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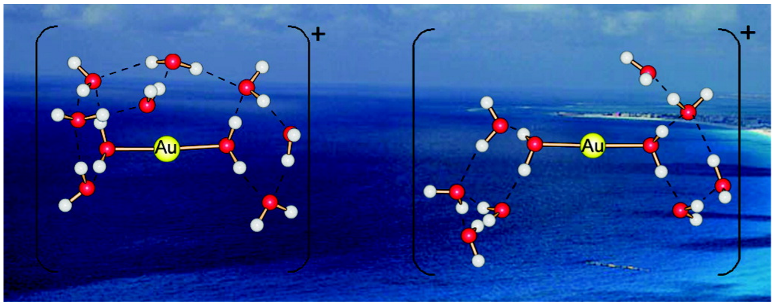

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# $H_2O$ Nucleation around $Au^+$

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***Abstract:*** First principles electronic structure calculations have been carried out to investigate the ground state geometry, electronic structure, and the binding energy of $[Au(H_2O)_n]^+$ clusters containing up to 10 $H_2O$ molecules. It is shown that the first coordination shell of $Au^+$ contains two $H_2O$ molecules forming a $H_2O-Au^+-H_2O$ structure with $C_2$ symmetry. Subsequent $H_2O$ molecules bind to the previous $H_2O$ molecules forming stable and fairly rigid rings, each composed of 4 $H_2O$ molecules, and leading to a dumbbell structure at $[Au(H_2O)_8]^+$. The 9th and the 10th $H_2O$ molecules occupy locations above the $Au^+$ cation mainly bonded to one $H_2O$ from each ring, leading to structures where the side rings are partially distorted and forming structures that resemble droplet formation around the $Au^+$ cation. The investigations highlight quantum effects in nucleation at small sizes and provide a microscopic understanding of the observed incremental binding energy deduced from collision induced dissociation that indicates that $[Au(H_2O)_n]^+$ clusters with 7−10 $H_2O$ molecules have comparable binding energy. The charge on the $Au^+$ is shown to migrate to the outside $H_2O$ molecules, suggesting an interesting screening phenomenon.

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## 1. Introduction

The condensation of water molecules around charged particles has been used, for a long time, to stimulate rain formation and was used, in a pioneering work by Wilson, to detect charged particles through condensate traces in cloud chambers.[1] Nucleation studies are also important in atmospheric chemistry as the formation of acid rain proceeds via condensation of water molecules around sulfate and other ions.[2] Although this phenomenon has been known for decades, it is only recently that the developments of the molecular beam experiments and the theoretical techniques have enabled accurate investigations into the condensation phenomenon. It is now well known that the presence of ions can help to overcome the nucleation barrier, leading to enhancement in nucleation rates. It is also suggested that the sign of the charge can affect the nucleation rates. Whereas cations form clusters with oxygen bonding to the ionic species and leading to fairly symmetric arrangements, the anions bind to H atoms leading to asymmetric arrangements.[3,4] One of the effects that has received attention, only recently,[5] is the quantum chemical nature of the ionic species. Studies by Nadykto et al.[5] indicate that the structure of the initial core of $H_2O$ molecules around the charged particles depends significantly on the charged state as well as the chemical nature of the charged particles. Their studies on $M(H_2O)_n$ clusters containing up to 6 $H_2O$ molecules indicate that the water molecules can have different coordination to the ions of different chemical and charged state.

In this work, we demonstrate a new feature to the $H_2O$ nucleation around a metal cation. Through studies on the nucleation of $H_2O$ around $Au^+$, we show that the quantum chemical nature of the cation not only effects the initial attachment of $H_2O$ molecules but also leads to the formation of stable rigid $H_2O$ rings that are different from those in, for example, ice. The present investigations are partly motivated by the recent experiments by Poisson et al.,[6] who investigated the binding of $H_2O$ molecules to $Au^+$ cations through collision induced dissociation (CID) of $[Au(H_2O)_n]^+$ clusters. Their investigations revealed interesting trends in the incremental binding energy (B.E.) of a $H_2O$ molecule (energy required to remove the weakest bonded $H_2O$ molecule). Their results indicate that the first two water molecules bind strongly to the $Au^+$ (B.E. of 40.1 and 44.9 kcal/mol, respectively). The B.E. decreases from 23.0 to 16.1 kcal/mol from 3 to 6 $H_2O$ molecules, and for larger clusters $[Au(H_2O)_n]^+$ with $n = 7$, 8, 9, and 10, the B.E. remains at a constant value of around 10.4 kcal/mol,

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(1) Wilson, C. T. R. *Philos. Trans. R. Soc. London* **1897**, *189*, 265; Das Gupta, N. N.; Ghosh, S. K. *Rev. Mod. Phys.* **1946**, *18*, 225.
(2) Onianwa, P. C.; Odukoya, O. O.; Alabi, H. A. *Bull. Chem. Soc. Ethiop.* **2002**, *16*, 141; Aas, W, et al. *Atmos. Environ.* **2007**, *41*, 1706.
(3) Garret, B. C. *Science* **2004**, *303*, 1146.
(4) Kathmann, S. M.; Schenter, G. K.; Garret, B. C. *Phys. Rev. Lett.* **2005**, *94*, 116104.
(5) Nadykto, A. B.; Natsheh, A. A.; Yu, F.; Mikkelsen, K. V.; Ruuskanen, J. *Phys. Rev. Lett.* **2006**, *96*, 125701.
(6) Poisson, L.; Lepetit, F.; Mestdagh, J. -M.; Visticot, J.-P. *J. Phys. Chem. A* **2002**, *106*, 5455.

