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Manuscript Title	Probing the Hydrogen Bonding in Microsolvated Clusters of $Au_{1,2}^{-}(Solv)_n$ ($Solv=C_2H_5OH$, $n\text{-}C_3H_7OH$; n=1-3 for Au^-; n=1 for Au_2^-)
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Figures	None

Probing the Hydrogen Bonding in Microsolvated Clusters of $Au_{1,2}^-$(Solv)n (Solv=C_2H_5OH, n-C_3H_7OH; n=1-3 for Au^-; n=1 for Au_2^-)

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Supporting Information

Table S1. The electronic energy (include zero point energy correction) and Gibbs free energy difference between trans and gauche isomers for $Au^-(C_2H_5OH)$ under several theoretical methods.

Relative Energy	Theoretical Methods				
	mPW2PLYP	MP2	B3LYP	B3PW91	HF
$\Delta E_{ZPE}{}^a$ (kcal/mol)	0.28	1.19	−0.014	0.065	−0.31
$\Delta E_{Gibbs}{}^b$ (kcal/mol)	0.010	0.67	−0.18	−0.15	−0.39

^{a} The total electronic energy difference including ZPE correction, $\Delta E_{ZPE}=E_{trans}-E_{gauche}$
^{b} The Gibbs free energy difference, $\Delta E_{Gibbs}=E_{trans}-E_{gauche}$, at temperature 200 K.

In this table, there are three methods support the gauche conformer is the most stable one, the energy differences are 0.28 kcal/mol, 1.19 kcal/mol and 0.065 kcal/mol for mPW2PLYP, MP2 and B3PW91 method, respectively. Under HF and B3LYP methods, the results are different. The trans conformer is more stable than gauche conformer by 0.31 kcal/mol for HF method. For B3LYP method, electronic energies of both conformers are almost the same, the difference is only 0.014 kcal/mol. However, if the zero-point energy (ZPE) correction is not included, for B3LYP method, the total electronic energy of gauche isomer is lower than trans one by 0.003 kcal/mol. However, when the thermal correction of free energy is considered, the relative stability of these two conformer is changed in B3PW91 method.

In order to understand the energies difference between trans and gauche isomers, the total electronic energy analysis was performed by decomposed to six components, that are ET, EV, EJ, EK, Ec and ENuc, respectively. The difference of every energy component between trans and

gauche isomer was calculated under various theoretical methods, the calculation results were list

in Table S2. In these energy components, the ET term is the electronic kinetic energy, the EV term

is the electron-nucleus attraction energy, the EJ term is the coulomb term of electrons, EK term is

the electronic exchange energy, Ec term is the correlation energy correction, and Etot is total

electronic energy which include the correlation energy correction. In additional, ENTVJK term is

the sum of ET, EV, EJ, EK and ENuc.

Table S2. The participation energy difference analysis between tans and gauche isomers of

$Au^-(C_2H_5OH)$ complex.

Theoretical methods	Energy difference terms ΔE^a (kcal/mol)							
	$\Delta ENuc$	ΔET	ΔEV	ΔEJ	ΔEK	ΔEc	$\Delta ENTVJK$	$\Delta Etot$
HF	−1953.17	1.12	3969.79	−2017.72	−0.30	0.00	−0.28	−0.28
MP2	−3744.07	−0.83	7588.92	−3846.12	0.76	2.66	−1.35	1.31
mPW2PLYP	−2973.25	0.58	6035.66	−3063.48	−0.02	0.80	−0.51	0.36
B3LYP	−2456.92	0.68	4989.76	−2533.32	−0.41	0.26	−0.21	0.05
B3PW91	−2633.13	0.89	5346.99	−2714.46	−0.56	0.40	−0.27	0.14

[a] $\Delta E = E_{trans} - E_{gauch}$

As shown in Table S2, if do not consider the Ec term, the electronic energy of trans isomer is

lower than gauche one under all the theoretical method here, the results are list the $\Delta ENTVJK$

column. When the Ec term is included, the results are converted. It is probably that the electrons

correlation interaction, which maybe include dispersion force, or hyperconjugation effect,

determined the gauche conformer is more stable than trans one in the $Au^-(C_2H_5OH)$ complex.

Hartree-Fock method is not reliable in most electronic structure analysis because the electronic

correlation energy is not considered.