^+ are 7.15 and 8.69 eV, respectively.

| n | $\text{Cu}^+(\text{H}_2\text{O})_n$ | $r(\text{M}^+-\text{O})$ | $r(\text{O}-\text{O})$ | $\angle(\text{OM}^+\text{O})$ | $\angle(\text{HOH})$ | A | B | C | $q_{\text{NBO}}^{\text{M}^+}$ | α | EA_v |
|-----|-------------------------------------|--------------------------|------------------------|-------------------------------|----------------------|--------|------|------|-------------------------------|----------|---------------|
| 1 | 1+0(C_{2v}) | 1.950 | ... | ... | 106.8 | 414.43 | 8.80 | 8.62 | 0.98 | 26.72 | 5.62 |
| 2 | 2+0(C_2) | 1.898 | ... | 178.0 | 107.0 | 195.59 | 3.60 | 3.60 | 0.86 | 46.27 | 3.83 |
| 3 | 2+1(C_1) | 1.883 | 2.613 | 177.7 | 106.9 | 14.46 | 1.44 | 1.33 | 0.84 | 65.38 | 3.35 |
| 4 | 2+2(C_2) | 1.871 | 2.628 | 177.9 | 106.9 | 4.53 | 0.86 | 0.75 | 0.83 | 80.14 | 2.85 |
| 5 | 2+3(C_1) | 1.864 | 2.665 | 177.9 | 106.7 | 2.09 | 0.65 | 0.54 | 0.81 | 98.36 | 2.54 |
| 6 | 2+4(C_1) | 1.856 | 2.689 | 178.1 | 106.4 | 1.31 | 0.47 | 0.44 | 0.80 | 116.65 | 2.28 |
| n | $\text{Au}^+(\text{H}_2\text{O})_n$ | $r(\text{M}^+-\text{O})$ | $r(\text{O}-\text{O})$ | $\angle(\text{OM}^+\text{O})$ | $\angle(\text{HOH})$ | A | B | C | $q_{\text{NBO}}^{\text{M}^+}$ | α | EA_v |
| 1 | 1+0(C_s) | 2.133 | ... | ... | 106.3 | 357.37 | 6.36 | 6.28 | 0.93 | 38.16 | 7.07 |
| 2 | 2+0(C_2) | 2.053 | ... | 177.2 | 106.5 | 171.31 | 3.13 | 3.13 | 0.71 | 59.50 | 4.42 |
| 3 | 2+1(C_1) | 2.041 | 2.585 | 177.2 | 106.6 | 11.66 | 1.32 | 1.20 | 0.68 | 78.29 | 3.76 |
| 4 | 2+2(C_2) | 2.030 | 2.605 | 177.9 | 106.4 | 2.94 | 0.92 | 0.71 | 0.66 | 96.62 | 3.12 |
| 5 | 2+3(C_1) | 2.024 | 2.638 | 177.8 | 106.0 | 2.31 | 0.60 | 0.52 | 0.64 | 114.66 | 2.74 |
| 6 | 2+4(C_1) | 2.019 | 2.663 | 178.3 | 105.8 | 1.32 | 0.48 | 0.43 | 0.62 | 134.37 | 2.40 |

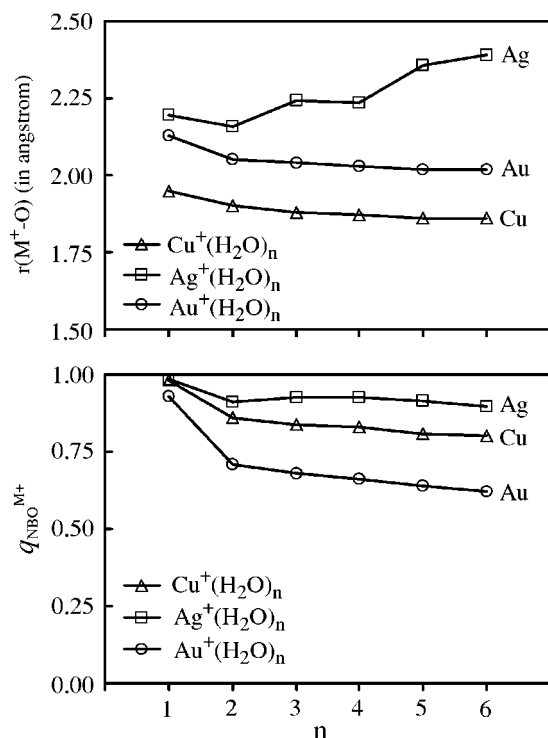


FIG. 5. MP2/aVDZ M^+-O distances and NBO charges of metal ions M^+ for $Cu^+(H_2O)_n$, $Ag^+(H_2O)_n$ and $Au^+(H_2O)_n$.

