Optimization of a new reactive force field for silver-based materials

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SUPPORTING INFORMATION

	parameters	description	Ref. 24	new
1	r_0^sigma	Sigma bond covalent radius	**2.3644**	**2.4518**
2	Val_i	Valency	2.0000	2.0000
3	n/a	Atomic mass	63.5460	107.8682
4	r_vdW	van der Waals radius	**1.9896**	**2.0128**
5	D_ij	van der Waals dissociation energy	**0.4000**	**0.3165**
6	gamma_i	gammaEEM; EEM shielding	0.4200	0.4200
7	r_0^pi	Pi bond covalent radius	0.1000	0.1000
8	Val_i^e	Number of valence electrons	1.0000	1.0000
9	alpha_ij	van der Waals parameter	**11.3629**	**11.0461**
10	1/gamma_w	van der Waals shielding	**100.0000**	**99.9077**
11	Val_j^angle	Valency for 1,3-BO correction	1.0000	1.0000
12	p_ovun5	Undercoordination energy	0.0000	0.0000
13	p_i^xel2	eReaxFF, atom type parameter	0.0000	0.0000
14	chi_i	EEM electronegativity	0.5000	1.0082
15	eta_i	EEM hardness	6.0000	8.9305
16	n/a	Donor or acceptor switch in H-bonds	0.0000	0.0000
17	r_0^pi	Double pi bond covalent radius	-1.0000	-1.0000
18	p_lp2	Lone pair energy	0.0000	0.0000
19	n/a	Atomic heat of formation	80.7000	80.7000
20	p_boc4	Bond order correction	**34.9923**	**35.750**
21	p_boc3	Bond order correction	**2.3973**	**5.2466**
22	p_boc5	Bond order correction	0.0000	0.0000
23	C_i	Atomic softness cutoff parameter	0.8563	0.8563
24	alpha, alpha_i	eReaxFF, constant, dependent on atom type	0.0000	0.0000
25	p_ovun2	Valence angle parameter	**-5.1872**	**-7.7845**
26	p_val3	Valence angle parameter	**3.8628**	**3.6694**
27	beta, beta_i	eReaxFF, constant, dependent on atom type	1.0000	1.0000
28	Val_i^'boc	Number of lone pairs	4.0000	4.0000
29	p_val5	Valence angle parameter	2.5791	2.5791
30	p_c1	Inner wall vdW repulsion parameter	0.0000	0.0000
31	p_c2	Inner wall vdW repulsion parameter	0.0000	0.0000
32	p_c3	Inner wall vdW repulsion parameter	0.0000	0.0000
33	C_i	Lg dispersion parameter	0.0000	0.0000
34	R_eij	VdW Radius for Lg dispersion correction	0.0000	0.0000

Table S1 : Atomic parameters for silver: comparison between ReaxFF(lit)[24] and the new force field. The optimized parameters a The optimized parameters are colored in red.

	parameters	Description	Ref. 24	new
1	D_e^sigma	Sigma-bond dissociation energy	**59.5179**	**67.7805**
2	D_e^pi	Pi-bond dissociation energy	0.0000	0.0000
3	D_e^pipi	Double pi-bond dissociation energy	0.0000	0.0000
4	p_be1	Bond energy parameter	**-0.2379**	**-0.4891**
5	p_bo5	Double pi bond parameter	-0.2000	-0.2000
6	Val'_i^boc	1,3-Bond order correction	0.0000	0.0000
7	p_bo6	Double pi bond order	16.0000	16.0000
8	p_ovun1	Overcoordination penalty	**0.3340**	**0.3130**
9	p_be2	Bond energy parameter	**0.2271**	**1.4433**
10	p_bo3	Pi bond order parameter	-0.2000	-0.2000
11	p_bo4	Pi bond order parameter	15.0000	15.0000
12	unused	n/a	1.0000	1.0000
13	p_bo1	Sigma bond order	**-0.2376**	**-0.1785**
14	p_bo2	Sigma bond order	**5.1970**	**4.8876**
15	delta'_i	Uncorrected BO overcoordination	0.0000	0.0000
16	p_ij^xel1	e ReaxFF param	0.0000	0.0000

Table S2 : Bond parameters for silver : comparison between ReaxFF(lit) and the new force field. The optimized parameters are displayed in red letters.

	parameters	description	new
1	D_e^sigma	Sigma-bond dissociation energy	129.5847
2	D_e^pi	Pi-bond dissociation energy	0.0000
3	D_e^pipi	Double pi-bond dissociation energy	0.0000
4	p_be1	Bond energy parameter	-0.6766
5	p_bo5	Double pi bond parameter	-0.2000
6	Val'_i^boc	1,3-Bond order correction	0.0000
7	p_bo6	Double pi bond order	16.0000
8	p_ovun1	Overcoordination penalty	-0.0198
9	p_be2	Bond energy parameter	0.1321
10	p_bo3	Pi bond order parameter	-0.2000
11	p_bo4	Pi bond order parameter	15.0000
12	unused	n/a	1.0000
13	p_bo1	Sigma bond order	-0.4592
14	p_bo2	Sigma bond order	5.2259
15	delta'_i	Uncorrected BO overcoordination	0.0000
16	p_ij^xel1	e ReaxFF param	0.0000