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that is, more than twice the B.E. between two isolated $H_2O$ molecules. Note that an $Au^+$ is marked by relativistic effects and the unoccupied 6s level is close to the filled 5d levels, and this can lead to appreciable s−d mixing, which, in turn, can substantially affect the interaction between $Au^+$ and $H_2O$. The previous theoretical studies by Hrušák et al.,[7] Feller et al.,[8] and Lee et al.[9] were carried out on clusters containing 1, up to 4, and up to 6 $H_2O$ molecules, respectively, and employed a post-Hartree−Fock approach with relativistic core potentials for the Au atom. The results of these investigations predict a nonplanar $C_s$ ground state for $[Au(H_2O)]^+$. This distortion of planarity is a correlation effect that is only correctly taken into account by density functional theory and post Hartree−Fock methods. The B.E. of $H_2O$ in $[Au(H_2O)]^+$ was predicted to be 36.0, 40.2, and 34.0 kcal/mol by Hrušák et al., Feller et al., and Lee et al., respectively. The B.E. of $H_2O$ in $[Au(H_2O)_2]^+$ was predicted to be 48.1 and 40.1 by Feller et al. and Lee et al., respectively. The increased B.E. of $[Au(H_2O)_2]^+$ over $[Au(H_2O)]^+$ is rather unusual but in good agreement with the measured CID energies of 40.1 ± 2.3 and 44.9 ± 3.4 kcal/mol for the two systems. The authors also studied $[Au(H_2O)_n]^+$ clusters containing 3, 4, 5, and 6 $H_2O$ molecules (Feller et al., $n = 1-4$; Lee et al., $n = 1-6$), and found that the additional molecules prefer to bond to the existing $H_2O$ molecules over hydrogen bridges in their ground states. Although the initial bonding of $H_2O$ to the $Au^+$ is an interesting finding, several of the key issues outlined above remain unanswered. For example, if the $H_2O$ added to $[Au(H_2O)_2]^+$ bind to the $H_2O$ molecules, then what kind of $H_2O$ networks evolve at each end? How does the B.E. evolve as successive $H_2O$ units are added? In particular, why is the binding energy in $[Au(H_2O)_n]^+$ with $n = 7$, 8, 9, and 10 clusters remaining at a constant value? Although the addition of $H_2O$ units results in $H_2O$ bound to the initial two $H_2O$ molecules in $[Au(H_2O)_2]^+$, at what size, the water begins to form a droplet surrounding the $Au^+$ cation? Another important issue that has not received much attention is the charge on the $Au^+$ cation. Does the charge remain localized on the Au atom or does the caging of the cation result in the transport of the charge to the outside atoms, forming a charged outer shell of water molecules?

In this work, we have carried out extensive first principle theoretical investigations of the $[Au(H_2O)_n]^+$ clusters containing up to 10 water molecules to address the above questions. As found in previous studies, the first two water molecules bind directly to the $Au^+$. The addition of subsequent $H_2O$ molecules results in the formation of two rings of water molecules each containing 4 units leading to a dumbbell structure for $[Au(H_2O)_8]^+$. The ninth $H_2O$ molecule occupies a position above the $Au^+$ cation, and one $H_2O$ molecule from each $(H_2O)_4$ binds to the ninth molecule, resulting in distorted $(H_2O)_4$ cages and the beginning of a semi-droplet formation around the cation. Notably, the charge on the cation is transported to the outer $H_2O$ molecules, leading to a positively charged outer shell screening the central Au atom. The calculated binding energies are in excellent agreement with experiments confirming the validity of the present findings. Because the optimized structures are very floppy systems, special care has to be taken. In the next section, we, therefore, describe in detail our computational approach. Results and discussions are then given in Section 3. In the last section, final conclusions are drawn.