of charge of Au^+ in $Au^+(H_2O)_n$ (from 0.93 a.u. for $n=1$ to 0.71 a.u. for $n=2$ to 0.62 a.u. for $n=6$ in Table IV) which is compared with the change of charge of Cu^+ in $Cu^+(H_2O)_n$ (from 0.98 a.u. for $n=1$ to 0.86 a.u. for $n=2$ to 0.80 a.u. for $n=6$).

The unique hydration properties of Cu^+ , Ag^+ , and Au^+ would be understood from their ion-water distances as shown in Fig. 5. For the monohydrated cations, the r_{Cu^+-O} is 1.95 Å and r_{Au^+-O} is 2.13 Å, while r_{Ag^+-O} is 2.20 Å. The r_{M^+-O} in $Cu^+(H_2O)_n$ for $n=1-6$ are 1.95, 1.90, 1.88, 1.87, 1.86, 1.86 Å; those in $Au^+(H_2O)_n$ are 2.13, 2.05, 2.04, 2.03, 2.02, 2.02 Å; those in $Ag^+(H_2O)_n$ with di-coordination are 2.20, 2.16, 2.14, 2.12, 2.10, 2.09 Å. The metal-oxygen distances [$r(M^+-O)$] decrease with the increase of water molecules due to the considerable electronegativities of Cu, Ag, and Au atoms and the charge transfer from the metal to water molecules. This is highly contrasted with the cases of hydrated alkali metal ions where the metal-oxygen distances increase with the increase of water molecules. The decreased lengths of $Cu^+-O/Ag^+-O/Au^+-O$ distances for $n=2-6$ with di-coordination with respect to that of monohydrated complex are 0.05/0.04/0.08, 0.07/0.08/0.09, 0.08/0.08/0.10, 0.09/0.10/0.11, and 0.09/0.10/0.11 Å. On the other hand, the oxygen-oxygen distances [$r(O-O)$] between H-bonded water molecules increase with increasing number of water molecules, while the bond angles of hydrating water molecules are little changed.

C. IR spectra

Generally, the IR spectra for OH stretch frequencies of aqueous clusters show the characteristic features of hydrated