Table S3: Bond parameters for Ag-S of the new force field. The optimized parameters are displayed in red letters.

	parameters	description	new
1	D_ij	VdW energy	0.2440
2	r_vdW	VdW radius	2.0564
3	alpha_ij	VdW parameter	11.8537
4	r_0^sigma	Sigma bond length	2.1389
5	r_0^pi	Pi bond length	-1.0000
6	r_0^pipi	PiPi bond length	-1.0000
7	C_i, C_lg,ij	Lg dispersion parameter	-1.0000

Table S4: Off-diagonal parameters for Ag-S of the new force field. The optimized parameters are displayed in red letters.

	parameters	Description	new
1	Theta_0,0	180°-(equilibrium angle)	107.9986
2	p_val1	Valence angle parameter	-21.7445
3	p_val2	Valence angle parameter	15.6034
4	p_coa1	Valence conjugation	0.0000
5	p_val7	Undercoordination	2.4513
6	p_pen1	Penalty energy	0.0000
7	p_val4	Valence angle parameter	1.9208

Table S5: Torsion parameters for S-Ag-Ag of the new force field. The optimized parameters are displayed in red letters.

	parameters	Description	new
1	Theta_0,0	180°-(equilibrium angle)	53.9262
2	p_val1	Valence angle parameter	53.8120
3	p_val2	Valence angle parameter	20.9984
4	p_coa1	Valence conjugation	0.0000
5	p_val7	Undercoordination	4.9781
6	p_pen1	Penalty energy	0.0000
7	p_val4	Valence angle parameter	2.1841

Table S6: Torsion parameters for Ag-S-Ag of the new force field. The optimized parameters are displayed in red letters.

Isomers	potentials	E_{rel} / kcal/mol	d(Au-S) /Å	d(Au-Au) /Å	Au-S-Au/Å
EE_{edge}	***Järvi***	0	2.58	3.02	72
	Bae	0	2.48	3.16	79
	Monti	0	2.48	3.03	75
	DFT	0	2.37	3.25	87
VE	***Järvi***	15	2.59	3.01	71
	Bae	1	E : 2.49 V : 2.47	3.14	78
	Monti	9	E : 2.48 V : 2.49	3.01	75
	DFT	10	E : 2.43 V : 2.39	2.90	74
V	***Järvi***	56	2.54	-	-
	Bae	-30	2.42	-	-
	Monti	99	2.28	-	-
	DFT	23	2.28	-	-
FE_{down}	***Järvi***	76	E : 2.67 F : 2.63	2.97	68
	Bae	51	E : 2.50 F : 2.44	3.68	97
	Monti	129	E : 2.66 F : 2.55	3.01	71
	DFT	39	E : 2.46 F : 2.37	3.05	78
EE_{down}	***Järvi***	43	E : 2.61 V : 2.71	3.07	72
	Bae	-2	no bond Au-S	2.89	-
	Monti	114	E : 2.43 V : 2.38	3.02	77
	DFT	66	E : 2.50 V : 3.02	2.87	70

Table S7: Relative energies (kJ / mol), S-S and Au-Au interatomic distances (Å) and Au-S-Au angles (°) for each cluster optimized with three ReaxFF available (*Järvi, Bae, Monti*) as well as the DFT reference values.

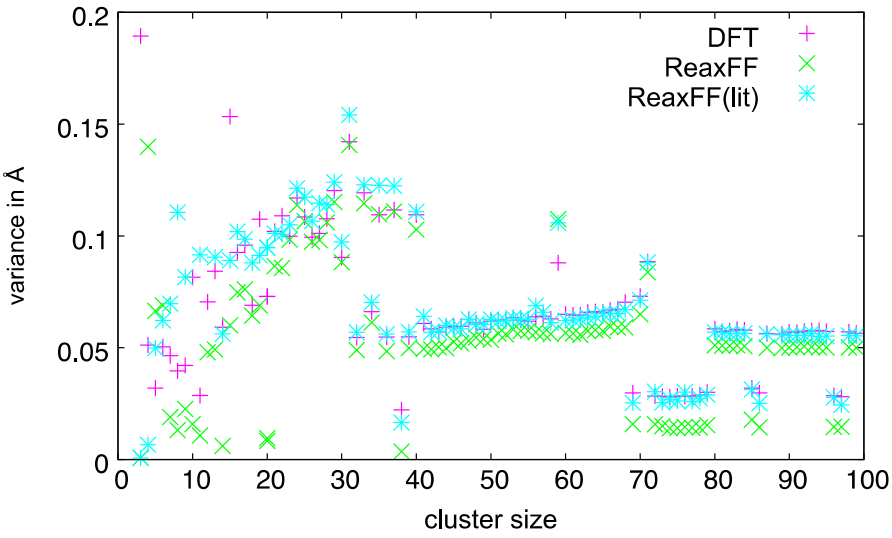


Figure S1: Standard deviation of the first-neighbor distances between silver atoms as a function of the cluster size (from 2 to 99 silver atoms) for DFT, the published reactive force field (ReaxFF (lit)),[24] and the one developed here (ReaxFF).

