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Supporting Information

Large Scale Quantum Dynamics Investigations on the Sensing Mechanism of H_2O, Acetone, NO_2 and O_3 Adsorption on the $(MA)_2Pb(SCN)_2I_2$ Surface

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Table S1 The adsorption energies of four adsorption complexes

Time(ps)	$MAPbI_3$ -H_2O	$(MA)_2Pb(SCN)_2I_2$ -H_2O	$(MA)_2Pb(SCN)_2I_2$ -$CO(CH_3)_2$	$(MA)_2Pb(SCN)_2I_2$ -NO_2
0	-2.499	-1.209	2.868	2.436
5	-4.639	-6.412	-1.032	-0.698
10	-5.304	-5.232	-1.145	-1.432
15	-7.625	-5.847	-1.180	-3.087
20	-6.360	-9.916	-1.428	-7.061
25	-6.206	-9.047	-1.296	-9.807
30	-8.336	-6.017	-1.658	-7.572
35	-6.531	-6.377	-1.323	-8.172
40	-7.589	-9.202	-1.233	-8.315
45	-8.814	-7.374	-1.135	-7.622
50	-10.555	-8.630	-1.019	-9.145
55	-8.164	-7.994	-1.887	-8.409
60	-9.370	-8.811	-1.308	-7.695
65	-7.651	-8.213	-0.117	-9.802
70	-7.253	-8.808	-2.027	-8.046
75	-7.818	-8.607	-1.274	-8.241
80	-7.984	-7.781	-1.631	-9.882
85	-7.949	-8.375	-0.970	-9.993
90	-7.387	-8.866	-0.686	-10.292
95	-9.179	-10.057	-0.982	-9.700
100	-8.178	-9.528	-1.499	-10.011
105	-9.694	-9.083	-1.308	-9.543
110	-10.856	-7.786	-1.757	-9.279
115	-10.144	-9.134	-1.555	-9.690
120	-9.006	-9.369	-1.248	-10.716
125	-10.596	-10.888	-1.553	-9.622
130	-9.041	-9.741	-1.072	-9.948
135	-8.168	-7.547	-2.562	-9.697
140	-11.364	-8.082	-3.071	-10.066
145	-10.497	-8.317	-1.941	-10.067
150	-10.738	-7.451	-1.591	-10.762
155	-11.095	-8.948	-1.741	-9.766
160	-11.521	-10.689	-2.412	-11.073
165	-8.921	-10.719	-2.498	-9.874
170	-9.341	-10.690	-2.712	-9.918
175	-8.724	-9.924	-1.954	-9.822
180	-10.173	-10.756	-2.366	-9.424
185	-9.458	-11.808	-2.276	-9.977
190	-7.779	-10.597	-3.526	-10.462
195	-9.635	-11.095	-2.572	-10.157
200	-8.019	-12.986	-3.132	-10.264
205	-7.987	-7.149	-2.640	-9.880
210	-8.297	-9.075	-3.468	-9.769
215	-12.274	-7.723	-2.054	-10.534
220	-8.514	-9.794	-2.480	-10.077

