Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Hydrogen Bonding in Microsolvation：Photoelectron Imaging and Theoretical Studies on Au_x^-–$(H_2O)_n$ and Au_x^-–$(CH_3OH)_n$ (x=1, 2; n = 1, 2) Complexes

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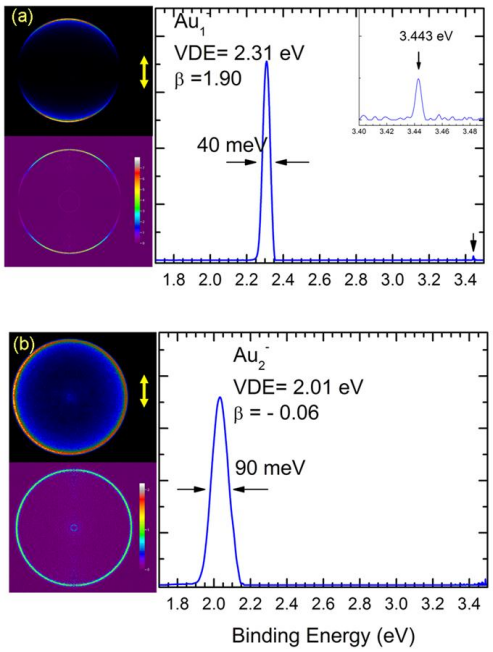

Figure S1 The raw images (top on the left) and the reconstructed (bottom on the left) images and photoelectron spectra of Au_1^- and Au_2^- taken at 355nm (3.49 eV). The double arrows show the directions of the laser polarization. The number in spectra shows full width of half-maximum (FWHM).

The photoelectron velocity-map images and the photoelectron spectra (PES) of Au^- and Au_2^- obtained at 355 nm (3.49 eV) are shown in Figure S1. The ground state transitions of Au^- and Au_2^- located at 2.31 and 2.01 eV are observed. The full width at half-maximum (FWHM) of the ground state transition of Au^- is 40 meV, close to our instrumental resolution which is dependent on electron kinetic energy (eKE).

Table S1 Natural charge of NHBs obtained by NBO analysis (MP2/aug-cc-pVTZ(pp)).

	X	H	O
Au^-–(H_2O)	-0.95	0.49	-1.00
Cl^-–(H_2O)	-0.96	0.52	-1.00
Au^-–(CH_3OH)	-0.92	0.49	-0.84
Cl^-–(CH_3OH)	-0.95	0.52	-0.84

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Optimized Cartesian Coordinates and binding Energies at the MP2/aug-cc-pVTZ(pp) level of theory level of theory

Au^--(H_2O) isomer 1 E_b = -14.29 kcal/mol

Au	0.354543	0.000946	0.000000
H	-1.927313	-0.275221	0.000019
O	-2.901076	-0.084660	-0.000002
H	-2.872957	0.877766	0.000004

Au^--(H_2O)$_2$ isomer 2 E_b = -29.12 kcal/mol

Au	-0.154206	-0.395581	0.054124
H	0.262924	1.960472	0.074381
O	0.025527	2.913013	0.043653
H	-0.931288	2.827538	-0.078299
O	-2.679799	1.527875	-0.028557
H	-1.950134	0.860899	-0.171013
H	-2.741684	1.503404	0.932994

Au^--(CH_3OH) isomer 3 E_b = -16.00 kcal/mol

Au	-0.00049	0.00000	0.0001
H	0.01265	0.00000	2.18671
O	0.25876	0.00000	3.15568
C	1.66969	0.00000	3.17013
H	1.99029	0.00000	4.21408
H	2.08548	0.88258	2.67341
H	2.08548	-0.88258	2.67341

Au^--(CH_3OH)$_2$ isomer 4a E_b = -31.02 kcal/mol

Au	-0.08436476	-0.34912204	0.09200584
H	0.36288628	1.78041814	-0.16972179
O	0.31269066	2.76449112	-0.31747506
C	-1.05164283	3.02656239	-0.57390512
H	-1.17585982	4.10964218	-0.62526307
H	-1.69792870	2.63224328	0.21581766
H	-1.38355216	2.59057168	-1.52207805
H	0.63969652	-0.62334511	-1.98896016
O	0.85354957	-0.54557440	-2.95487289
C	0.28137228	0.68439347	-3.35862044
H	0.57631375	0.85852254	-4.39484220
H	0.62827421	1.51923581	-2.74395749
H	-0.81264701	0.66021237	-3.30809684