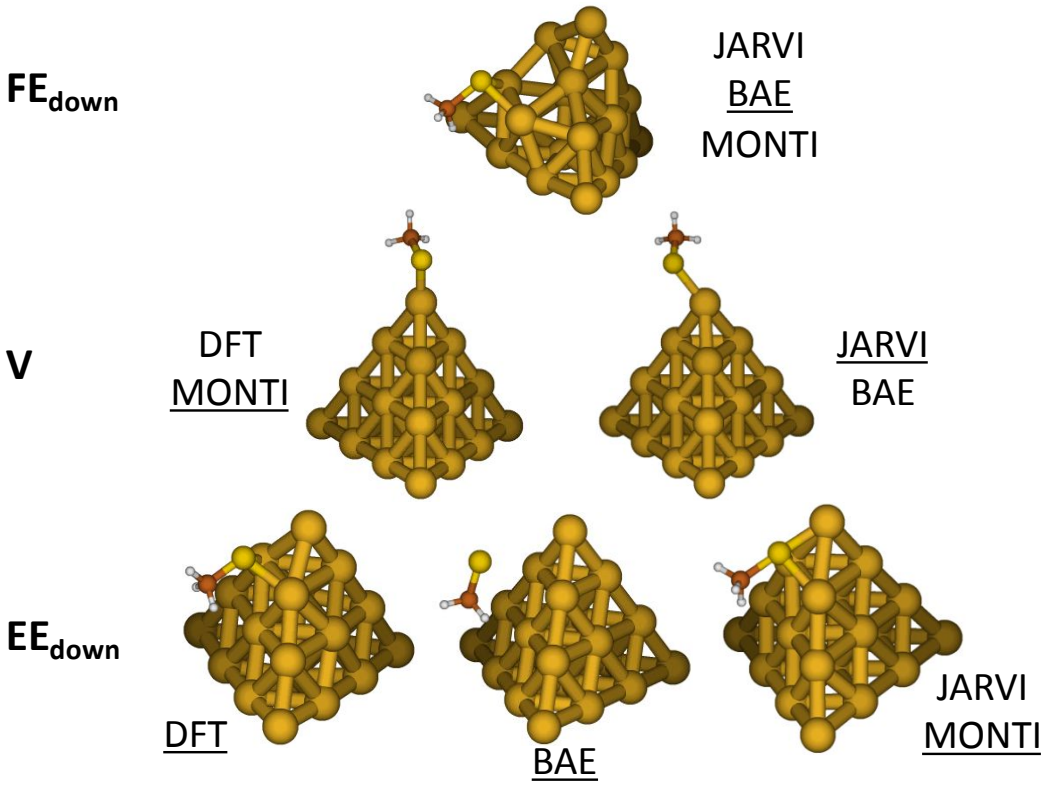


Figure S2: Examples of the different geometries obtained by ReaxFF and DFT for the FE_{down} (first line), V (second line) and EE_{down} (third line) isomers for MeS-Au_{20}. The shown structure corresponds to the underlined potential.

