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Supplementary Information: On the D_2/H_2 Adsorption Selectivity of Sodium Decorated Polycyclic Aromatic Hydrocarbons. I. Accurate Modelling Approaches and Low Pressure Selectivity

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1) Optimized structure for [H–Cor–Na]$^+$

Table S1: Cartesian coordinates of the optimized geometry used for [H-Cor-Na]$^+$ and CM5 atomic charges distribution (Marenich *et al*, J. Chem. Theor. Comp. 8, 527 (2012))

Atom	x (Å)	y (Å)	z (Å)	q/e
C	-0.024283	-1.446066	-0.001979	-0.012847
C	-1.254332	-0.722875	-0.008805	-0.014314
C	-1.239843	0.710148	-0.000821	-0.014392
C	-0.009984	1.412485	0.005535	-0.015919
C	1.240062	0.687345	0.001530	-0.016566
C	1.220306	-0.741653	0.007505	-0.010870
C	-0.037612	-2.863509	0.001760	0.002645
C	-2.486673	-1.422550	-0.012204	0.002369
C	-2.476570	1.419827	0.010913	0.000956
C	-0.002390	2.849522	0.021016	-0.009478
C	2.470234	1.363205	0.001600	0.010574
C	2.439288	-1.471135	0.022097	0.001709
C	-1.284620	-3.532785	-0.010721	-0.028897
C	-2.464631	-2.839090	-0.017846	-0.028203
C	-3.698385	-0.679128	-0.012539	-0.031386
C	-3.687724	0.689134	0.000191	-0.030484
C	-2.443205	2.841606	0.030056	-0.031830
C	-1.266355	3.525083	0.037646	-0.028705
C	1.193635	3.537657	0.011004	-0.014992
C	2.520415	2.868077	-0.045378	-0.047242
C	3.656318	0.622778	0.015982	-0.033156
C	3.649851	-0.756712	0.027632	-0.026650
C	2.389752	-2.897324	0.022330	-0.029473
C	1.203395	-3.563172	0.011701	-0.030075
H	-1.293392	-4.614656	-0.018234	0.062155
H	-3.405692	-3.372680	-0.030776	0.062224
H	-4.637451	-1.215669	-0.025196	0.061241
H	-4.621301	1.236184	-0.001546	0.061806
H	-3.381683	3.380253	0.033334	0.061709
H	-1.267804	4.606947	0.046030	0.060987
H	1.180127	4.619600	0.014795	0.057620
H	3.165630	3.244558	0.759725	0.057506
H	4.601826	1.150068	0.010763	0.061333
H	4.583781	-1.302533	0.033651	0.062170
H	3.322358	-3.445598	0.025416	0.062044
H	1.186737	-4.644941	0.006225	0.062168
H	3.044484	3.179895	-0.961256	0.064137
Na	-0.061469	-0.028301	2.328867	0.640237

2) Energy levels of H_2/D_2 adsorbed to $[H–Cor–Na]^+$ and [CCCor–Na], and within PsAt/RB Models

Table S2: Lowest energy levels of H_2/D_2 bound to $[H–Cor–Na]^+$ (PsAt model), presented as differences with respect to the ground state energy, $E_l - E_0$, in K. E_0 =-871.08 and -940.26 K for H_2 and D_2, respectively.

	$E_l - E_0$ (K)			$E_l - E_0$ (K)	
l	H_2	D_2	l	H_2	D_2
0	0.000	0.000	20	161.020	103.049
1	10.603	10.896	21	163.149	120.223
2	15.248	17.670	22	167.049	120.803
3	18.071	20.067	23	168.351	121.728
4	19.514	20.462	24	175.221	129.243
5	24.330	22.409	25	179.981	134.432
6	30.570	23.621	26	180.783	136.450
7	40.706	32.133	27	181.717	137.216
8	41.476	34.637	28	192.678	139.478
9	55.636	39.685	29	193.152	140.110
10	55.724	40.104	30	207.587	140.246
11	74.161	48.410	31	207.744	142.253
12	74.324	49.114	32	217.633	149.231
13	96.212	59.661	33	217.674	150.327
14	96.237	59.772	34	229.085	157.056
15	121.421	72.426	35	229.692	157.318
16	121.466	72.453	36	233.926	160.980
17	149.456	86.873	37	240.453	161.010
18	149.828	86.933	38	244.732	167.118
19	153.574	103.024	39	247.557	167.345

Table S3: Lowest energy levels of H_2/D_2 bound to [CCCor−Na] (PsAt model), presented as differences with respect to the ground state energy, $E_l - E_0$, in K. E_0 =-788.49 and -848.97 K for H_2 and D_2, respectively.