## 2. Theoretical and Computational Methods

Any theoretical approach to describe the present systems has to correctly reproduce water−water interactions as well as include the relativistic effects in Au. It is now well known that the use of gradient-corrected functionals is mandatory for a reliable description of hydrogen bridges within the density functional theory (DFT) methodologies.[10] In the present work, we have used the revised PBE functional[11] proposed by Hammer et al. (PBE99).[12] For the O and H atoms, we employed the DFT optimized DZVP basis set,[13] whereas the Au atom was described by a scalar relativistic effective core potential (ECP) with 19 valence electrons as proposed by Schwerdtfeger et al.,[14] in combination with the correlation consistent aug-cc-pVTZ-PP valence basis set.[15] To avoid the calculation of four-center electron repulsion integrals, the variational fitting of the Coulomb potential[16−17] was employed. The auxiliary density was expanded in primitive Hermite Gaussian functions using the GEN-A2 auxiliary function set for O and H atoms and the GEN-A2* auxiliary function set for Au. The GEN-A2 auxiliary function set contains s, p, and d auxiliary functions and adapts automatically to the chosen orbital basis set.[18] The GEN-A2* auxiliary function set possesses a similar structure as the GEN-A2 set but includes also f and g functions. The exchange-correlation potential was calculated with the orbital density. The methodology was first tested via studies on small water clusters $(H_2O)_n$ with $n = 2-5$, for which accurate ab initio benchmark calculations are available.[19−21] For example, for a water dimer, the present approach leads to an O−O distance of 2.99 Å that is in excellent agreement with the observed experimental bond length of 2.98 Å.[22] The present approach predicts a fragmentation energy for $(H_2O)_2$ to be 2.4 kcal/mol including basis set superposition errors and zero point energy corrections. This is again in good agreement with the experimental binding energy of 3.59 ± 0.5 kcal/mol.[23] For larger $(H_2O)_n$ clusters with $n = 3-5$, we find that our optimized structures are in good agreement with the ones from existing high level ab-initio calculations.[21] In particular, the ordering of the low lying isomers for the trimer, tetramer, and pentamer water clusters is correctly reproduced in the present approach. Additionally, we performed a comparison of the binding energies including basis set superposition corrections for the ground state geometries of the $(H_2O)_n$ clusters with $n = 2-5$, with respect to the results of Xantheas et al.[20] This comparison, presented in Table 1 of the Supporting Information, shows a very good agreement. On the basis of these results, we expect the accuracy of the present calculations to be around 1.0 kcal/mol.

To further test our computational methodology for the $[Au(H_2O)_n]^+$ systems, we investigate the basis set size convergence of the gold atom in the $[Au(H_2O)]^+$ molecule employing aug-cc-pVxZ-PP ($x$ = D, T,

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(7) Hrušák, J.; Schröder, D.; Schwarz, H. *Chem. Phys. Lett.* **1994**, *225*, 416.
(8) Feller, D.; Glendening, E. D.; de Jong, W. A. *J. Chem. Phys.* **1999**, *100*, 1475.
(9) Lee, H. M.; Min, S. K.; Lee, E. C.; Min, J. -H.; Odde, S.; Kim, K. S. *J. Chem. Phys.* **2005**, *122*, 064314.
(10) Sim, F.; St-Amant, A.; Papai, I.; Salahub, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 4391.
(11) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(12) Hammer, B.; Hansen, L. P.; Nørskov, J. K. *Phys. Rev. B.* **1999**, *59*, 7413.
(13) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.
(14) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, *91*, 1762.
(15) http://www.emsl.pnl.gov/forms/basisform.html.
(16) Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 4993.
(17) Mintmire, J. W.; Dunlap, B. I. *Phys. Rev. A* **1982**, *25*, 88.
(18) Calaminici, P.; Janetzko, F.; Köster, A. M.; Mejia-Olvera, R.; Zuñiga-Gutierrez, B. *J. Chem. Phys.* **2007**, *126*, 044108.
(19) Burnham, C. J.; Xantheas, S. S. *J. Chem. Phys.* **2002**, *116*, 1479.
(20) Xantheas, S. S.; Burnham, C. J.; Harrison, R. J. *J. Chem. Phys.* **2002**, *116*, 1493.
(21) Day, M. B.; Kirschner, K. N.; Shields, G. C. *J. Phys. Chem. A* **2005**, *109*, 6773.
(22) Odutola, J. A.; Dyke, T. R. *J. Chem. Phys.* **1980**, *72*, 5062.
(23) Curtiss, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703.