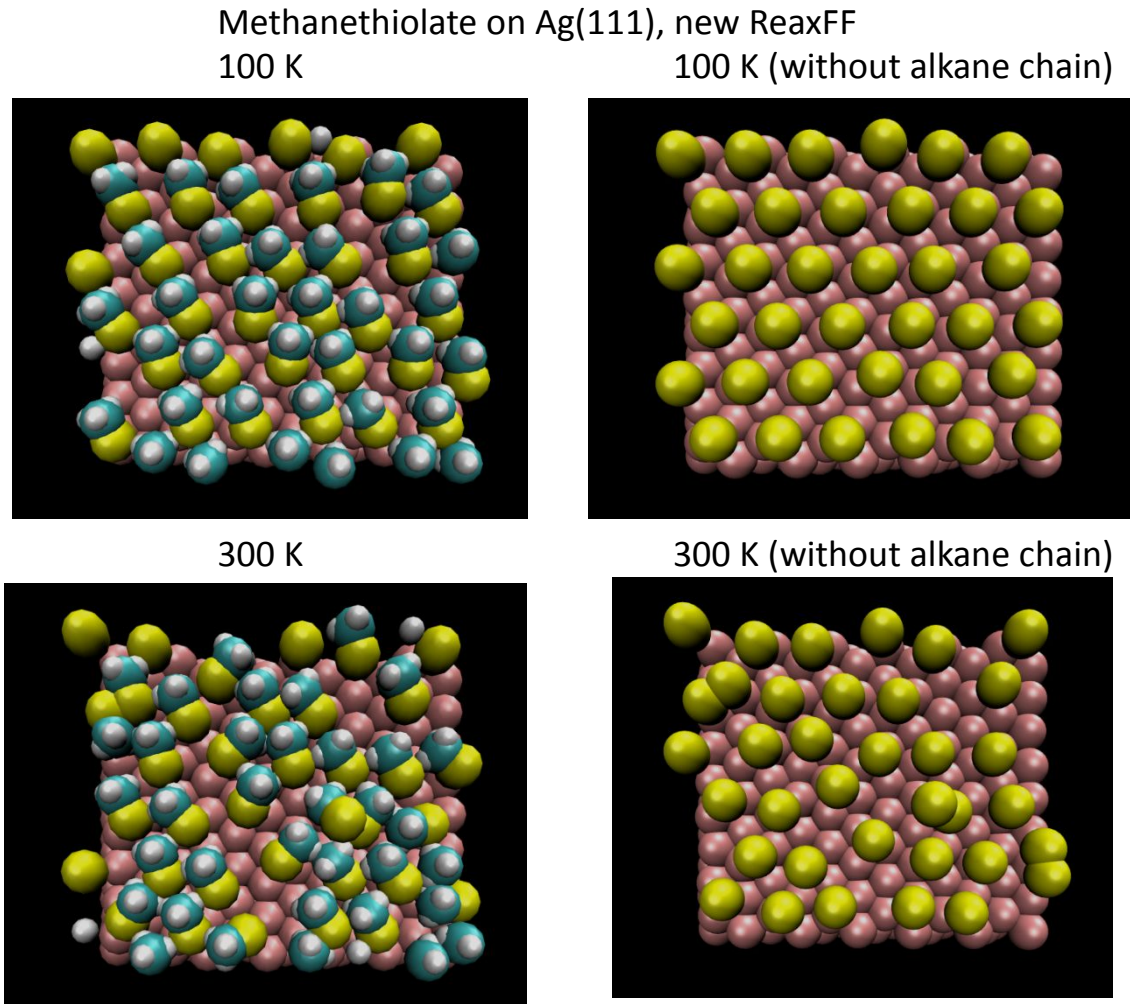


Figure S3: Snapshots of simulations of a SAM of methanethiolate on silver using the new ReaxFF at 100 and 300 K. On the right, the alkane chains have been removed to see the assembly of sulfur atoms.