	$E_l - E_0$ (K)			$E_l - E_0$ (K)	
l	H_2	D_2	l	H_2	D_2
0	0.000	0.000	20	143.946	81.282
1	1.387	0.502	21	144.152	97.196
2	1.412	0.504	22	146.122	97.198
3	5.240	1.720	23	150.789	112.278
4	5.346	1.724	24	151.536	113.149
5	8.767	2.502	25	151.866	113.198
6	21.270	16.326	26	155.352	114.536
7	27.735	18.626	27	157.282	114.762
8	27.821	18.630	28	164.637	114.821
9	40.711	24.383	29	166.850	115.137
10	40.792	24.387	30	176.674	116.560
11	57.160	31.515	31	178.151	122.692
12	57.248	33.432	32	181.432	125.526
13	76.647	42.360	33	181.486	125.848
14	76.685	42.363	34	190.080	131.567
15	98.924	53.799	35	193.384	131.872
16	98.968	53.801	36	195.219	133.201
17	123.853	66.793	37	196.462	133.208
18	123.915	66.801	38	196.682	138.689
19	142.803	81.280	39	199.724	140.239

Table S4: Lowest energy levels of even-J RB H_2/D_2 bound to [H-Cor-Na]$^+$, presented as differences with respect to the ground state energy, $E_l - E_0$, in K. E_0 =-1116.32 and -1250.73 K for H_2 and D_2, respectively.

	$E_l - E_0$ (K)			$E_l - E_0$ (K)	
l	H_2	D_2	l	H_2	D_2
0	0.000	0.000	30	221.789	147.214
1	13.734	14.948	31	222.024	152.588
2	17.541	15.517	32	239.239	155.727
3	20.513	19.520	33	239.378	158.340
4	22.091	22.484	34	245.322	163.627
5	27.596	23.443	35	245.805	164.323
6	33.759	26.101	36	270.820	170.359
7	44.905	33.374	37	272.390	171.573
8	45.726	35.687	38	273.244	175.646
9	61.530	41.282	39	279.909	177.679
10	61.581	43.064	40	280.177	184.527
11	81.979	51.809	41	280.337	185.009
12	82.079	52.403	42	282.216	185.309
13	106.205	62.470	43	283.220	188.248
14	106.264	64.974	44	286.767	192.280
15	133.949	76.433	45	288.591	198.329
16	134.026	78.878	46	293.034	200.025
17	160.271	92.596	47	295.613	200.223
18	164.999	94.214	48	296.662	200.270
19	165.205	108.636	49	298.972	200.518
20	170.010	112.234	50	299.352	201.241
21	171.780	122.095	51	301.059	204.348
22	176.246	127.556	52	305.850	204.423
23	177.575	129.325	53	306.232	206.483
24	185.308	133.494	54	308.273	207.706
25	191.473	138.300	55	311.057	207.875
26	198.089	139.785	56	313.350	208.098
27	198.286	141.610	57	316.681	208.285
28	205.746	144.127	58	324.210	210.694
29	206.147	144.627	59	324.384	211.262

Table S5: Lowest energy levels of odd-J RB H_2/D_2 bound to [H-Cor-Na]$^+$, presented as differences with respect to the ground state energy, $E_l - E_0$, in K. E_0 =-1016.77 and -1208.07 K for H_2 and D_2, respectively. To estimate the evaporation energy, one needs to subtract the energy for the J=1 state of the gas phase species, which is 163.80 and 82.00 K for, respectively, H_2 and D_2.