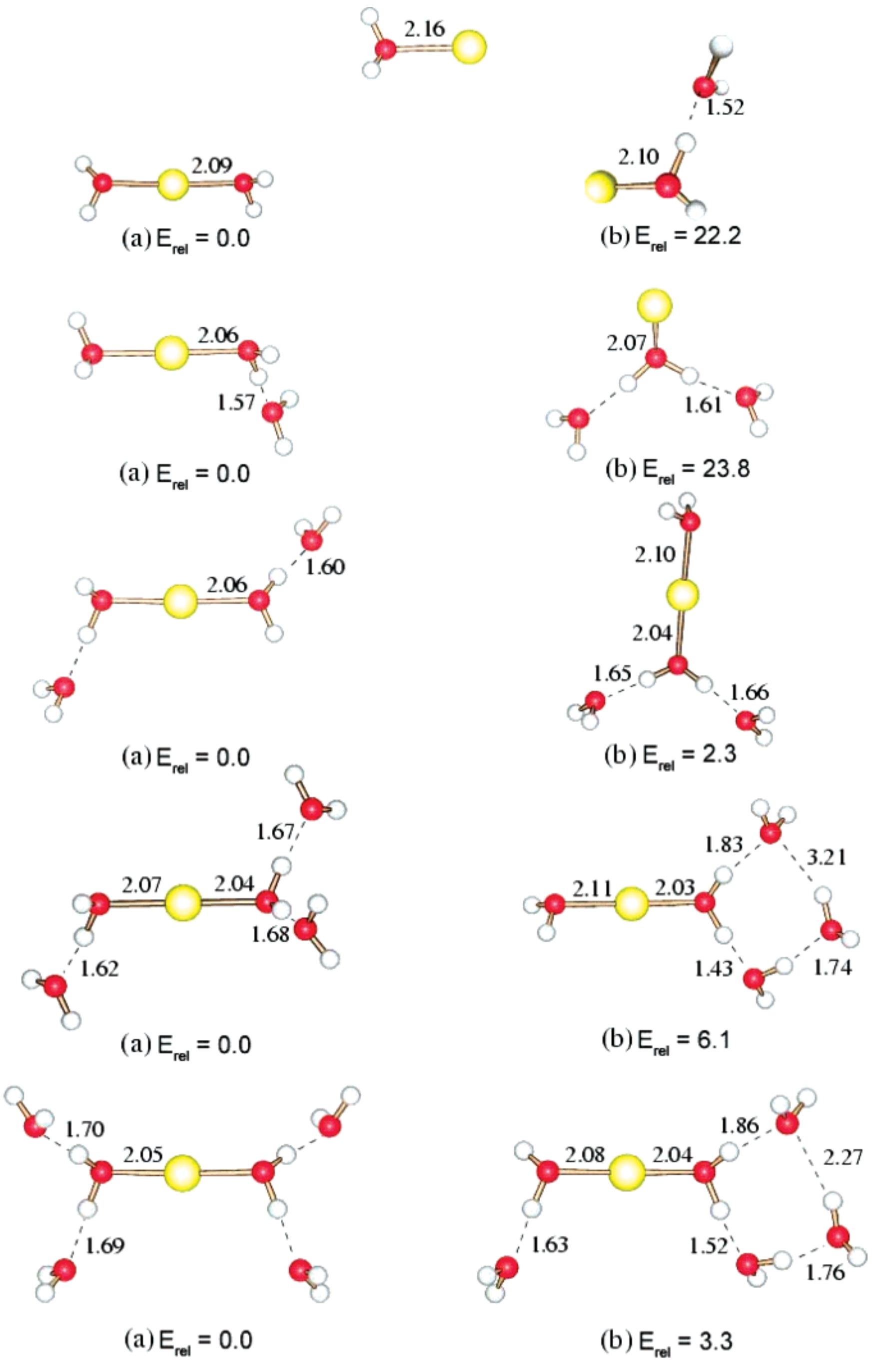

***Figure 1.*** (a) Ground state structures and (b) energetically next higher isomers for $[Au(H_2O)_n]^+$ with $n = 1-6$. Also given are the relative energies in kcal/mol.

Q, and 5) valence basis sets.[15] As shown in Table 2 of the Supporting Information, the aimed accuracy of around 1 kcal/mol in the binding energy was reached with the aug-cc-pVTZ-PP valence basis set. Additionally, we performed calculations on the free Au atom. The experimental ionization potential (IP) and electron affinity (EA) of Au are 9.23 and 2.31 eV, respectively,[24] and the calculated IP and EA of Au were 9.41 and 2.17 eV, respectively, with the aug-cc-pVTZ-PP valence basis set. On the basis of these results, we selected this basis set in all our $[Au(H_2O)_n]^+$ calculations. The potential energy surface in larger $[Au(H_2O)_n]^+$ clusters is very flat. We therefore employed a relative large adaptive grid[25] with a grid tolerance of $10^{-6}$ a.u. for the converged self-consistent field (SCF) energy[26] and a very tight convergence criterion (RMSQ force $\leq 10^{-6}$ a.u.) for the geometry optimization. To determine the ground state, the configuration space was sampled by starting from several initial configurations and optimizing the geometry by moving atoms in the direction of forces till they dropped below the threshold value. For the local structure optimization, the Levenberg−Marquardt method[27,28] was employed. All structures were fully optimized in redundant coordinates without symmetry constrains,[29] and the resulting ground states were characterized via a frequency analysis. The frequencies for the structures depicted in Figures 1 and 2 are reported in Table 3 of the Supporting Information.