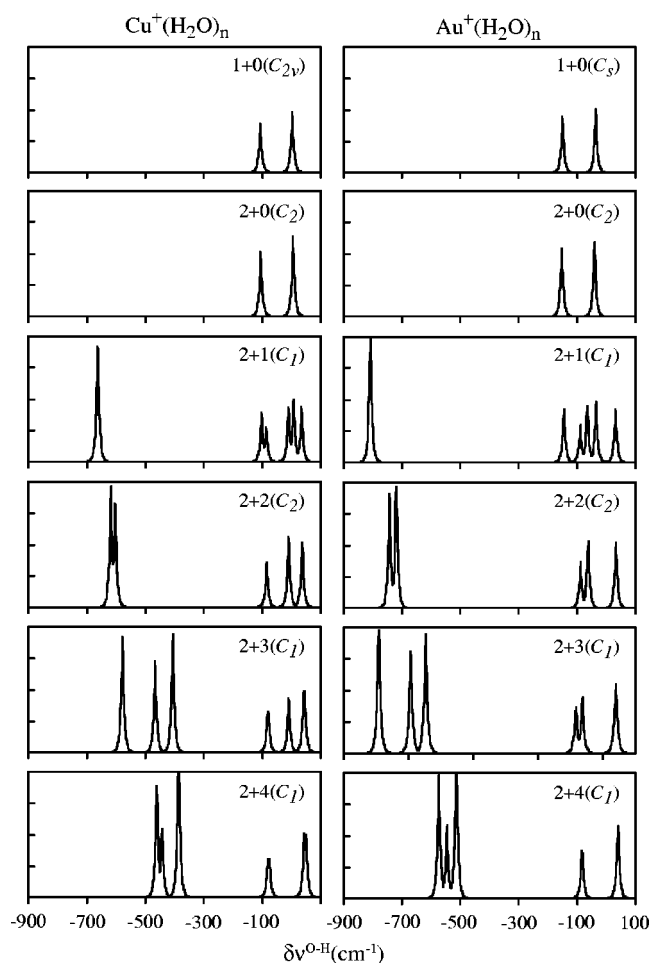


FIG. 6. MP2/aVDZ IR spectral shifts for the OH stretch frequencies of $Cu^+(H_2O)_n$ and $Au^+(H_2O)_n$ with respect to the average value of asymmetric and symmetric OH stretching frequencies of the water monomer.

systems. Figure 6 represents the IR spectra of hydrated copper and gold monocations. The shifts of OH stretching frequencies of aqueous clusters with respect to those of water monomer have often been used to identify the ion-water and H-bond interactions. The reference value for the shifts was chosen as the average value (~ 3700 cm^{-1}) of the experimental symmetric and antisymmetric frequencies of the water monomer.³⁵ Their MP2/aVDZ characteristic frequencies are listed in Table V, where the frequencies are scaled by 0.96 in order to reproduce realistic experimental values.

The OH stretch frequencies of $Cu^+(H_2O)[1+0(C_{2v})]$ are 3703 and 3598 cm^{-1} , and those of $Au^+(H_2O)$ are 3666 and 3557 cm^{-1} . The dihydrated systems show similar frequencies to the monohydrated systems. In the cases of $Cu^+(H_2O)_n$ and $Au^+(H_2O)_n$ for $n \geq 3$, the highest frequencies are blueshifted with the increasing number of n (Table V). This is due to the enhanced metal-water interactions by the enhanced charge transfer from the metals to the relayed H-bonded water, as can be noted from the increasing metal-water frequencies. On the other hand, the OH stretch frequencies of the solely H-bonded terminal water are redshifted. In the case of trihydrated systems, the OH stretch frequency redshifts of the solely H-bonded terminal water in $Cu^+(H_2O)_3$ and

TABLE V. MP2/aVDZ frequencies (cm^{-1}) and the IR intensities in subscripts (10 km/mol). All frequencies are scaled by 0.96. The scaled MP2/aVDZ frequencies of the water monomer are ν_3 : 3764 (7) b_2 ; 3636 (0) a_1 , and ν_2 : 1549 (7) a_1 .