	$E_l - E_0$ (K)			$E_l - E_0$ (K)	
l	H_2	D_2	l	H_2	D_2
0	0.000	0.000	30	128.363	79.270
1	5.283	7.495	31	128.532	79.709
2	14.307	13.864	32	146.527	89.239
3	17.146	19.642	33	146.607	89.283
4	18.760	20.390	34	158.468	94.681
5	20.549	21.821	35	158.565	95.571
6	21.621	22.867	36	161.530	105.098
7	24.915	25.272	37	164.525	106.050
8	26.256	28.221	38	171.341	111.384
9	28.552	28.658	39	172.214	113.084
10	30.123	29.710	40	175.282	122.668
11	33.528	31.098	41	176.544	124.174
12	37.587	33.507	42	177.453	125.776
13	39.009	35.465	43	178.387	130.126
14	44.034	37.280	44	178.667	131.352
15	45.395	38.159	45	179.533	132.109
16	53.497	41.947	46	183.347	136.988
17	54.019	43.791	47	184.205	138.063
18	59.100	45.071	48	186.292	139.602
19	59.355	46.307	49	188.806	141.418
20	71.179	51.712	50	191.327	142.281
21	71.247	52.282	51	191.622	143.732
22	78.400	53.377	52	198.573	144.145
23	78.679	55.575	53	198.648	145.044
24	92.705	61.948	54	201.611	146.248
25	92.741	62.647	55	203.214	148.592
26	101.649	65.435	56	211.089	149.544
27	101.734	66.509	57	211.244	150.639
28	117.845	74.425	58	216.096	151.823
29	117.962	75.173	59	216.293	152.503

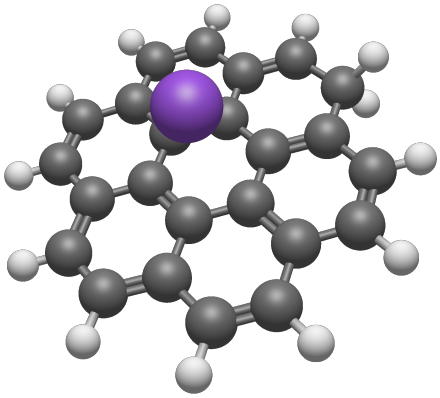
Table S6: Lowest energy levels of even-J RB H_2/D_2 bound to [CCCor−Na], presented as differences with respect to the ground state energy, $E_l - E_0$, in K. E_0 =-1097.86 and -1239.25 K for H_2 and D_2, respectively.

	$E_l - E_0$ (K)			$E_l - E_0$ (K)	
l	H_2	D_2	l	H_2	D_2
0	0.000	0.000	30	221.095	143.389
1	1.625	0.442	31	221.827	147.128
2	1.929	1.012	32	229.319	152.849
3	6.728	2.185	33	229.837	153.484
4	6.790	2.604	34	239.906	159.371
5	11.415	3.477	35	241.483	160.018
6	25.328	19.225	36	241.758	161.259
7	33.729	21.815	37	244.832	167.115
8	33.775	22.594	38	246.327	167.870
9	49.978	29.400	39	246.566	173.610
10	50.049	29.582	40	246.673	181.409
11	69.991	38.644	41	251.068	182.862
12	71.035	40.366	42	262.596	183.556
13	94.722	51.277	43	266.749	184.582
14	94.748	52.152	44	267.850	184.902
15	122.430	65.532	45	270.563	185.233
16	122.506	66.049	46	271.112	186.111
17	153.469	81.278	47	271.264	186.218
18	153.571	81.919	48	271.280	186.895
19	172.938	96.309	49	286.041	187.248
20	174.896	102.777	50	286.323	187.321
21	175.032	117.262	51	298.539	187.921
22	180.563	120.491	52	300.777	188.104
23	180.750	130.523	53	304.514	189.267
24	187.275	130.903	54	305.689	189.451
25	187.322	132.682	55	309.829	189.631
26	188.296	132.963	56	309.883	190.032
27	197.559	134.903	57	318.603	190.214
28	207.826	135.681	58	318.824	190.509
29	208.497	135.879	59	318.968	190.656

Table S7: Lowest energy levels of odd-J RB H_2/D_2 bound to [CCCor−Na], presented as differences with respect to the ground state energy, $E_l - E_0$, in K. E_0 =-1011.53 and -1206.11 K for H_2 and D_2, respectively. To estimate the evaporation energy, one needs to subtract the energy for the J=1 state of the gas phase species, which is 163.80 and 82.00 K for, respectively, H_2 and D_2.