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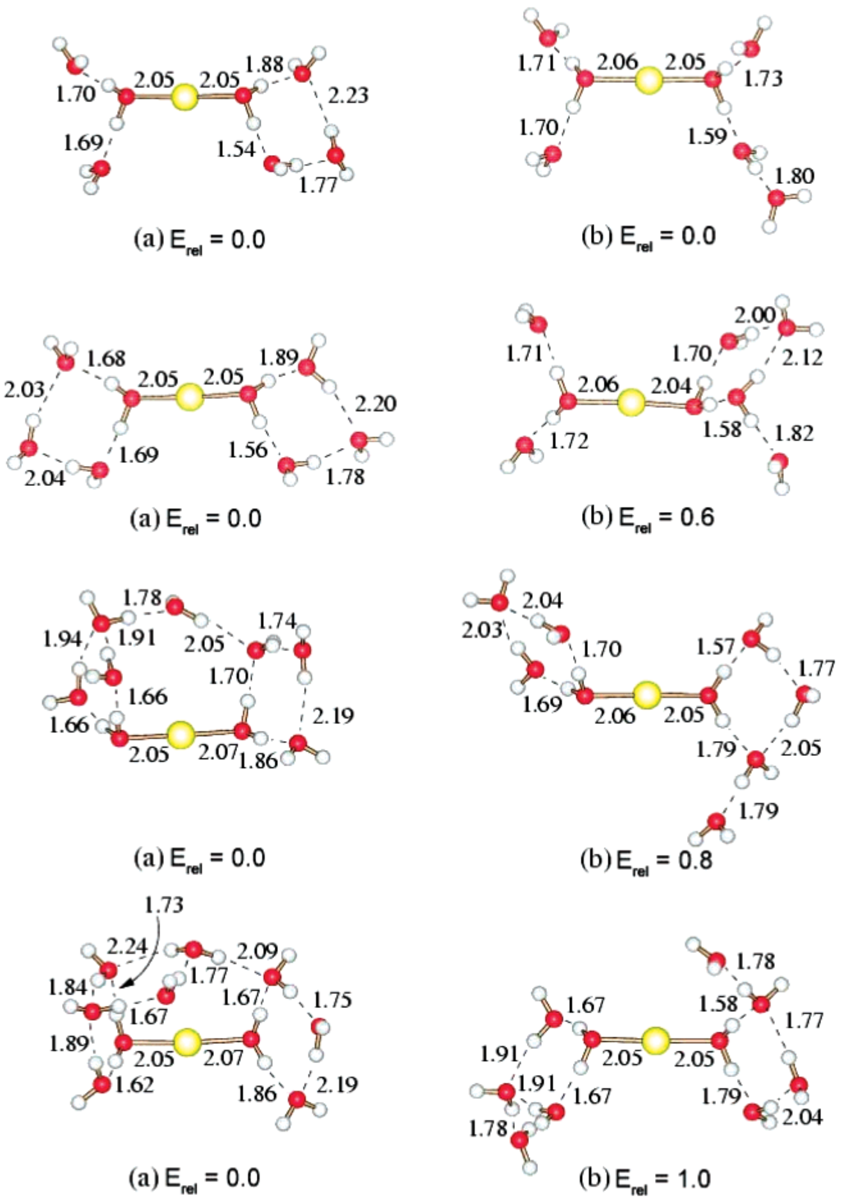
(24) *Table of Periodic Properties of the Elements*; Sargent-Welch Scientific: Skokie, IL, 1992.
(25) Köster, A. M.; Flores-Moreno, R.; Reveles, J. U. *J. Chem. Phys.* **2004**, *121*, 681.
(26) Krack, M.; Köster, A. M. *J. Chem. Phys.* **1998**, *108*, 3226.
(27) Levenberg, K. *Quart. Appl. Math* **1944**, *2*, 164.
(28) Marquardt, D. W. *SIAM J.* **1963**, *11*, 431.
(29) Reveles, J. U.; Köster, A. M. *J. Comput. Chem.* **2004**, *25*, 1109.



(a) $E_{rel}$ = 0.0 (b) $E_{rel}$ = 0.0

(a) $E_{rel}$ = 0.0 (b) $E_{rel}$ = 0.6

(a) $E_{rel}$ = 0.0 (b) $E_{rel}$ = 0.8

(a) $E_{rel}$ = 0.0 (b) $E_{rel}$ = 1.0

***Figure 2.*** (a) Ground state structures and (b) energetically next higher isomers for $[Au(H_2O)_n]^+$ with $n = 7-10$. Also given are the relative energies in kcal/mol.

Even though these harmonic frequencies are not suitable for free energy calculations by the ideal gas approximation due to non-negligible anharmonicity contributions in these systems, as shown by Kathmann et al.,[30,31] their positive values ensure that minimum structures were obtained by the local optimization. All calculations were performed using the deMon2k program.[32] We also performed a natural bond orbital (NBO) charge analysis[33] of the $[Au(H_2O)_n]^+$ clusters using the Gaussian 03 program.[34] For these calculations, we employed our same theoretical model but the PBE functional,[11] instead of the revised PBE99 functional.[12]

## 3. Results and Discussion

Figure 1 and 2 show the ground states (a), and the energetically next higher isomers (b) for $[Au(H_2O)_n]^+$ containing up to 10 water molecules. The corresponding incremental B.E., representing the B.E. of the most weakly bonded $H_2O$ molecule to the preceding cluster, are listed in Table 1. For comparison, the B.E. from a collision induced dissociation (CID) experiment,[6] and from all previous theoretical studies, namely at the CCSD level of theory by Hrušák et al.,[7] and at the MP2 level of theory by Feller et al.[8] and Lee et al,[9] are also listed in Table 1, and shown graphically in Figure 3. As mentioned previously, the first two $H_2O$ molecules bind directly to the $Au^+$ cation. Note that the second $H_2O$ molecule binds more strongly than the first one. This observation was recently explained by Lee et al.[35] based on the presence of a low-lying, electrophilic HOMO *s* orbital in $Au^+$ for efficient charge transfer, and to an

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(30) Kathmann, S. M.; Schenter, G.; Garret, B. *J. Phys. Chem. C* **2007**, *111*, 4977.

(31) Kathmann, S. M.; Schenter, G. K.; Garret, B. C. *Phys. Rev. Lett.* **2007**, *98*, 109603.

(32) Köster, A. M.; Calaminici, P.; Casida, M. E.; Flores-Moreno, R.; Geudtner, G.; Goursot, A.; Heine, T.; Ipatov, A.; Janetzko, F.; M. del Campo, J.; Patchkovskii, S.; Reveles, J. U.; Salahub, D. R.; Vela, A. *deMon2k* V.2.3; Cinvestav: México, 2006; http://www.deMon-software.com.

(33) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* 1983, *78*, 4066; Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(34) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(35) Lee, H. M.; Diefenbach, M.; Suh, S. B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2005**, *123*, 074328.