| $\text{Cu}^+(\text{H}_2\text{O})_n$ | 1+0(C_{2v}) | 2+0(C_2) | 2+1(C_1) | 2+2(C_2) | 2+3(C_1) | 2+4(C_1) |
|-------------------------------------|-----------------|--------------|--------------|--------------|--------------|--------------|
| ν_3 | 3703 (25) b_2 | 3705 (24) | 3733 (15) | 3735 (12) | 3743 (15) | 3747 (17) |
| | | 3705 (23) | 3707 (22) | 3735 (17) | 3741 (11) | 3747 (10) |
| | | | 3690 (18) | 3690 (21) | 3739 (14) | 3741 (8) |
| | | | | 3691 (13) | 3691 (16) | 3741 (16) |
| | | | | | 3312 (163) | 3332 (145) |
| | | | | | 3330 (142) | |
| ν_1 | 3598 (12) a_1 | 3602 (0) | 3617 (4) | 3619 (6) | 3625 (3) | 3628 (2) |
| | | 3600 (25) | 3603 (12) | 3619 (2) | 3624 (3) | 3628 (4) |
| | | | 3066 (165) | 3124 (122) | 3622 (4) | 3623 (2) |
| | | | | 3109 (181) | 3254 (70) | 3623 (4) |
| | | | | | 3147 (156) | 3277 (34) |
| | | | | | 3259 (147) | |
| ν_2 | 1577 (8) a_1 | 1572 (16) | 1597 (2) | 1596 (3) | 1597 (0) | 1597 (3) |
| | | 1572 (1) | 1571 (9) | 1596 (0) | 1593 (2) | 1596 (0) |
| | | | 1547 (8) | 1549 (3) | 1559 (5) | 1558 (2) |
| | | | | 1548 (15) | 1549 (9) | 1558 (10) |
| | | | | | 1545 (9) | 1551 (10) |
| | | | | | 1551 (7) | |
| $\nu_{\text{M-W}}^{\text{st}}$ | 383 (1) a_1 | 488 (1) | 523 (1) | 539 (1) | 555 (1) | 569 (1) |
| | | 365 (0) | 395 (0) | 432 (1) | 441 (0) | 462 (0) |
| $\text{Au}^+(\text{H}_2\text{O})_n$ | 1+0(C_s) | 2+0(C_2) | 2+1(C_1) | 2+2(C_2) | 2+3(C_1) | 2+4(C_1) |
| ν_3 | 3666 (24) a'' | 3662 (26) | 3730 (16) | 3731 (24) | 3738 (13) | 3739 (27) |
| | | 3661 (20) | 3667 (22) | 3731 (6) | 3739 (16) | 3739 (3) |
| | | | 3638 (18) | 3641 (13) | 3736 (12) | 3737 (19) |
| | | | | 3640 (21) | 3639 (15) | 3737 (3) |
| | | | | | 3178 (162) | 3210 (185) |
| | | | | | 3208 (119) | |
| ν_1 | 3557 (16) a'' | 3558 (2) | 3615 (5) | 3616 (5) | 3621 (3) | 3622 (3) |
| | | 3554 (31) | 3561 (15) | 3616 (5) | 3621 (5) | 3621 (3) |
| | | | 2928 (193) | 3013 (193) | 3619 (4) | 3620 (4) |
| | | | | 2991 (154) | 3134 (96) | 3620 (4) |
| | | | | | 3040 (201) | 3179 (40) |
| | | | | | 3152 (195) | |
| ν_2 | 1550 (6) a'' | 1552 (3) | 1582 (2) | 1584 (1) | 1589 (3) | 1591 (4) |
| | | 1552 (13) | 1552 (8) | 1583 (2) | 1580 (7) | 1590 (1) |
| | | | 1536 (7) | 1542 (5) | 1560 (5) | 1560 (0) |
| | | | | 1541 (12) | 1548 (4) | 1560 (9) |
| | | | | | 1545 (7) | 1546 (11) |
| | | | | | 1546 (5) | |
| $\nu_{\text{M-W}}^{\text{st}}$ | 337 (5) a'' | 454 (13) | 492 (2) | 497 (1) | 521 (1) | 522 (2) |
| | | 398 (0) | 415 (1) | 462 (2) | 474 (0) | 491 (0) |

$\text{Au}^+(\text{H}_2\text{O})_3$ [2+1(C_1)] are 663 and 808 cm^{-1} , respectively. For the multihydrated systems of 2+ n_2 conformers ($n_2 \geq 2$), the redshifts of the solely H-bonded terminal water are slightly redshifted compared with those of the trihydrated systems. Overall, the shapes of IR spectra of hydrated copper and gold monocations are similar due to the similar water structures. However, $\text{Au}^+(\text{H}_2\text{O})_n$ shows slightly larger redshifts than $\text{Cu}^+(\text{H}_2\text{O})_n$ which shows much larger redshifts than $\text{Ag}^+(\text{H}_2\text{O})_n$.¹⁹

The bending modes of $\text{Cu}^+(\text{H}_2\text{O})_{1,2}$ were calculated as 1577 and 1572(e) cm^{-1} , while those of $\text{Au}^+(\text{H}_2\text{O})_{1,2}$, as 1550 and 1552(e) cm^{-1} . In Table V, the largest bending frequencies of $\text{Cu}^+(\text{H}_2\text{O})_n$ for $n=3-6$ are ~ 1597 cm^{-1} , while those

of $\text{Au}^+(\text{H}_2\text{O})_n$ for $n=3-6$ are 1582, 1584, 1589, and 1591 cm^{-1} , which are slightly increased with increasing n . These frequencies correspond to the primary waters. For $\text{Au}^+(\text{H}_2\text{O})_n$, the weak blueshifts of the bending modes with increasing n are induced by weak OH bonds because of the charge transfer by the strong inductive effect.