Table S2 The charge transfer of four adsorption complexes

Time(ps)	$MAPbI_3$ -H_2O	$(MA)_2Pb(SCN)_2I_2$ -H_2O	$(MA)_2Pb(SCN)_2I_2$ -$CO(CH_3)_2$	$(MA)_2Pb(SCN)_2I_2$ -NO_2
0	0.601	0.289	0.159	1.512
5	0.579	0.231	0.045	1.795
10	0.557	0.162	0.049	2.344
15	0.595	0.251	0.094	2.607
20	0.629	0.249	0.111	3.324
25	0.768	0.226	0.085	3.724
30	0.626	0.281	0.039	3.514
35	0.649	0.372	0.057	3.615
40	0.564	0.323	0.080	3.417
45	0.606	0.430	0.055	3.524
50	0.671	0.455	0.069	3.572
55	0.682	0.288	0.060	3.629
60	0.688	0.221	0.075	3.652
65	0.609	0.263	0.058	3.678
70	0.643	0.332	0.091	3.592
75	0.679	0.409	0.084	3.462
80	0.691	0.430	0.099	3.693
85	0.683	0.517	0.067	3.702
90	0.671	0.483	0.122	3.709
95	0.538	0.315	0.101	3.948
100	0.609	0.466	0.128	3.787
105	0.566	0.463	0.101	3.980
110	0.679	0.352	0.123	3.610
115	0.756	0.308	0.104	3.710
120	0.826	0.383	0.220	3.805
125	0.628	0.271	0.182	3.616
130	0.694	0.363	0.142	3.893
135	0.889	0.367	0.176	3.742
140	0.791	0.200	0.129	3.681
145	1.010	0.330	0.098	3.885
150	0.830	0.506	0.199	3.948
155	0.745	0.426	0.213	3.781
160	0.749	0.378	0.139	4.050
165	0.873	0.406	0.177	3.890
170	0.709	0.423	0.126	3.852
175	0.540	0.382	0.163	3.857
180	0.713	0.472	0.165	3.834
185	0.611	0.333	0.185	3.746
190	0.626	0.367	0.178	3.706
195	0.719	0.374	0.170	3.707
200	0.743	0.400	0.206	3.813
205	0.653	0.517	0.156	3.697
210	0.674	0.509	0.148	3.827
215	0.757	0.279	0.144	3.857
220	0.733	0.436	0.144	3.701

Table S3 The adsorption energy and charge transfer of $(MA)_2Pb(SCN)_2I_2$-O_3

Time(ps)	Adsorption energy(eV)	Charge transfer(e)
0	1.972	2.455
5	-20.658	8.829
10	-31.452	12.281
15	-63.329	18.133
20	-130.557	21.129
25	-111.628	22.881
30	-133.063	24.908
35	-103.884	26.281
40	-109.523	26.293
45	-104.157	26.895
50	-107.833	27.233
55	-113.751	27.041
60	-104.764	26.930
65	-112.054	28.563
70	-112.938	28.403
75	-111.294	28.415
80	-109.973	28.994
85	-113.547	28.657
90	-115.034	29.302
95	-109.175	30.143
100	-119.000	28.509
105	-113.218	29.614
110	-117.334	28.953
115	-124.627	29.799
120	-118.589	30.143
125	-120.079	30.408
130	-113.964	30.135
135	-115.283	30.256
140	-119.989	30.812
145	-121.627	31.008
150	-119.291	31.147
155	-122.759	30.211
160	-123.352	30.221
165	-122.244	30.536
170	-120.142	30.649
175	-124.971	31.971
180	-124.063	30.978
185	-121.596	31.769
190	-120.632	31.509
195	-120.879	31.360
200	-120.061	31.728
205	-124.405	31.245
210	-124.917	31.185
215	-124.564	31.467
220	-124.694	31.096

The fluctuations of the adsorption energy in Fig. 8 a) could be introduced by the rotations of water molecules and the MA groups around their equilibrium positions during the adsorption process. To better understand the reason of the fluctuation of the adsorption energy of the $MAPbI_3$-H_2O and $(MA)_2Pb(SCN)_2I_2$-H_2O systems, the structural snapshots respectively corresponding to the maximum (210 ps) and minimum (215 ps) adsorption energy in the $MAPbI_3$-H_2O are shown for an example in

Fig.S1:

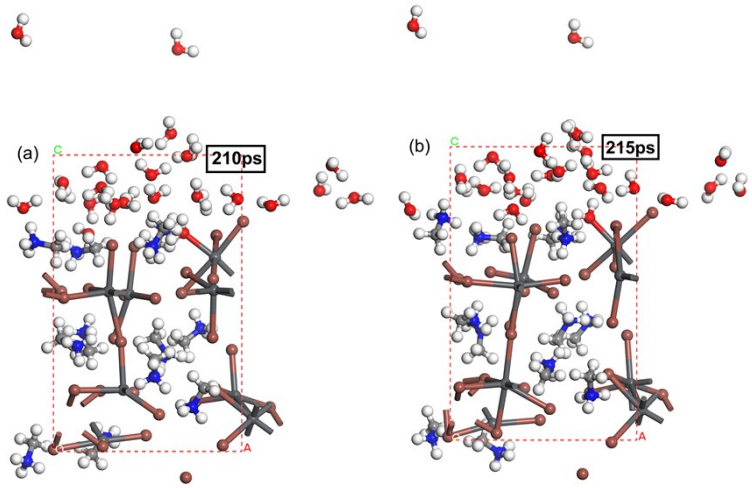

Fig. S1 The snapshots of 210 and 215 ps of the $MAPbI_3$-H_2O adsorption

From this figure, it can be seen clearly that the all the atoms, either from the perovskite skeleton or water molecules, do NOT display obvious displacement in the two pictures, which is consistent with the flat root mean square deviations (RMSD) curves (Fig. 2(a) in the manuscript). However, in Fig. 8(a), the fluctuation of the adsorption energy is somewhat obvious, it might be initiated by the rotations of water molecules and the MA groups in the perovskite skeleton and followed by the changes of the interactions between MA-H_2O.

To prove the influence of the rotation of water molecules on the adsorption energy calculations, simplified $MAPbI_3$-H_2O models were built and the adsorption energy were computed with the same parameter settings in the manuscript. As seen in Fig. S2, the only difference of the two models is the orientation of the two water molecules toward the surface of $MAPbI_3$. The adsorption energy changes are given in Table S4.

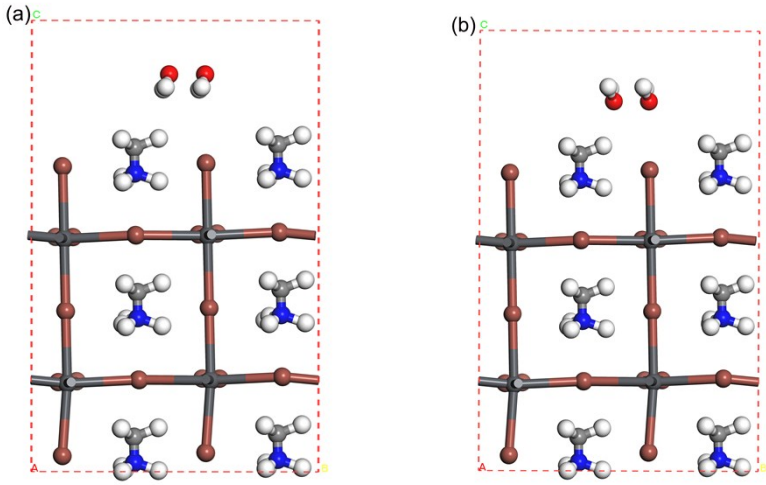

Fig. S2 The simplified $MAPbI_3$-H_2O adsorption models

Table S4. The energy of each component and the adsorption energy

		Model (a)	Model (b)
$E_{(perovskite+gas)}$	(eV)	-528.746	-528.498
$E_{(perovskite)}$	(eV)	-508.063	-508.063
$E_{(gas)}$	(eV)	-20.448	-20.466
E_{ad}	(eV)	-0.235	0.032

From both Fig. S2 and Table S4, it is clear that the adsorption energy of the whole system could be affected by the rotation of two water molecules by a difference of 0.267 eV. Considering there are 26 and 27 water molecules in the $MAPbI_3$-H_2O and $(MA)_2Pb(SCN)_2I_2$-H_2O, respectively, the influence of the rotations could be much bigger.

As discussed in the manuscript, due to the much larger size, the free rotation of CH_3COCH_3 on the surface of $(MA)_2Pb(SCN)_2I_2$ is difficult. Because of the stable interactions between NO_2 and SCN^- sulphur atoms in the $(MA)_2Pb(SCN)_2I_2$-NO_2 complex, the influence of the NO_2 rotations on the adsorption energy could be decreased greatly. This is why the adsorption energy curves of the above mentioned two complexes fluctuate less.