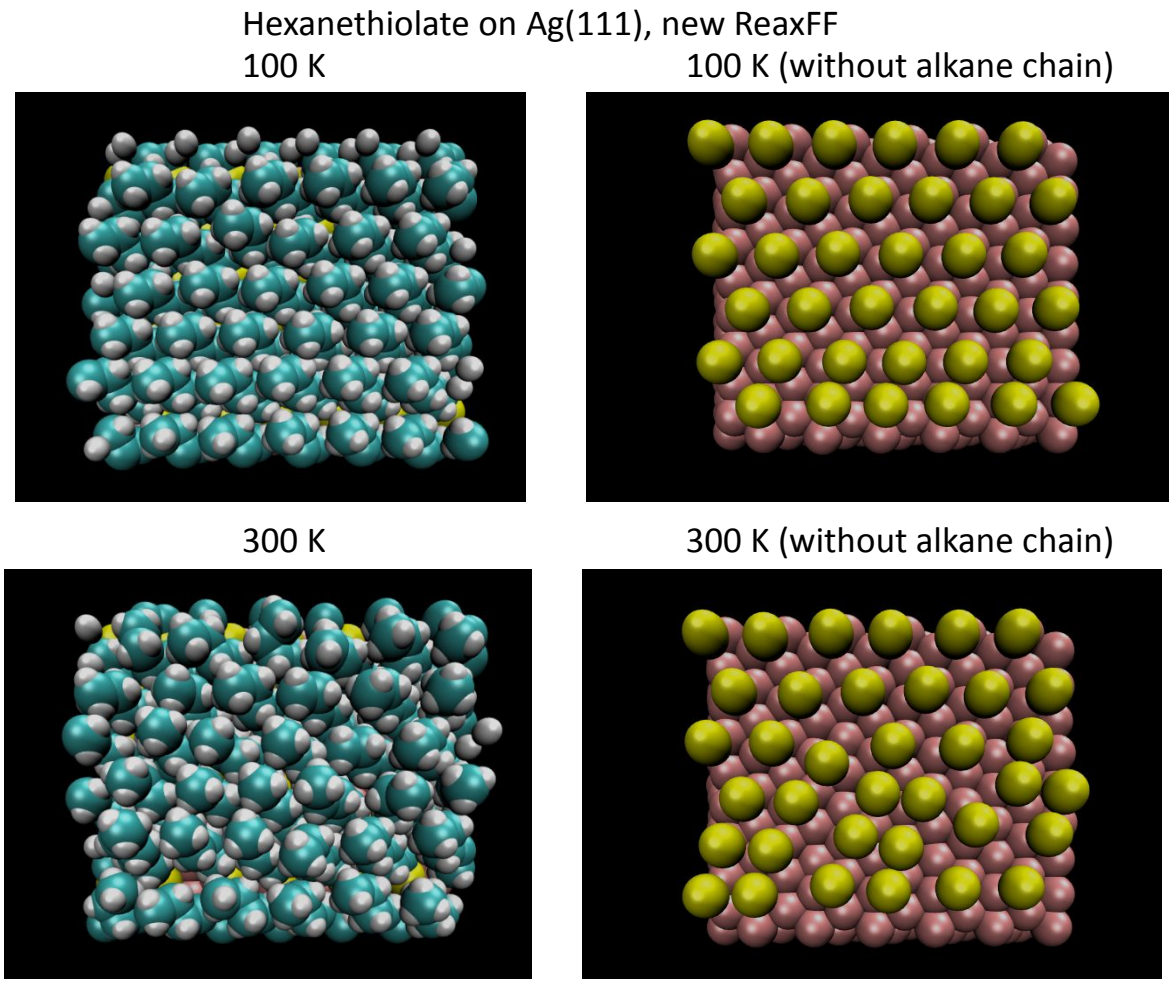


Figure S4: Snapshots of simulations of a SAM of hexanethiolate on silver using the new ReaxFF at 100 and 300 K. On the right, the alkane chains have been removed to see the assembly of sulfur atoms.

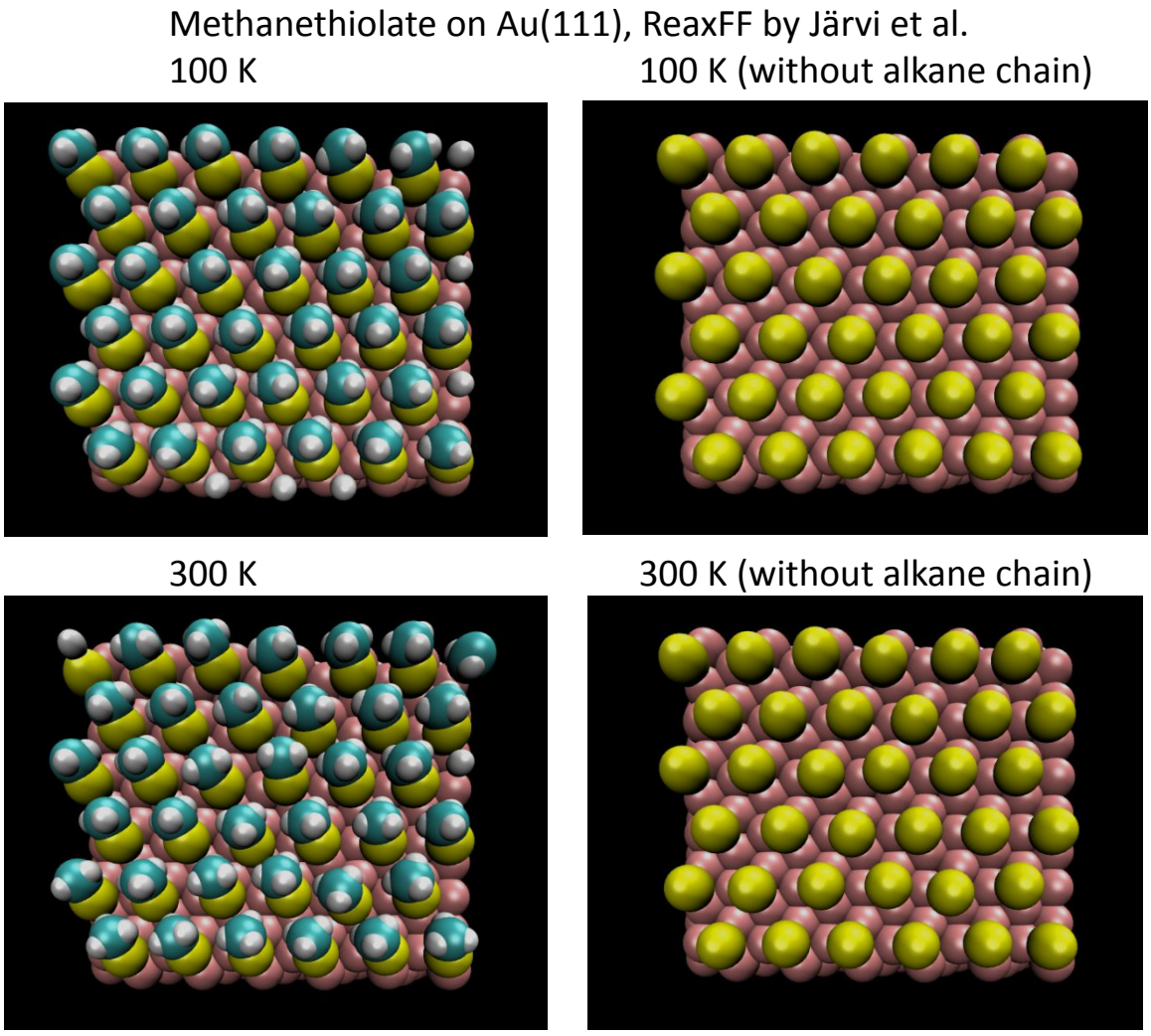


Figure S5: Snapshots of simulations of a SAM of methanethiolate on gold using the ReaxFF proposed by Järvi et al. at 100 and 300 K. On the right, the alkane chains have been removed to see the assembly of sulfur atoms.