***Table 1.*** Incremental Binding Energies (B.E.), Basis Set Superposition Errors Corrections (ΔBSSE), Zero Point Energies Corrections (ΔZPE), and Corrected Incremental Binding Energies (C.B.E) of the Studied $[Au(H_2O)_n]^+$ Clusters[a]

| cluster | B.E. [kcal/mol] | ΔBSSE [kcal/mol] | ΔZPE [kcal/mol] | C.B.E. [kcal/mol] | literature [kcal/mol] |
|---|---|---|---|---|---|
| $[Au(H_2O)]^+$ | 41.6 | −2.5 | −1.9 | 37.2 | *40.1 ± 2.3*,[b] 34.0,[c] 40.2,[d] 36.0[e] |
| $[Au(H_2O)_2]^+$ | 45.2 | −2.7 | −2.7 | 39.8 | *44.9 ± 3.4*,[b] 40.1,[c] 48.1[d] |
| $[Au(H_2O)_3]^+$ | 20.0 | −1.1 | −2.0 | 16.9 | *23.0 ± 4.6*,[b] 17.4,[c] 16.8[d] |
| $[Au(H_2O)_4]^+$ | 18.5 | −1.1 | −2.0 | 15.4 | *20.7 ± 4.6*,[b] 16.1[b],[c] 20.3[c] |
| $[Au(H_2O)_5]^+$ | 15.3 | −1.1 | −1.9 | 12.3 | *18.4 ± 3.4*,[b] 14.1[c] |
| $[Au(H_2O)_6]^+$ | 14.1 | −1.1 | −1.9 | 11.1 | *16.1 ± 3.4*,[b] 12.8[c] |
| $[Au(H_2O)_7]^+$ | 10.9 | −0.7 | −2.7 | 7.5 | *10.4 ± 2.3*[b] |
| $[Au(H_2O)_8]^+$ | 11.8 | −0.8 | −2.9 | 8.1 | *10.4 ± 2.3*[b] |
| $[Au(H_2O)_9]^+$ | 12.3 | −1.4 | −3.4 | 7.5 | *10.4 ± 2.3*[b] |
| $[Au(H_2O)_{10}]^+$ | 11.7 | −0.8 | −3.0 | 7.9 | *10.4 ± 2.3*[b] |

[a] Experimental B.E. from literature and previous available theoretical values are included for comparison. The experimental B.E. values are in italics. [b] Poisson et al. (Experimental), ref 6. [c] Lee et al. (ab initio, MP2), ref 9. [d] Feller et al. (ab initio, MP2), ref 8. [e] Hrušák et al. (ab initio, CCSD(T)), ref 7.

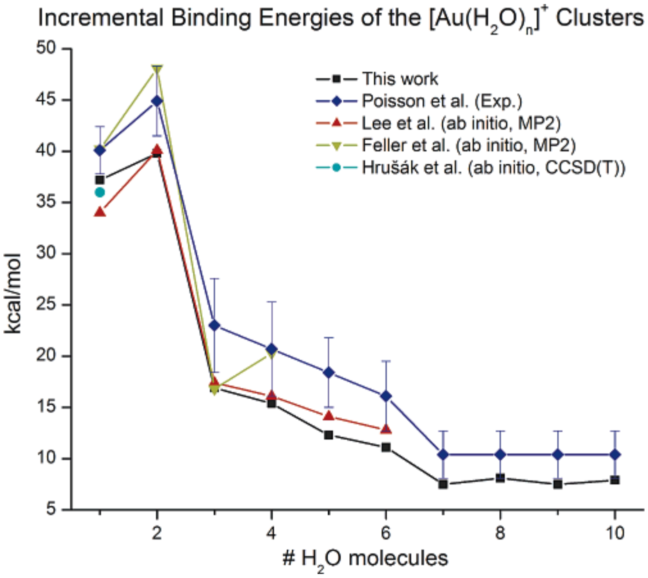

***Figure 3.*** Incremental binding energies (B.E.) from a CID experiment, previous theoretical studies, and this work for the studied $[Au(H_2O)_n]^+$ clusters.