$Au^-(CH_3OH)_2$ isomer 4b E_b = -29.72 kcal/mol

Au	1.03490072	-0.17743525	0.04727870
H	-0.65237417	0.85444929	-0.61378974
O	-1.53946069	1.34195594	-0.67814658
C	-1.69769102	1.98305317	0.57881475
H	-2.75870108	1.98839368	0.83609503
H	-1.33909292	3.01642862	0.54190811
H	-1.13800301	1.45055103	1.35209132
H	-2.72100952	0.01885099	-0.68387266
O	-3.30475161	-0.75132143	-0.51391829
C	-2.59512708	-1.56680994	0.40891424
H	-2.85510809	-2.60959071	0.21817669
H	-2.87184713	-1.32983020	1.44298952
H	-1.51233741	-1.44380419	0.30796491

$Au_2^-(H_2O)$ isomer 5 E_b = -12.55 kcal/mol

Au	1.25970800	-0.18156500	0.00001200
O	-0.00246400	3.00016500	0.00000200
H	0.73558200	2.36800900	0.00000900
Au	-1.25947700	-0.18210200	-0.00001200
H	-0.73415100	2.36038700	-0.00000600

$Au_2^-(H_2O)_2$ isomer 6a E_b = -24.44 kcal/mol

Au	1.112812	-0.576594	0.058444
H	0.907314	1.671816	1.427755
O	0.300269	2.431158	1.434119
H	1.154960	2.865285	-0.426042
O	1.604778	2.649017	-1.257575
Au	-1.344793	-0.041792	-0.086334
H	-0.483043	1.990741	1.053138
H	1.506873	1.683280	-1.263882

$Au_2^-(H_2O)_2$ isomer 6b E_b = -23.83 kcal/mol

Au	-1.26053000	0.00058900	-0.18202400
Au	1.26032900	-0.00059800	-0.18228600
O	0.00336200	2.72239600	1.50292400
H	-0.73482100	2.17846500	1.18443000
O	-0.00176000	-2.72238800	1.50287400
H	-0.73715400	-2.17569400	1.18244900
H	0.73637100	-2.17798500	1.18507100
H	0.73871700	2.17587100	1.18212800

Au_2^--(CH_3OH) isomer 7 E_b = -12.52 kcal/mol

Au	1.05748	-0.76101	0.20322
Au	-1.28584	0.10782	-0.08678
O	2.07651	2.32869	-0.4238
H	1.84725	1.37764	-0.34892
C	1.06413	3.02647	0.2836
H	1.23674	4.09174	0.12479
H	0.0655	2.76138	-0.07203
H	1.10254	2.82019	1.35744

Au_2^--(CH_3OH)$_2$ isomer 8a E_b = -19.42 kcal/mol

Au	-1.249756	-0.529637	0.154805
Au	1.245363	-0.538747	-0.154860
O	-1.274198	2.250372	-1.670546
O	1.292745	2.240305	1.671060
H	-1.308534	1.422431	-1.146865
H	1.320649	1.412419	1.146948
C	0.098540	2.507883	-1.932289
H	0.138607	3.380406	-2.585360
H	0.658792	2.722399	-1.018816
H	0.581368	1.664628	-2.431560
C	-0.077998	2.508349	1.932348
H	-0.567796	1.668370	2.430328
H	-0.111654	3.380441	2.586388
H	-0.636003	2.728412	1.018792

Au_2^--(CH_3OH)$_2$ isomer 8b E_b = -19.04 kcal/mol

Au	-0.325011	-1.076533	-0.058623
H	-1.255918	0.898016	-0.760830
O	-1.787968	1.726297	-0.824995
C	-1.384752	2.538520	0.273612
H	-1.825179	3.523456	0.122544
H	-0.297124	2.619245	0.318850
H	-1.740020	2.130822	1.224013
H	-3.529139	1.265163	-0.587606
O	-4.409948	0.945161	-0.305892
C	-4.167241	-0.018843	0.705317
H	-3.339442	-0.684292	0.445504
H	-5.073974	-0.611813	0.825113
H	-3.933536	0.449951	1.667154
Au	1.640070	0.493238	0.057595

Cl^-- (H_2O)

Cl	-1.12180900	0.00490500	0.00000100
H	1.01650100	-0.20820600	0.00000100
O	1.99888200	-0.09263700	-0.00000400
H	2.06320000	0.86591600	0.00000500

Cl^-- (CH_3OH)

Cl	1.43797600	-0.79399200	0.00000000
O	-0.82331400	1.28432800	0.00000000
C	-1.88474300	0.35784300	0.00000000
H	-2.82097400	0.91964900	0.00000000
H	-1.86482100	-0.28878400	0.88281800
H	-1.86482100	-0.28878400	-0.88281800
H	0.00000000	0.73409100	0.00000000