Despite that copper-water interactions are weaker than gold-water interactions, it is interesting to note that the frequencies of metal ion-water stretch modes ($\nu_{\text{M-W}}$) of copper-water clusters are higher than those of gold-water clusters. This indicates that the copper-water interactions have higher curvature of the potential wells. These ion-water stretch frequencies are blueshifted with the increase of water molecules

by the enhanced interactions due to the charge transfer. These stretch frequencies are larger than those of silver-water monocations.¹⁹

IV. CONCLUDING REMARKS

The structures of monohydrated to hexahydrated copper and gold monocations have been investigated using high level *ab initio* calculation methods. At both 0 K and room temperature, the most stable conformers of $\text{Cu}^+(\text{H}_2\text{O})_n/\text{Au}^+(\text{H}_2\text{O})_n$ for $n=1-6$ are $1+0(C_{2v})/1+0(C_s)$, $2+0(C_2)$, $2+1(C_1)$, $2+2(C_2)$, $2+3(C_1)$, and $2+4(C_1)$, respectively. The Cu^+ and Au^+ ions have smaller HOMO-LUMO energy gaps (*d*- and *s*-orbital energy splitting) and lower LUMO energies than the Ag^+ ion. In contrast to the silver monocation water clusters which have the coordination numbers of 3–4, these copper and gold monocation water clusters show di-coordinated structures. The dihydration energies of copper and gold monocations are larger than those of silver monocations. Especially gold-water cations favor the coordination number of only 2. Thus, even tricoordination of gold and copper monocations by water would not be practically feasible. It is very interesting that the linearlike di-coordinated structures appear in the highly electronegative noble metal monovalent water cations. The OH stretching frequency analysis has been made to facilitate the IR spectroscopic study.

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¹*Comprehensive Coordination Chemistry*, edited by S. G. Wilkinson, R. D. Gillard, and J. A. McCleverty (Pergamon, Oxford, 1987), Vols. 1–7, *Cation Binding by Macromolecules*, edited by Y. Inoue and G. W. Gokel, (Marcel Dekker, New York, 1990); *Ion Solvation*, edited by Y. Marcus, (Wiley-Interscience, New York, 1985); J. R. Newsom, G. W. Neilson and J. E. Enderby, *J. Phys. Chem.* **13**, L923 (1980).

²B. Brutschy, *Chem. Rev. (Washington, D.C.)* **100**, 3891 (2000); B. Reimann, K. Buchhold, H.-D. Barth, B. Brutschy, P. Tarakeshwar, and K. S. Kim, *J. Chem. Phys.* **117**, 8805 (2002); P. Tarakeshwar, K. S. Kim, and B. Brutschy, *ibid.* **114**, 1295 (2001).

³K. S. Kim, P. Tarakeshwar, and J. Y. Lee, *Chem. Rev. (Washington, D.C.)* **100**, 4145 (2000); S. Odde, B. J. Mhin, S. Lee, H. M. Lee, and K. S. Kim, *J. Chem. Phys.* **120**, 9524 (2004); S. Odde, C. Pak, H. M. Lee, and K. S. Kim, *ibid.* **121**, 204 (2004).

⁴P. Jayaweera, A. T. Blades, M. G. Ikonou, and P. Kebarle, *J. Am. Chem. Soc.* **112**, 2452 (1990); L. Poisson, L. Dukan, O. Sublemontier, F. Lepetit, F. Reau, P. Pradel, J.-M. Mestdag, and J.-P. Visticot, *Int. J. Mass. Spectrom.* **220**, 111 (2002).

⁵P. M. Holland and A. W. Castleman, Jr., *J. Chem. Phys.* **76**, 4195 (1982).

⁶N. F. Dalleska, K. Honma, L. S. Sunderlin, and P. B. Armentrout, *J. Am. Chem. Soc.* **116**, 3519 (1994); P. J. Marinelli and R. R. Squires, *ibid.* **111**, 4101 (1989); C. A. Thompson and L. Andrews, *J. Phys. Chem.* **100**, 12214 (1996); T. F. Magnera, D. E. David, and J. Michl, *J. Am. Chem. Soc.* **111**, 4100 (1989); T. F. Magnera, D. E. David, D. Stulik, R. G. Orth, H. T. Jonkman, and J. Michl, *ibid.* **111**, 5036 (1989).