unusual skewed overlap of p−6s−p orbitals. As the orbital overlap is saturated with two water molecules, this property is responsible for the low coordination of the gold ion. This is in agreement with the experimental values obtained by CID.[6] The third $H_2O$ molecule prefers to bind to a $H_2O$ molecule leading to the beginning of the second hydration shell. As this $H_2O$ binds via a hydrogen bridge, the B.E. drops from the direct binding to $Au^+$ by more than a factor of 2. The subsequent water molecules bind with decreasing binding energy until the completion of the second hydration shell at $[Au(H_2O)_6]^+$. For $[Au(H_2O)_5]^+$, whereas the ground state structure corresponds to the $H_2O$ molecules occupying the second hydration shell, the next higher structure corresponds to the completion of a ring of $H_2O$ molecules on one side. The energy difference between the ground state and the next higher structure given in Figure 1a and b decreased with increasing size. For the case of $[Au(H_2O)_5]^+$ and $[Au(H_2O)_6]^+$, we find an energy difference of 6 and 3 kcal/mol, respectively. The ring closure marks the beginning of the third hydration shell that surrounds $[Au(H_2O)_6]^+$. The stability of the open structures compared to the rings can be reconciled as the $H_2O$ molecules in the former occupy the second hydration shell. Nevertheless, the ring structures present less floppy frameworks marked by an increase in the low lying frequencies (see Table 3 of the Supporting Information). For $[Au(H_2O)_7]^+$, the third hydration shell is filled with $H_2O$ and the ground state structure corresponds to the completion of a **ring** of $H_2O$ molecules. The stable ring is composed of 4 molecules where the orientation of the $H_2O$ molecule is progressively modified as one goes around the ring. However, this system is degenerated with respect to the isomer where the ring is open. The completion of the rings on the two sides occurs at $[Au(H_2O)_8]^+$, which presents a dumbbell structure. Note also that the ring structures are more stable than the corresponding open ring isomers with a small energy difference of 1 kcal/mol. In particular, the comparison of the structures in $[Au(H_2O)_8]^+$ is quite interesting. The structure in Figure 2b is only 0.6 kcal/mol less stable than that in Figure 2a, and the two configurations can be regarded as isoenergetic. The structures are, however, quite different. The isomer (b) corresponds to an opening of the ring on the left and attachment of the $H_2O$ molecule to a 4-membered ring on the other side. At a first glance, this looks like the exchange of a water molecule from a third to a more outer hydration shell. However, the small energy difference between (a) and (b) structures contradicts this impression. In fact, all water molecules in $[Au(H_2O)_n]^+$ clusters for $n \geq 7$ and outside the central shell $[Au(H_2O)_6]^+$, irrespective of the isomer, possess very similar binding energies. Therefore, the classification of higher hydration shells beyond the second one is meaningless as it leads to similar energies. This result is in qualitative agreement with the CID results that approach a limiting energy of 10.4 ± 2.3 kcal/mol for $[Au(H_2O)_n]^+$ systems with $n \geq 7$. From our optimized structures, it is seen that the ground state for $[Au(H_2O)_9]^+$ and $[Au(H_2O)_{10}]^+$ can be looked upon as two four-member rings joined together via a Au ion, and one and two water molecules, respectively. In $[Au(H_2O)_9]^+$, the distance between the gold atom and the water molecule connecting the four-membered rings is around 4.4 Å, whereas in $[Au(H_2O)_{10}]^+$, the distances between the gold atom and the water molecules connecting the rings are around 4.1 and 5.5 Å, respectively. Note that the structures corresponding to the unconnected rings are less stable for both systems. However, the energy difference is small, and a correct ordering of the structures requires inclusion of the zero point energies. We also carried out supplementary studies to examine the rigidity of the four-member rings. To this end, we calculated the vibrational frequencies of the two isomers of $[Au(H_2O)_8]^+$ cluster. We found that the lowest vibrational frequency of isomer (a) was much higher than that of (b), indicating a rigidity of the closed rings. The same holds for the cage structures (a) of $[Au(H_2O)_9]^+$ and $[Au(H_2O)_{10}]^+$. They possess lowest frequencies of more than 10 $cm^{-1}$, whereas the corre-