	$E_l - E_0$ (K)			$E_l - E_0$ (K)	
l	H_2	D_2	l	H_2	D_2
0	0.000	0.000	30	124.430	81.299
1	1.582	0.311	31	124.444	82.129
2	1.886	1.122	32	151.634	82.592
3	6.535	1.832	33	152.097	83.177
4	6.585	3.748	34	152.173	94.931
5	10.981	4.273	35	152.402	98.214
6	25.220	18.669	36	173.731	99.594
7	29.009	21.000	37	175.661	100.687
8	30.408	22.585	38	175.747	112.471
9	31.283	28.419	39	180.476	113.108
10	32.559	29.825	40	181.798	118.691
11	33.219	30.386	41	183.214	119.526
12	36.689	30.891	42	183.525	126.776
13	36.770	32.004	43	184.874	128.423
14	41.002	32.353	44	187.091	129.988
15	49.555	35.546	45	187.800	131.164
16	49.660	35.985	46	197.412	132.277
17	54.466	38.374	47	200.615	132.501
18	62.829	40.686	48	202.165	136.792
19	63.175	48.974	49	203.379	137.323
20	69.510	51.572	50	206.707	139.113
21	70.079	51.768	51	206.960	144.082
22	79.378	52.010	52	209.575	146.705
23	79.505	52.665	53	211.034	149.306
24	93.672	59.090	54	216.506	149.423
25	93.724	60.484	55	216.872	149.836
26	99.809	64.336	56	218.614	152.213
27	100.370	67.817	57	219.032	156.737
28	120.910	69.104	58	221.271	157.640
29	121.325	70.954	59	225.673	159.763

3) Minimum energy path of H_2 adsorbed on $[H–Cor–Na]^+$ (PsAt)



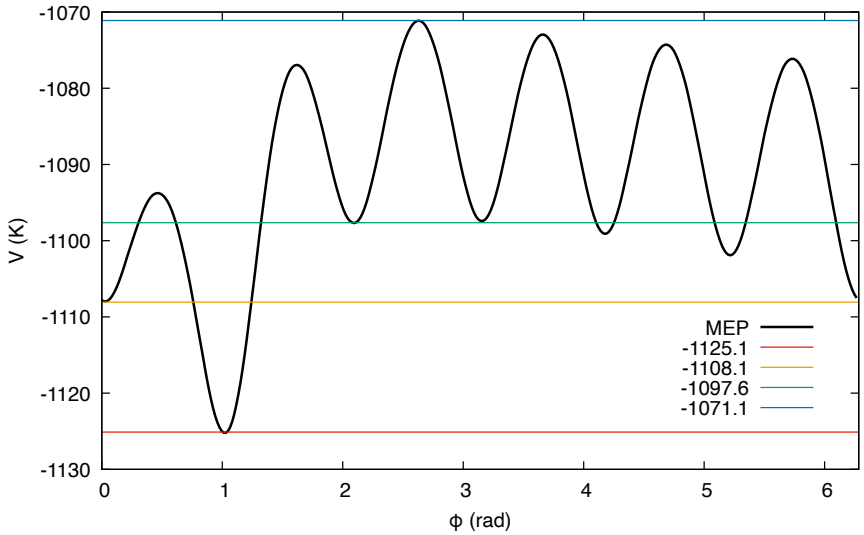


Figure S1: Minimum energy path (MEP), as a function of the angle φ (in rad), for the H_2-$[H{-}Cor{-}Na]^+$ interaction within the PsAt approximation. Horizontal lines indicate the potential energy of selected maxima and minima along the path for comparison purpose. The deeper well observed at $\varphi \approx 1$ rad is due to the vicinity of the proton that protrudes over the coronene plane (see scheme above). The ground state wavefunctions of H_2/D_2-$[H{-}Cor{-}Na]^+$ are localized on top of this well. The lack of a C_6 symmetry in this MEP explains the angular distributions of the low-lying wavefunctions, an effect that fades out for the higher energy states (see Fig. 3 of the main article).