⁷T. Yamaguchi, O. Lindqvist, J. B. Boyce, and T. Claesson, *Acta Chem. Scand.* **38**, 423 (1984); T. Yamaguchi, G. Johansson, B. Holmberg, M. Maeda, and H. Ohtaki, *ibid.* **38**, 437 (1984); M. Sandström, G. W. Neilson, G. Johansson, and T. Yamaguchi, *J. Phys. C* **18**, L1115 (1985); T. Yamaguchi, H. Wakita, and M. Nomura, *Chem. Commun.* **1988**, 433; Y. Tsutsui, K. Sugimoto, H. Wasada, Y. Inada, and S. Funahashi, *J. Phys. Chem. A* **101**, 2900 (1997).

⁸L. Poisson, P. Pradel, F. Lepetit, F. Reau, J.-M. Mestdag, and J.-P. Visticot, *Eur. Phys. J. D* **14**, 89 (2001); L. Poisson, F. Lepetit, J.-M. Mestdag, and J.-P. Visticot, *J. Phys. Chem. A* **106**, 5455 (2002).

⁹T. D. Vaden, B. Forinash, and J. M. Lisy, *J. Chem. Phys.* **117**, 4628 (2002); O. M. Carbacos, C. J. Weinheimer, and J. M. Lisy, *ibid.* **110**, 8429 (1999); J. M. Lisy, *Int. Rev. Phys. Chem.* **16**, 267 (1997); C. J. Weinheimer and J. M. Lisy, *J. Chem. Phys.* **105**, 2938 (1996); G. N. Patwari and J. M. Lisy, *ibid.* **118**, 8555 (2003).

¹⁰I. Dzidic and P. Kebarle, *J. Phys. Chem.* **74**, 1466 (1970); A. T. Blades, P. Jayaweera, M. G. Ikonou, and P. Kebarle, *J. Chem. Phys.* **92**, 5900 (1990); P. Jayaweera, A. T. Blades, M. G. Ikonou, and P. Kebarle, *J. Am. Chem. Soc.* **112**, 2452 (1990); H. Deng and P. Kebarle, *J. Phys. Chem. A* **102**, 571 (1998); N. Tang and A. W. Castleman, *J. Chem. Phys.* **57**, 3638 (1972); S. M. Hurley, T. E. Dermota, D. P. Hydustry, and A. W. Castleman, *Science* **298**, 202 (2002).

¹¹N. Turki, A. Milet, A. Rahmouni, O. Ouamerali, R. Moszynski, E. Kochanski, and P. E. S. Wormer, *J. Chem. Phys.* **109**, 7157 (1998); C. Chaudhuri, Y.-S. Wang, J. C. Jiang, Y. T. Lee, H.-C. Chang, and G. Niedner-Schatteburg, *Mol. Phys.* **99**, 1161 (2001); M. Masamura, *J. Chem. Phys.* **117**, 5257 (2002).

¹²W. H. Robertson, E. G. Diken, E. A. Price, J.-W. Shin, and M. A. Johnson, *Science* **299**, 1367 (2003); J. M. Weber, J. A. Kelley, S. B. Nielsen, P. Ayotte, and M. A. Johnson, *ibid.* **287**, 2461 (2000); L. Lehr, M. T. Zanni, C. Frischkorn, R. Weinkauff, and D. M. Neumark, *ibid.* **284**, 635 (1999); J.-H. Choi, K. T. Kuwata, Y.-B. Cao, and M. Okumura, *J. Phys. Chem. A* **102**, 503 (1998).

¹³J. Kim, S. Lee, S. J. Cho, B. J. Mhin, and K. S. Kim, *J. Chem. Phys.* **102**, 839 (1995); H. M. Lee, J. Kim, S. Lee, B. J. Mhin, and K. S. Kim, *ibid.* **111**, 3995 (1999); S. Lee, J. Kim, J. K. Park, and K. S. Kim, *J. Phys. Chem.* **100**, 14329 (1996); B. J. Mhin, J. Kim, and K. S. Kim, *Chem. Phys. Lett.* **216**, 305 (1993); B. J. Mhin, S. Lee, S. J. Cho, K. Lee, and K. S. Kim, *ibid.* **197**, 77 (1992); H. M. Lee, P. Tarakeshwar, J. Park, M. R. Kolaski, Y. J. Yoon, H.-B. Yi, W. Y. Kim, and K. S. Kim, *J. Phys. Chem. A* **108**, 2949 (2004).

¹⁴E. D. Glendening and D. Feller, *J. Chem. Phys.* **99**, 3060 (1995); D. Feller, E. D. Glendening, D. E. Woon, and M. W. Feyereisen, *ibid.* **103**, 3526 (1995).