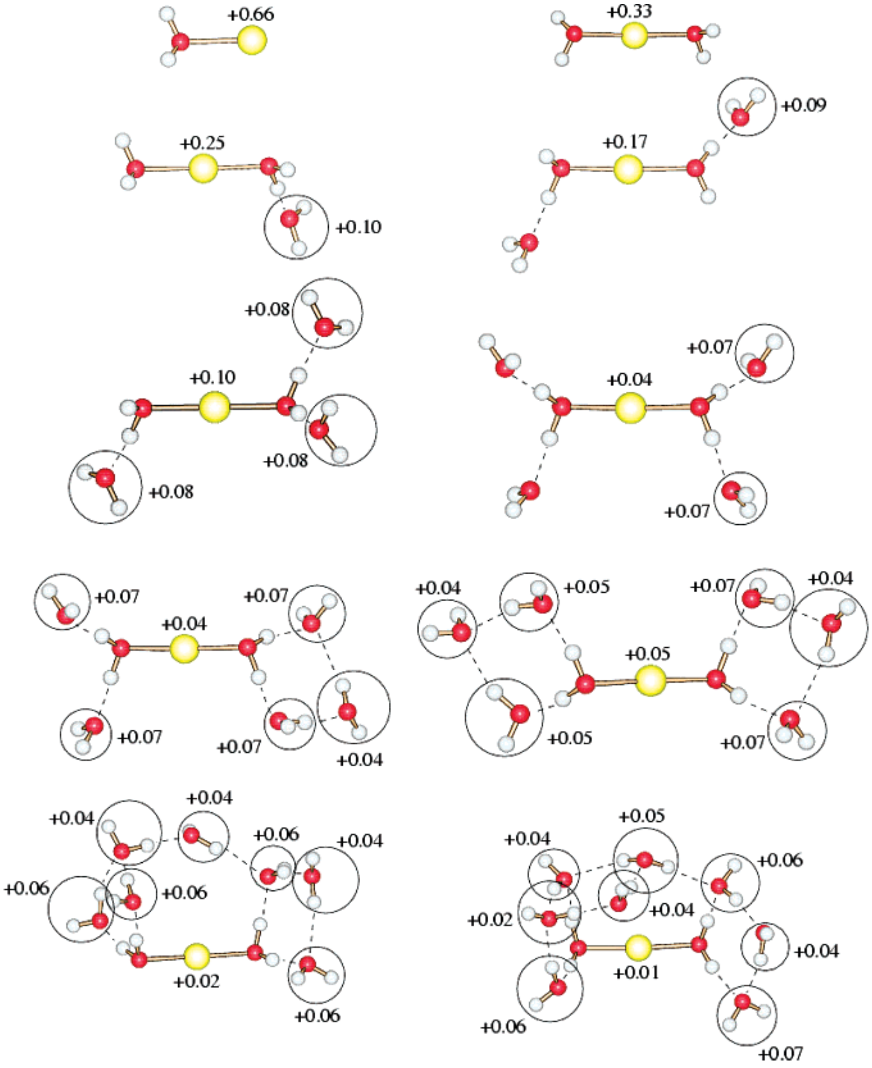

***Figure 4.*** Mulliken population charges of the $[Au(H_2O)_n{}^+]$ with $n = 1,10$ clusters.

sponding open structures have very small (but positive), lowest frequencies. Therefore, the connection of the four membered rings by bridging water molecules increases the rigidity of the structures considerably.

In the above, we have primarily focused on the geometry and the energetics of the various structures. The next issue is the nature of bonding and the charge at the Au site. As was previously pointed out by Lee et al.,[35] the Au atom has a large electron affinity of 2.31 eV, and the cation has an energetically very-low-lying lowest unoccupied molecular orbital (LUMO). Further, the gap between the 6s and the filled 5d orbitals is small, leading to some s−d mixing. Because the LUMO is low, it can receive charge from the surrounding $H_2O$ molecules. To illustrate this, we carried out a Mulliken population analysis of the electronic charge density in all clusters, and the results are marked on Figure 4. Here, the charges of the Au atom and the water molecules (indicated by circles in Figure 4), bonded by hydrogen bridges to the $[Au(H_2O)_2]^+$ moiety, are analyzed. Positive Mulliken charges indicate depletion of charge. Starting from an $Au^+$, the attachment of the first $H_2O$ molecule leads to a charge transfer from the $H_2O$ molecule to the $Au^+$ ion, and the positive charge in the Au site is reduced to 0.66 $e^-$ according to the Mulliken charge. As a second $H_2O$ is added, the positive charge in the Au site is reduced to only 0.33 $e^-$, and the basic $[Au(H_2O)_2]^+$ moiety is formed. The continual addition of $H_2O$ molecules results in a progressive decrease of the charge on Au, and for $[Au(H_2O)_6]^+$, the positive charge is almost entirely localized at the outer $H_2O$ molecules as the net charge at the Au site in $[Au(H_2O)_6]^+$ is less than 0.04 $e^-$ and remains basically constant until $[Au(H_2O)_{10}]^+$, as Figure 4 shows. The charges of the Au atom and of the water molecules bonded by hydrogen bridges (all the water molecules excluding the two directly bonded to the Au atom) sum up to an almost constant value in all clusters, namely the 0.33 $e^-$ of positive charge, and the same total charge is present on Au in the basic $[Au(H_2O)_2]^+$ moiety. This indicates that the two water molecules in the first hydration shell act only as intermediators and that the observed charge transfer is indeed a migration of positive charge from the Au atom to the surface of the $[Au(H_2O)_n]^+$ clusters. Because atomic charges are not observable, we also performed a natural bond orbital (NBO) charge analysis[33] for the $[Au(H_2O)_n]^+$ systems. Although our results showed that the magnitude of the Mulliken and NBO charges on the gold atom were different, the general trend was the same. In both charge analyses, positive charge migrates to the outer water molecules. However, a significant difference is observed for the gold charge. In the NBO analysis, the charge on this atom decreased only to 0.5 $e^-$ in $[Au(H_2O)_{10}]^+$, whereas in the Mulliken population analysis it decreased to almost zero. Therefore, the charge magnitudes may vary between different population analyses. Most surprisingly, however, the charge of the $[Au(H_2O)_2]^+$ moiety was similar in both population analyses. The present findings are consistent with previous results by Lee et al.[9] who found, based on a NBO charge analysis, that an increasing charge transfer occurs from the $H_2O$ molecules and reduces the positive charge on the Au atom.

## 4. Conclusions

The present studies indicate that the nature of $H_2O$ nucleation around $Au^+$ is different from that around cations of alkali atoms where multiple $H_2O$ units can bind to the cation.[5] The water molecules initially form four-member rings around the $H_2O$ molecules at the end of the $H_2O-Au-H_2O^+$ motif with $C_2$ symmetry. For $[Au(H_2O)_9]^+$ and $[Au(H_2O)_{10}]^+$, the sharing of the 9th and 10th $H_2O$ molecules between the rings at the two ends evidences the low temperature solvation around the cation. Beginning with $[Au(H_2O)_6]^+$, the additional water molecules are all bound to two other $H_2O$ molecules forming the series $[Au(H_2O)_{7-10}]^+$ and leading to almost similar B.E. The addition of $H_2O$ molecules does lead to a gradual filling of LUMO of $Au^+$, and therefore, the positive charge of the Au cation migrates to the cluster surface. It will be interesting to extend these studies to larger $Au_n^+$ clusters to investigate if the asymmetric $H_2O$ addition can lead to the solvation of the individual atoms. These will be reported later.

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**Supporting Information Available:** Supplemental tables with the comparison of binding energies of ground state water clusters with up to five water molecules, gold valence basis set size convergence, and frequencies of the ground state structures for the $[Au(H_2O)_n]^+$clusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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