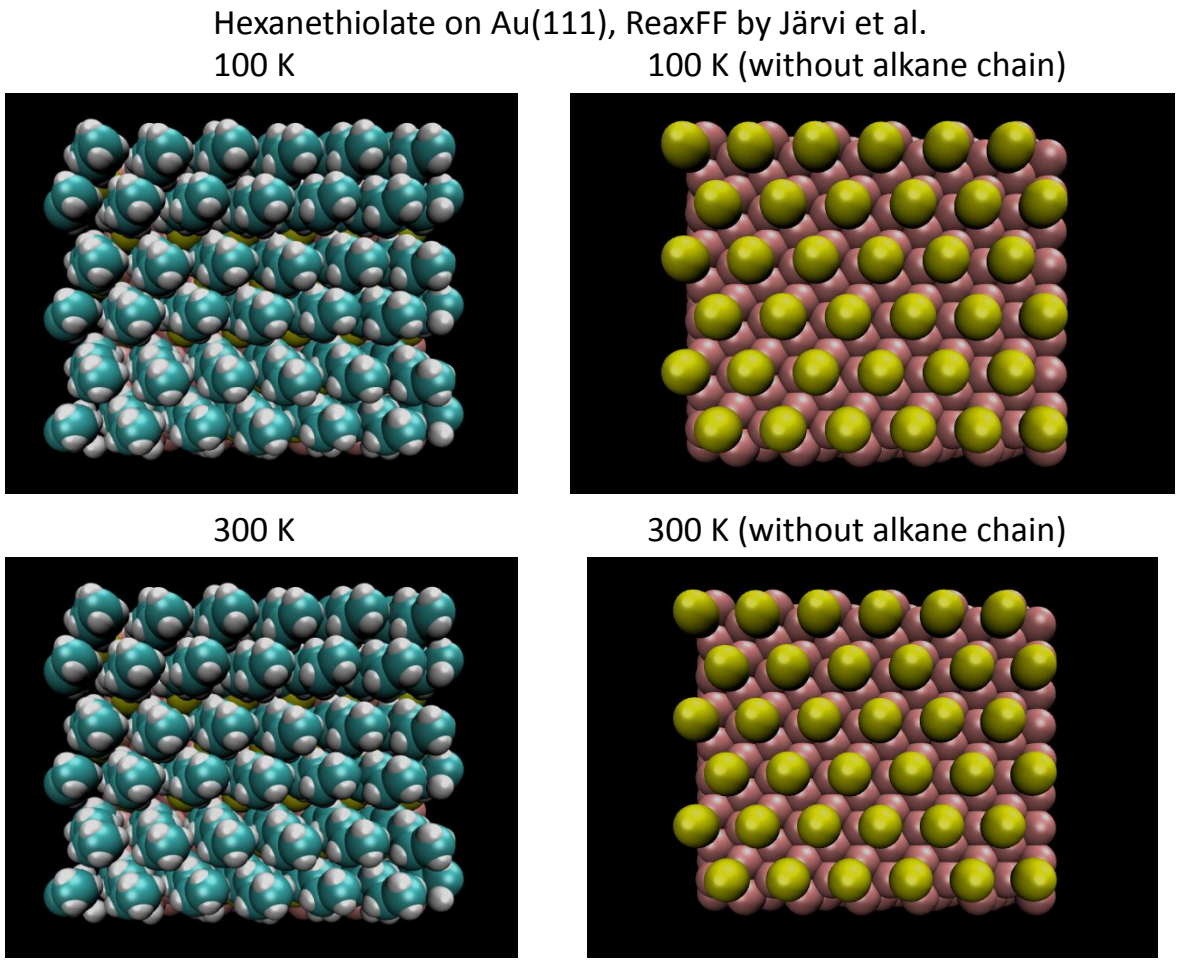


Figure S6: Snapshots of simulations of a SAM of hexanethiolate on gold using the ReaxFF proposed by Järvi et al. at 100 and 300 K. On the right, the alkane chains have been removed to see the assembly of sulfur atoms.