¹⁵Y.-S. Wang, H.-C. Chang, J.-C. Jiang, S. H. Lin, Y. T. Lee, and H.-C. Chang, *J. Am. Chem. Soc.* **120**, 8777 (1998); J.-C. Jiang, Y.-S. Wang, H.-C. Chang, S. H. Lin, Y. T. Lee, G. Niedner-Schatteburg, and H.-C. Chang, *ibid.* **122**, 1398 (2000).

¹⁶M. T. Rodgers and P. B. Armentrout, *J. Phys. Chem. A* **101**, 1238 (1997); J. Jensen, *J. Am. Chem. Soc.* **114**, 9533 (1992); D. R. Garmer and M. Krauss, *ibid.* **114**, 6487 (1992).

¹⁷H. M. Lee, D. Kim, and K. S. Kim, *J. Chem. Phys.* **116**, 5509 (2002); H. M. Lee and K. S. Kim, *Mol. Phys.* **100**, 875 (2002); H. M. Lee and K. S. Kim, *J. Chem. Phys.* **114**, 4461 (2001); H. M. Lee, S. B. Suh, and K. S. Kim, *ibid.* **119**, 7685 (2003); H. M. Lee and K. S. Kim, *ibid.* **117**, 706 (2002); H. M. Lee, S. B. Suh, and K. S. Kim, *ibid.* **118**, 9981 (2003); H. M. Lee, S. Lee, and K. S. Kim, *ibid.* **119**, 187 (2003).

¹⁸E. D. Glendening and D. Feller, *J. Phys. Chem.* **100**, 4790 (1996); Y.-K. Han and H. Y. Jeong, *ibid.* **100**, 18004 (1996); M. Sodupe, C. W. Bauschlicher, Jr., and H. Partridge, *J. Chem. Phys.* **95**, 9422 (1991); M. Beyer, C. Berg, H. W. Gortlitz, T. Schindler, U. Achatz, G. Albert, G. Niedner-Schatteburg, and V. E. Bondyby, *J. Am. Chem. Soc.* **118**, 7386 (1996); C. W. Bock, A. K. Katz, and J. P. Glusker, *ibid.* **117**, 3754 (1995); A. K. Katz, J. P. Glusker, S. A. Beebe, and C. W. Bock, *ibid.* **118**, 5752 (1996); D. B. Kitchen and L. C. Allen, *J. Phys. Chem.* **93**, 7265 (1989); Y. P. Yongyai, S. Kokpol, and B. M. Rode, *Chem. Phys.* **156**, 403 (1991); G. D. Markham, J. P. Glusker, C. L. Bock, M. Trachtman, and C. W. Bock, *J. Phys. Chem.* **100**, 3488 (1996).

¹⁹E. C. Lee, H. M. Lee, P. Tarakeshwar, and K. S. Kim, *J. Chem. Phys.* **119**, 7725 (2003).

²⁰D. Feller, E. D. Glendening, and W. A. de Jong, *J. Chem. Phys.* **110**, 1457 (1999).

²¹C. W. Bauschlicher, Jr., S. R. Langhoff, and H. Partridge, *J. Chem. Phys.* **94**, 2068 (1991); M. Rosi and C. W. Bauschlicher, Jr., *ibid.* **90**, 7264 (1989); **92**, 1876 (1990); N. Sahoo and T. P. Das, *ibid.* **93**, 1200 (1990); J. Hrusak, D. Schroder, and H. Schwarz, *Chem. Phys. Lett.* **225**, 416 (1994); D. Schroder, H. Schwarz, J. Hrusak, and P. Pyykko, *Inorg. Chem.* **37**, 624 (1998).

²²A. N. Widmer-Cooper, L. F. Lindoy, and J. R. Reimers, *J. Phys. Chem. A* **105**, 6567 (2001); B. S. Fox, M. K. Beyer, and V. E. Bondyby, *J. Am. Chem. Soc.* **124**, 13613 (2002).