4) Probability densities of some odd-J (RB) H_2-[H–Cor–Na]$^+$ bound states

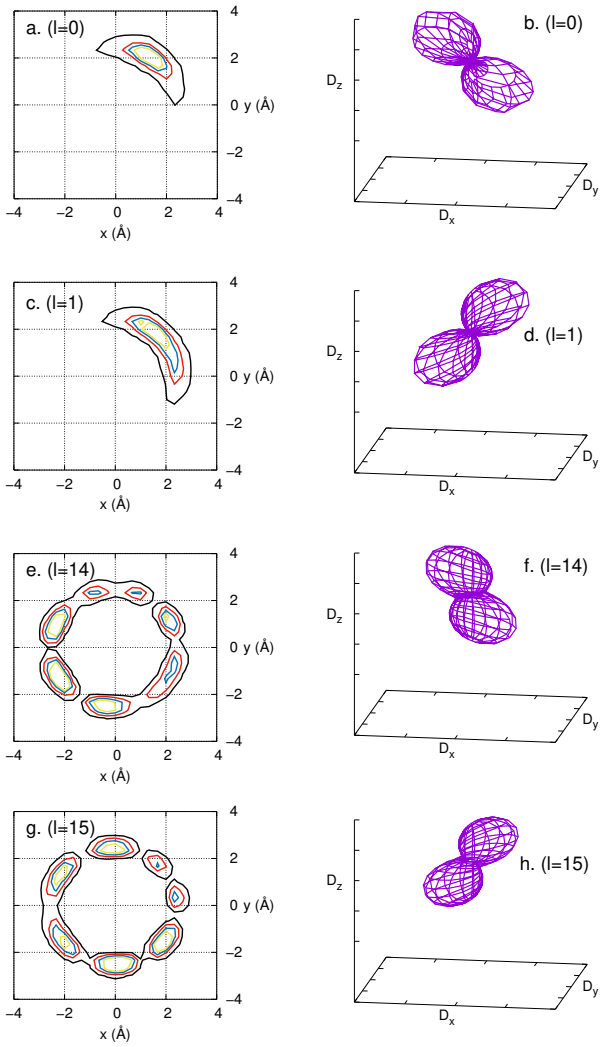


Figure S2: Probability densities of selected states of H_2 adsorbed on [H−Cor−Na]$^+$, within the RB model, J=odd block ($l = 0, 1, 14, 15$). Densities projected onto the (x, y) plane are presented in the left panels whereas, in the right panels, they have been projected onto the orientation of the molecule (θ, ϕ) and are displayed as polar plots (i.e., $\mathcal{D}_l(\theta, \phi)$ is the radius of a representation in spherical coordinates). The first two levels ($l = 0$, 1), having similar distributions along (x, y) (a. and c.), differ in the $\mathcal{D}_l(\theta, \phi)$ densities (b. and d.), which resemble p-like orbitals pointing to different directions, hence suggesting two distinct preferred orientations of the H_2 axis. A similar behavior is found for the couple of l= 14, 15 levels (e.-h. panels).