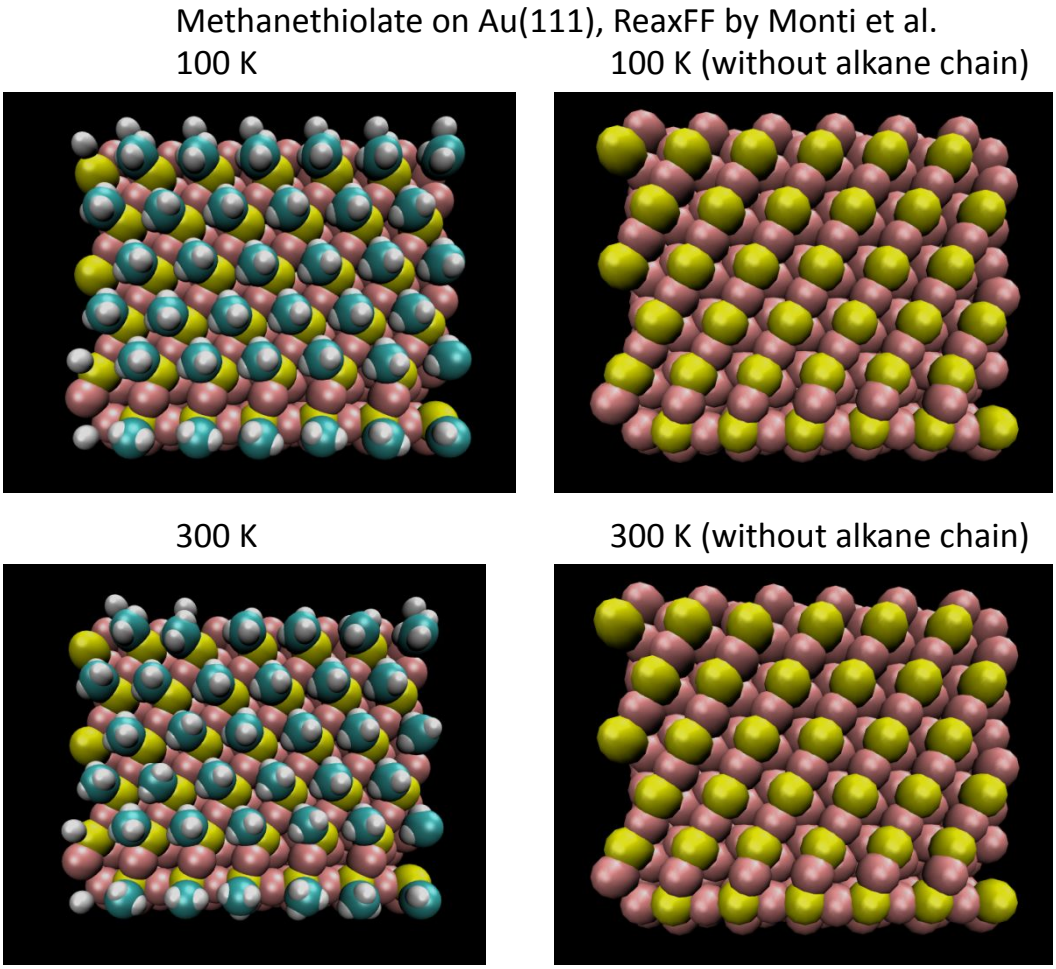
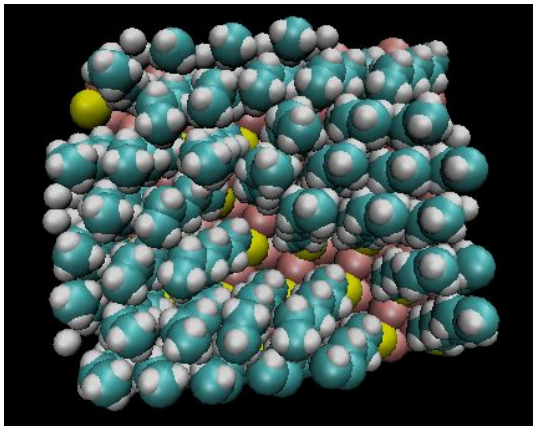


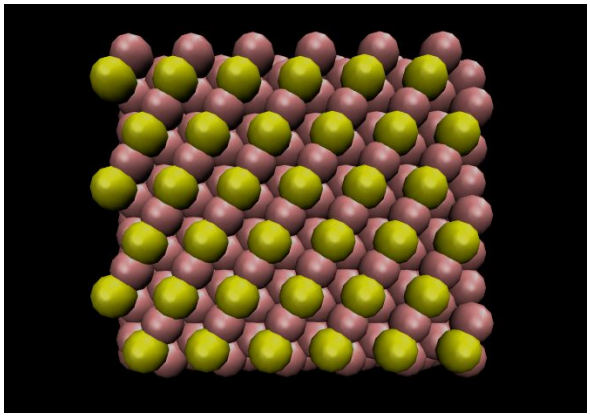
Figure S7: Snapshots of simulations of a SAM of methanethiolate on gold using the ReaxFF proposed by Monti et al. at 100 and 300 K. On the right, the alkane chains have been removed to see the assembly of sulfur atoms.

Hexanethiolate on Au(111), ReaxFF by Monti et al.