- ²³B. H. Hong, J. Y. Lee, C.-W. Lee, J. C. Kim, and K. S. Kim, *J. Am. Chem. Soc.* **123**, 10748 (2001); K. S. Kim, S. B. Suh, J. C. Kim, *et al.*, *ibid.* **124**, 14268 (2002); B. H. Hong, S. C. Bae, C.-W. Lee, S. Jeong, and K. S. Kim, *Science* **294**, 349 (2001); S. B. Suh, B. H. Hong, P. Tarakeshwar, S. J. Youn, S. Jeong, and K. S. Kim, *Phys. Rev. B* **67**, 241402 (2003); K. S. Kim, *Bull. Korean Chem. Soc.* **24**, 757 (2003); S. B. Suh, J. C. Kim, Y. C. Choi, and K. S. Kim, *J. Am. Chem. Soc.* **126**, 2186 (2004); P. Tarakeshwar and K. S. Kim, in *Encyclopedia of Nanotechnology*, edited by H. S. Nalwa, (American Science, California, 2004), Vol. 7, pp. 367–404; P. Tarakeshwar, D. Kim, H. M. Lee, S. B. Suh, and K. S. Kim, in *Computational Material Science*, edited by J. Leszczynski (Elsevier, Amsterdam, 2004), pp. 119–170; P. Tarakeshwar, D. Kim, H. M. Lee, S. B. Suh, and K. S. Kim, in *Dekker Encyclopedia of Nanoscience and Nanotechnology*, edited by J. A. Schwarz, C. Contescu, and K. Putyera (Marcel Dekker, New York, 2004), Vol. 3, pp. 2423–2433.
- ²⁴P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, and P. D. W. Boyd, *J. Chem. Phys.* **91**, 1762 (1989).
- ²⁵D. Kruger, H. Fuchs, R. Rousseau, D. Marx, and M. Parrinello, *J. Chem. Phys.* **115**, 4776 (2001); J. M. Seminario, A. G. Zacarias, and P. A. Derosa, *ibid.* **116**, 1671 (2002); C. Majumdar, T. Briere, H. Mizuseki, and Y. Kawazoe, *ibid.* **117**, 7669 (2002).
- ²⁶M. Dolg, U. Wedig, H. Stoll, and H. Preuss, *J. Chem. Phys.* **86**, 866 (1987); A. Antusek, M. Urban, and A. J. Sadlej, *ibid.* **119**, 7247 (2003).
- ²⁷H. M. Lee, M. Ge, B. R. Sahu, P. Tarakeshwar, and K. S. Kim, *J. Phys. Chem. B* **107**, 9994 (2003); T. Nautiyal, S. J. Youn, and K. S. Kim, *Phys. Rev. B* **68**, 033407 (2003); P. Pyykko, *Chem. Rev. (Washington, D.C.)* **88**, 563 (1988).
- ²⁸A. J. H. Wachters, IBM Tech. Report No. RJ584 1969; *J. Chem. Phys.* **52**, 1033 (1970); P. J. Hay, *ibid.* **66**, 4377 (1977); H. Partridge, *ibid.* **90**, 1043 (1989).
- ²⁹*Table of Periodic Properties of the Elements* (Sargent-Welch Scientific, Skokie, IL, 1992).
- ³⁰J. Kim and K. S. Kim, *J. Chem. Phys.* **109**, 5886 (1998); H. M. Lee, S. B. Suh, J. Y. Lee, P. Tarakeshwar, and K. S. Kim, *ibid.* **112**, 9759 (2000); K. S. Kim, B. J. Mhin, U.-S. Choi, and K. Lee, *ibid.* **97**, 6649 (1992); K. S. Kim, J. Y. Lee, H. S. Choi, J. Kim, and J. H. Jang, *Chem. Phys. Lett.* **265**, 497 (1997).
- ³¹S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 553 (1970).
- ³²M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision A.1., Gaussian, Inc., Pittsburgh, PA, 2003.
- ³³S. J. Lee, H. Y. Chung, and K. S. Kim, *Bull. Korean Chem. Soc.* **25**, 1061 (2004).
- ³⁴Though the B3LYP level gives the coordination number 2 for $\text{Ag}^+(\text{H}_2\text{O})_n$, the MP2 level calculations provide coordination number 3–4. This reason is that the DFT level gives too small E_{gap} for Ag^+ (Ref. 19).
- ³⁵P. E. Fraley and K. N. Rao, *J. Mol. Spectrosc.* **29**, 348 (1969); U. Buck and F. Huisken, *Chem. Rev. (Washington, D.C.)* **100**, 3863 (2000).