5) Sum over states for H_2/D_2 adsorbed on $[H–Cor–Na]^+$

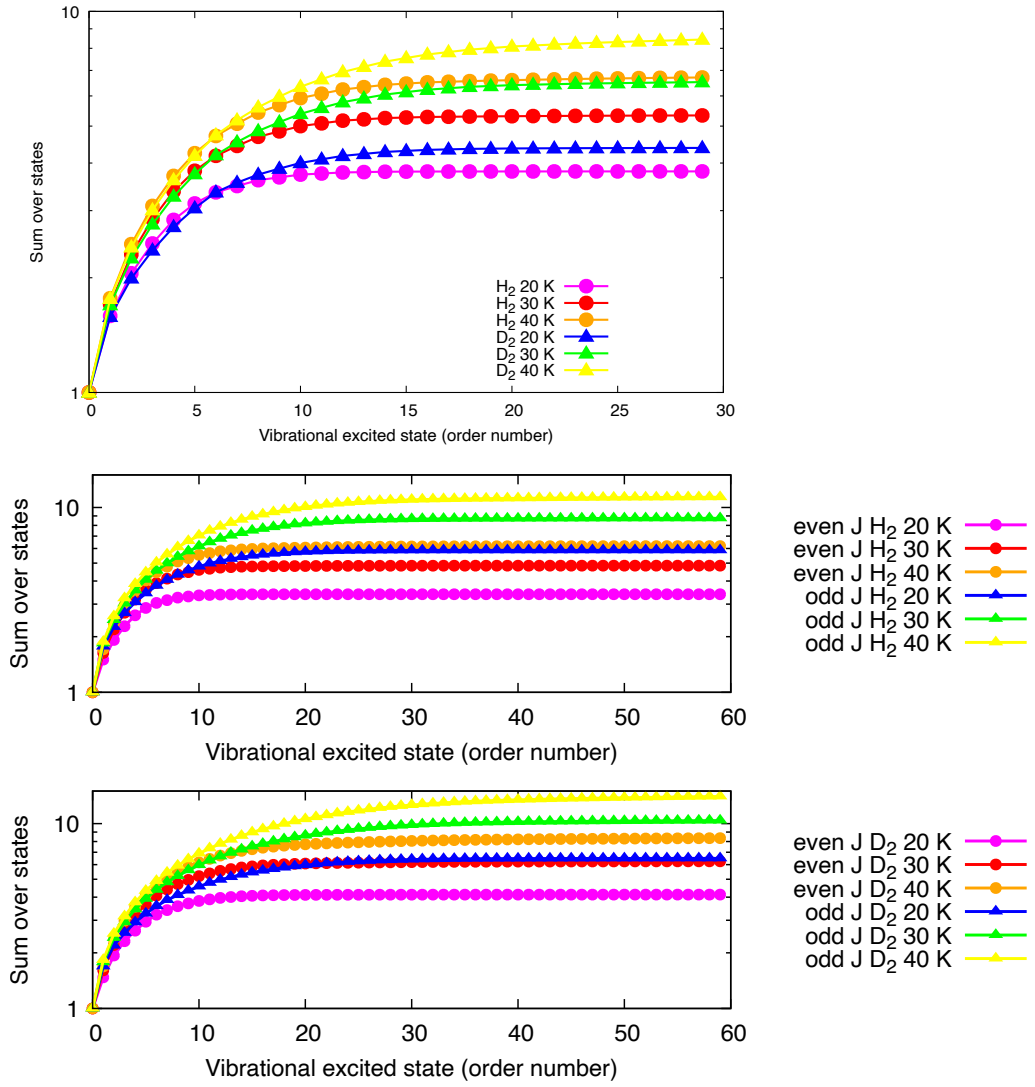


Figure S3: Sum over states, $\sum_{l=0}^{l_{max}} \exp[-(E_l - E_0)/k_bT]$, as functions of l_{max}, computed with the eigenenergies of H_2 and D_2 adsorbed on the Na–decorated plane of $[H{-}Cor{-}Na]^+$, for three different temperatures, $T = 20$, 30 and 40 K. These sums are part of the last factor of Eq. 5 of the article. Upper panel: H_2 and D_2 within the PsAt approximation. Middle and bottom panel: H_2 and D_2, respectively, within the RB approach (even- and odd-J). It can be seen that, depending on the temperature, molecule and approach, a certain number of l levels are needed to converge the sum: for instance, for PsAt H_2 at 20 K, the sum converges with about 10 levels whereas about 30 levels are needed to converge the sum for odd-J RB D_2 at 40 K. In any case, it can be seen that the total number of states considered (i.e. 30 and 60 within the PsAt and RB approaches) are sufficient for an accurate determination of the sum of states.

