

Supplementary material for “Vibrational predissociation spectra of the $^{35}\text{Cl}^-(\text{H}_2)$ complex and its isotopologue $^{35}\text{Cl}^-(\text{D}_2)$ ”

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Table S1: Variation of the A_1 rovibrational energy levels for $J = 0$ with respect to the number of point in the DVR grid $R \in [3, 30]$ and the number of vibrational and rotational levels of the diatom included in the calculations.

Species	(v, j, k)										
	(1,4,50)	(1,5,50)	(1,6,50)	(1,7,50)	(2,6,50)	(3,6,50)	(4,6,50)	(3,6,100)	(3,6,150)	(3,6,200)	(3,6,250)
$\text{Cl}^-(\text{H}_2)$	Rovibrational energies (cm^{-1})										
	-404.911	-404.915	-404.915	-404.915	-411.579	-411.591	-411.591	-416.547	-416.544	-416.544	-416.544
	-257.401	-257.413	-257.413	-257.413	-267.275	-267.322	-267.322	-274.763	-274.754	-274.754	-274.754
	-194.898	-194.911	-194.911	-194.911	-202.959	-202.987	-202.987	-167.388	-167.384	-167.384	-167.384
	-110.065	-110.066	-110.066	-110.066	-111.076	-111.079	-111.079	-91.605	-91.617	-91.617	-91.617
	-48.292	-48.292	-48.292	-48.292	-48.573	-48.574	-48.574	-43.250	-43.271	-43.271	-43.271
	-17.393	-17.393	-17.393	-17.393	-17.489	-17.489	-17.489	-16.576	-16.592	-16.592	-16.592
	-4.717	-4.717	-4.717	-4.717	-4.748	-4.748	-4.748	-4.677	-4.684	-4.684	-4.684
$\text{Cl}^-(\text{D}_2)$	-0.724	-0.724	-0.724	-0.724	-0.731	-0.732	-0.732	-0.736	-0.737	-0.737	-0.737
								-0.001	-0.002	-0.002	-0.002
	-503.626	-503.676	-503.676	-503.676	-511.053	-511.070	-511.070	-521.711	-521.704	-521.704	-521.704
	-388.492	-388.736	-388.741	-388.741	-406.489	-406.610	-406.611	-401.982	-401.759	-401.759	-401.759
	-317.557	-317.574	-317.574	-317.574	-320.245	-320.250	-320.250	-299.995	-299.431	-299.431	-299.431
	-181.291	-181.292	-181.292	-181.292	-182.034	-182.035	-182.035	-214.246	-214.310	-214.310	-214.310
	-95.129	-95.129	-95.129	-95.129	-95.399	-95.400	-95.400	-144.288	-145.840	-145.839	-145.839
	-74.806	-75.025	-75.027	-75.027	-76.538	-76.539	-76.539	-90.754	-93.172	-93.171	-93.171
	-46.694	-46.695	-46.695	-46.695	-46.802	-46.802	-46.802	-74.073	-74.073	-74.073	-74.073
	-21.061	-21.062	-21.062	-21.062	-21.113	-21.113	-21.113	-52.870	-54.973	-54.972	-54.972
	-13.306	-13.439	-13.441	-13.441	-14.390	-14.391	-14.391	-28.080	-29.302	-29.302	-29.302
	-8.348	-8.349	-8.349	-8.349	-8.371	-8.371	-8.371	-13.199	-13.700	-13.700	-13.700
	-2.753	-2.753	-2.753	-2.753	-2.760	-2.760	-2.760	-7.066	-7.066	-7.066	-7.066
	-0.606	-0.606	-0.606	-0.606	-0.608	-0.608	-0.608	-5.246	-5.404	-5.403	-5.403
-0.073	-0.073	-0.073	-0.073	-0.074	-0.074	-0.074	-1.582	-1.625	-1.625	-1.625	
							-0.283	-0.291	-0.291	-0.291	

