Dihydrogen bond interactions as a result of H_2 cleavage at Cu, Ag and Au centres

Supplementary Information

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Abstract

A quantum chemical study of the H_2 activation at fluorides of coinage metals, MF (M = Cu, Ag and Au), and its splitting was performed. The following reaction path was analyzed: FM···H_2 → FH···HM → HM···FH, where both the molecular complexes and the corresponding transition states have been characterized at the CCSD(T)/aug-cc-pVQZ//MP2/aug-cc-pVQZ level of theory. Further single-point CASSCF/CASPT2 calculations, including spin-orbit coupling effects, were also performed to analyze the role of non-dynamical correlation. The scalar relativistic effects are included via aug-cc-pVQZ-PP basis sets used for the metals. The dihydrogen-bonded copper (FH···HCu) and silver (FH···HAg) complexes are observed as a result of the H_2 cleavage, while the corresponding FH···HAu gold complex is not found but the HAu···HF arrangement is observed, instead. The energetic and geometrical parameters of the complexes have been analyzed and both the Quantum Theory of Atoms in Molecules approach and the Natural Bond Orbitals method were additionally applied to analyze the intermolecular interactions.

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Table 1SI. Geometrical parameters (Å, degrees) for the complexes linked through DHB (HAu···HF link, for gold complex); H···H intermolecular distance (H···Au distance, in the case of gold complex), FH···H angle (FH···Au angle for gold) and MH···H angle (for Au, HAu···H).

Metal	H···H(Au)	FH···H(Au)	MH···H
Cu	1.682	175.2	103.3
Ag	1.717	176.5	103.7
Au	2.366	174.3	72.8

Table 2SI. QTAIM parameters: ρ_{BCP}, $\nabla^2\rho_{BCP}$ and H_{BCP} (in au).

Complex	BCP type	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}
FCu···H_2	Cu···σ	0.136	0.407	-0.076
FAg···H_2	Ag···σ	0.106	0.320	-0.043
FAu···H_2	Au···σ	0.162	0.170	-0.107
CuH···HF	H···H	0.025	0.042	-0.003
AgH···HF	H···H	0.023	0.037	-0.003
HAu···HF	Au···H	0.022	0.044	-0.003
HCu···FH	Cu···F	0.064	0.433	-0.014
HAg···FH	Ag···F	0.040	0.232	-0.003
HAu···FH	Au···F	0.049	0.276	-0.006

Table 3SI. Most relevant orbital-orbital overlaps for the complexes in gas phase and the corresponding interaction energies, E_{NBO} (in kcal/mol).

Complex	Orbital-orbital overlap	E_{NBO}
FCu···H_2	$\sigma_{HH} \rightarrow n_{Cu}^*$	100.9
FAg···H_2	$\sigma_{HH} \rightarrow n_{Ag}^*$	57.4
FAu···H_2	$\sigma_{HH} \rightarrow n_{Au}^*$	319.8
CuH···HF	$\sigma_{CuH} \rightarrow \sigma_{HF}^*$	11.8
AgH···HF	$\sigma_{AgH} \rightarrow \sigma_{HF}^*$	11.3
HAu···HF	$\sigma_{AuH} \rightarrow \sigma_{HF}^*$	2.7
	$n_{Au} \rightarrow \sigma_{HF}^*$	6.2
HCu···FH	$\sigma_{HF} \rightarrow \sigma_{CuH}^*$	2.5
	$n_F \rightarrow \sigma_{CuH}^*$	22.7
	$n_F \rightarrow n_{Cu}^*$	16.2
HAg···FH	$\sigma_{FH} \rightarrow \sigma_{AgH}^*$	1.1
	$n_F \rightarrow \sigma_{AgH}^*$	15.0
	$n_F \rightarrow n_{Ag}^*$	4.3
HAu···FH	$\sigma_{FH} \rightarrow \sigma_{AuH}^*$	1.3
	$n_F \rightarrow \sigma_{AuH}^*$	22.8
	$n_F \rightarrow n_{Au}^*$	2.3

MP2/aug-cc-pVQZ-PP geometries of complexes analyzed here

F-Cu…H_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.311181	-0.000023	-0.000009
2	9	0	1.392322	0.000031	0.000013
3	1	0	-1.753229	0.418378	0.000071
4	1	0	-1.753420	-0.417994	0.000071

F-Ag…H_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	47	0	-0.241500	-0.000003	0.000011
2	9	0	1.691399	0.000007	-0.000078
3	1	0	-1.936044	0.398749	0.000086
4	1	0	-1.936046	-0.398682	0.000093

F-Au…H_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	0.155783	0.000000	0.000006
2	9	0	-1.737230	0.000001	-0.000068
3	1	0	1.664108	-0.477565	0.000061
4	1	0	1.664104	0.477577	0.000070

Cu-H…H-F

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.036208	-0.824214	0.000000
2	1	0	-1.064958	0.097618	0.000000
3	1	0	-0.310963	1.601211	0.000000
4	9	0	0.036208	2.467041	0.000000

Ag-H…H-F

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	47	0	0.027290	-0.595144	0.000000
2	1	0	-1.167985	0.471515	0.000000
3	1	0	-0.360244	1.986572	0.000000
4	9	0	0.027290	2.834854	0.000000

H-Au…H-F

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	0.016684	-0.359987	0.000000
2	1	0	-1.418730	0.041582	0.000000
3	1	0	-0.049437	2.005555	0.000000
4	9	0	0.016684	2.932422	0.000000

H-Cu…F-H

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.470162	-0.000857	-0.000078
2	9	0	1.513030	-0.091516	0.000257
3	1	0	-1.889195	0.100973	-0.000343
4	1	0	1.906615	0.747536	0.000305

H-Ag…F-H

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	47	0	-0.379925	-0.001533	-0.000066
2	9	0	1.935738	-0.086294	0.000338
3	1	0	-1.947275	0.126049	-0.000342
4	1	0	2.382127	0.722658	0.000391

H-Au…F-H

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	-0.241108	-0.000636	-0.000042
2	9	0	2.045358	-0.091299	0.000358
3	1	0	-1.734749	0.097722	-0.000305
4	1	0	2.374065	0.774225	0.000392