6) Isotherms of D_2 adsorbed on $[H{-}Cor{-}Na]^+$ within the RB model (J=even): comparison with low-temperature approximate calculations

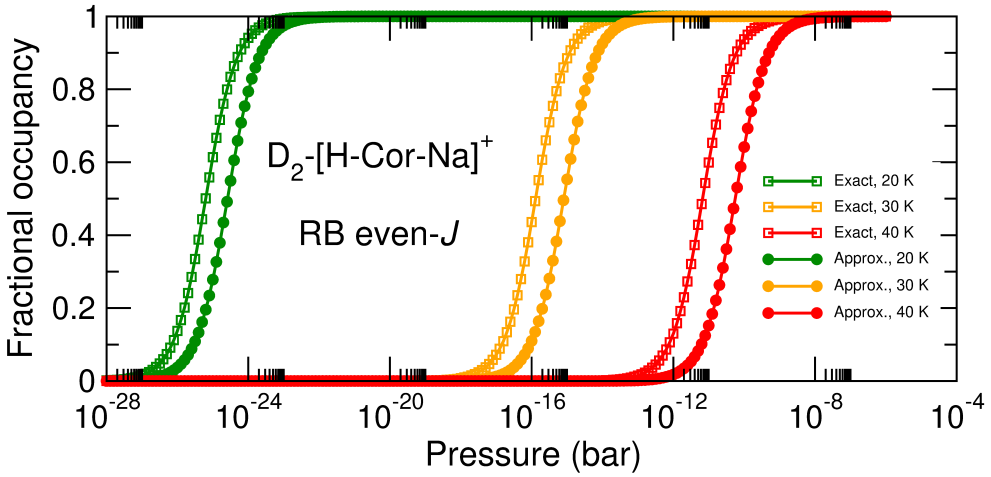


Figure S4: Adsorption isotherms of D_2 on $[H{-}Cor{-}Na]^+$ assuming non-interacting independent adsorption sites at 20, 30, and 40 K, within the even-J RB model: comparison between including all bound states needed (exact, open squares) and neglecting the contributions of the excited states (approximated, filled circles) in the partition functions of the adsorbed molecules. The approximated isotherms overestimate the pressures where the fractional occupancy rises, the effect being relatively small at low temperatures and becoming more important as temperature increases, as expected.

7) Excited states energies of H_2/D_2 adsorbed on [CC-Cor–Na]