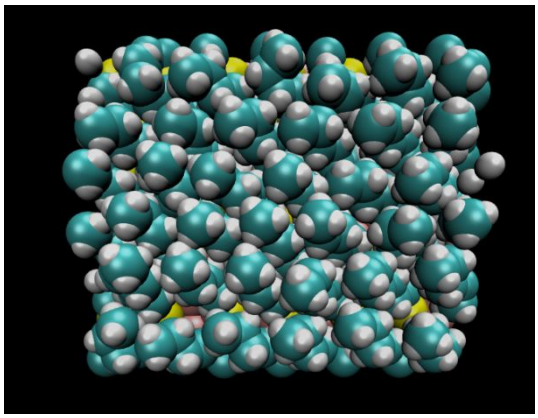
100 K



100 K (without alkane chain)



300 K



300 K (without alkane chain)

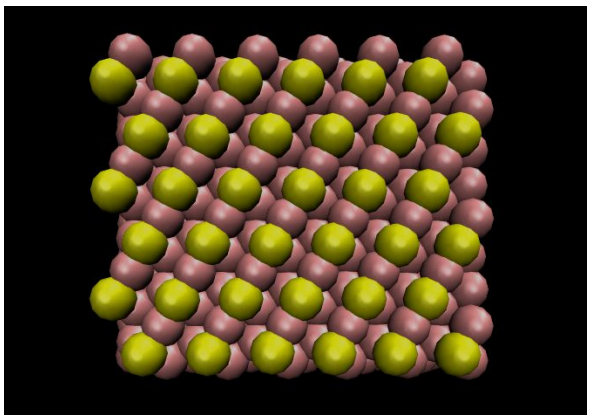


Figure S8: Snapshots of simulations of a SAM of hexanethiolate on gold using the two ReaxFF proposed by Monti et al. at 300 K. On the right, the alkane chains have been removed to see the assembly of sulfur atoms.

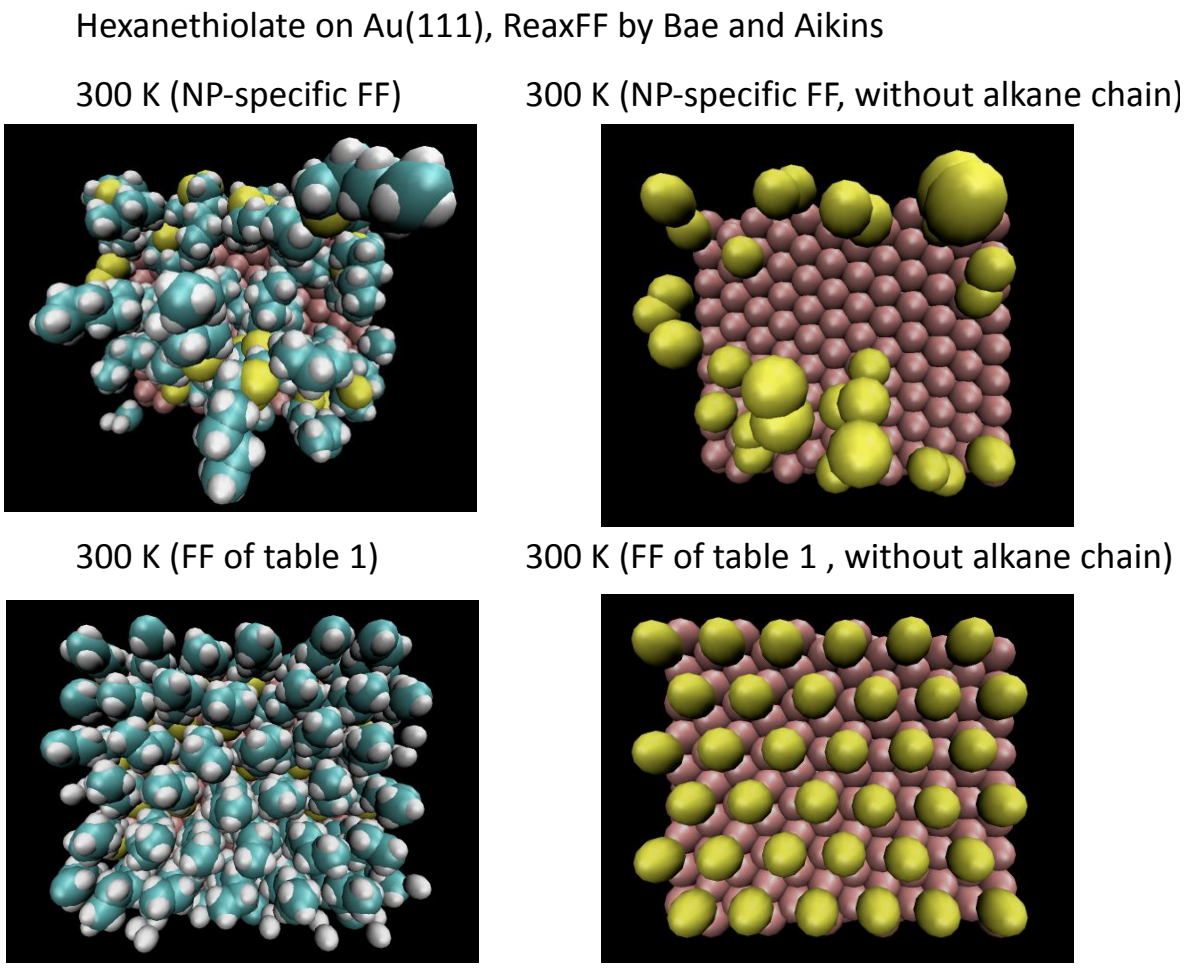


Figure S9: Snapshots of simulations of a SAM of hexanthiolate on gold using the two ReaxFF proposed by Bae et al. at 300K.