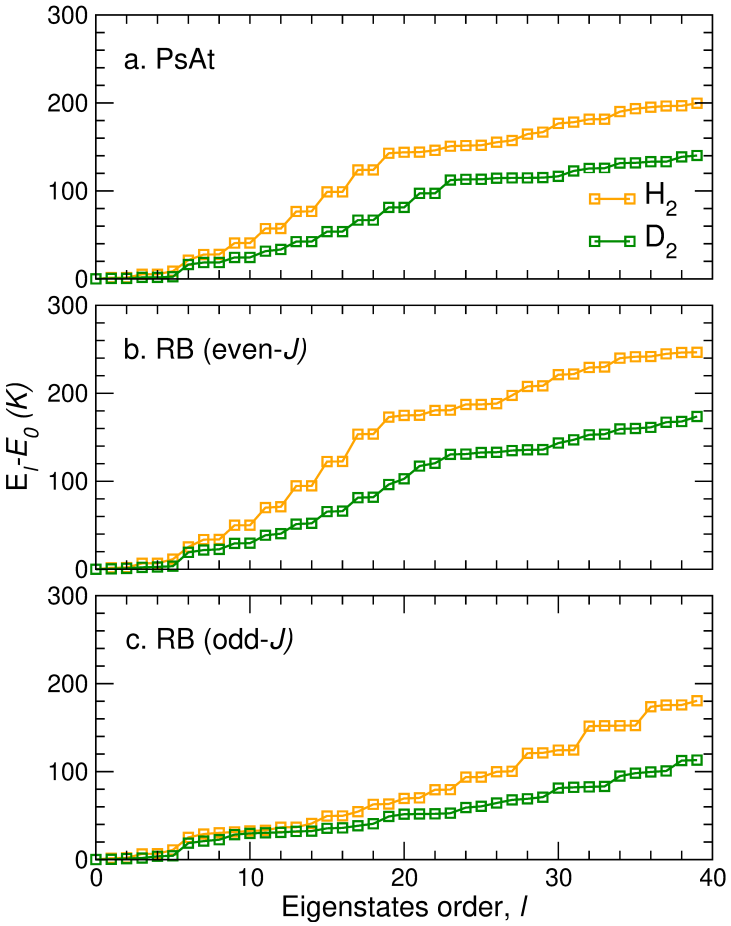


Figure S5: Energy levels of H_2 (yellow) and D_2 (green) adsorbed on [CCCor−Na], as differences with respect to the ground state energy, $\Delta E_{(l,0)} = E_l - E_0$ (in K), for the PsAt (a.), RB even-J (b.) and RB odd-J (c.) approaches. Notice the presence of degenerate pairs of excited states typical of a "particle on a ring" system and associated to opposite rotation directions.

8) Isotherms of H_2 and D_2 adsorbed on [CCCor–Na]

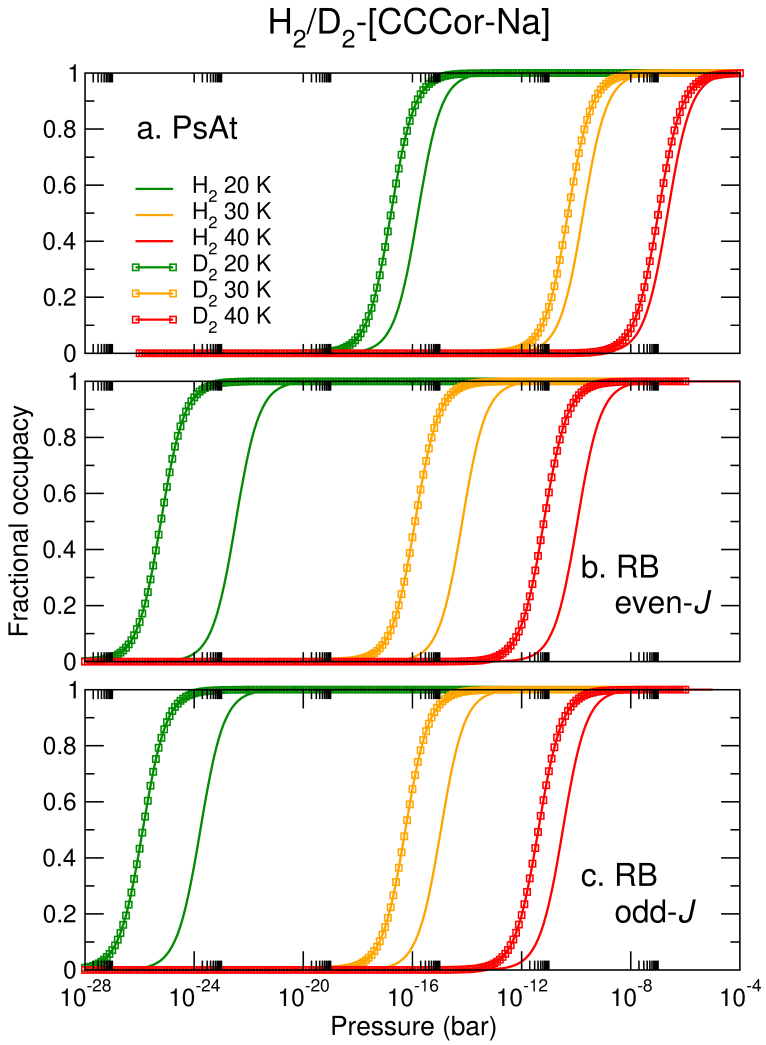


Figure S6: Adsorption isotherms of H_2/D_2 adsorbed on [CCCor−Na] at 20, 30, and 40 K, assuming non-interacting independent adsorption sites. Top panel: within the PsAt approach. Medium and lower panels: even-J and odd-J states, respectively, within a RB description for the adsorbed molecules. All needed excited states have been included in the calculations of the adsorption partition functions.