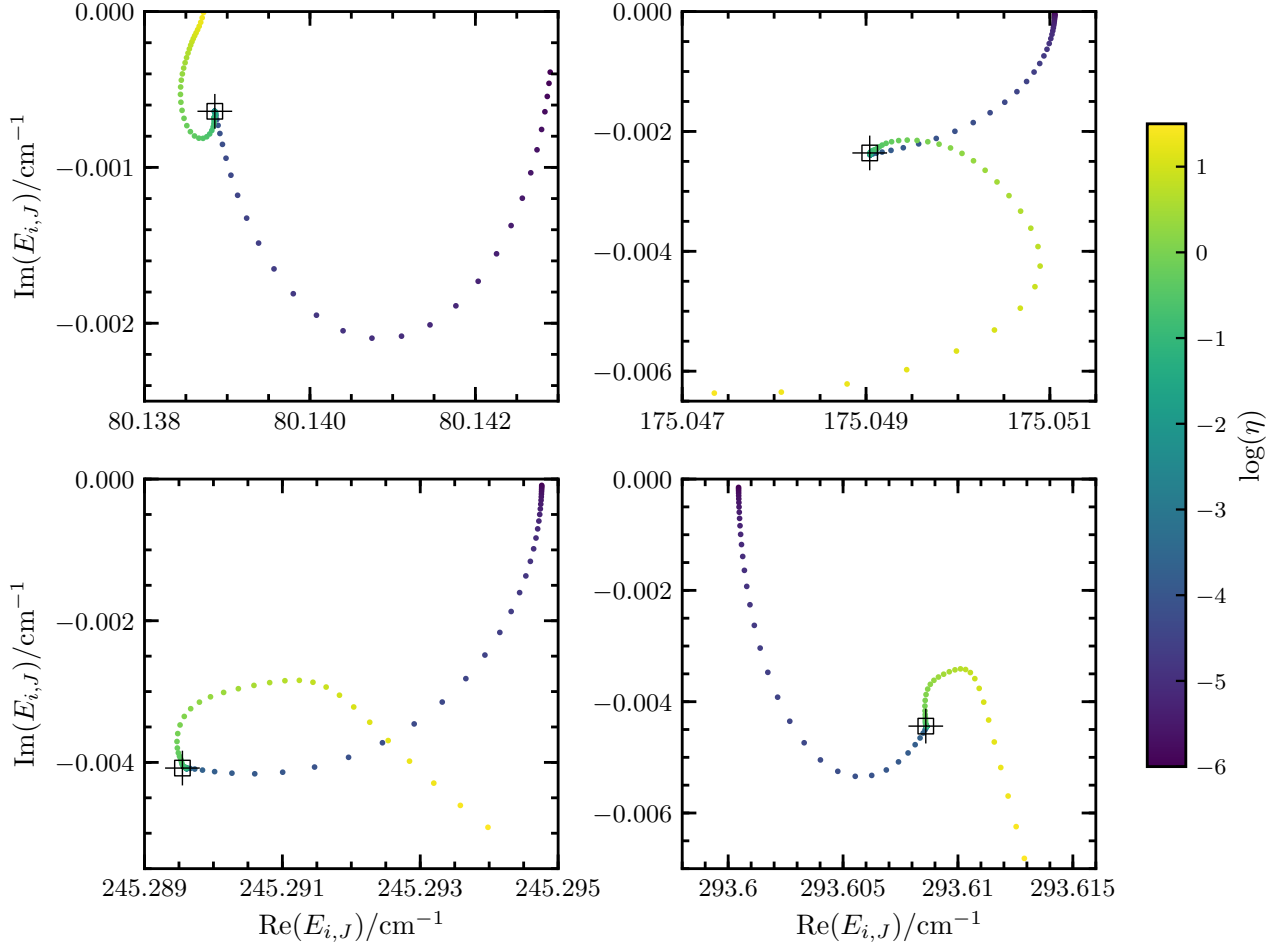


Figure S1: η -trajectories for the low lying resonant states of $\text{Cl}^-(\text{H}_2)$ for $J = 0$ and symmetry A_1 . The values of η grows exponentially according to $\log(\eta_k) = \log(\eta_{\min}) + \frac{k-1}{N} \log(\frac{\eta_{\max}}{\eta_{\min}})$ with $\eta_{\min} = 10^{-6}$, $\eta_{\max} = 31.62$ and the number of steps $N = 100$

Table S2: Lowest energy levels of $\text{Cl}^-(\text{H}_2)$ for $J = 0$ with their assigned vibrational quantum numbers v_1, v_2, l_2 whenever possible, parity p , representation Γ_{rovib} of the group G_4 . Energies are given in cm^{-1} with respect to the energy of separated monomers Cl^- and *para*- H_2 . For each set of quantum numbers (v_1, v_2, l_2, p) , we give the energies of the *para* and *ortho* states whenever possible. ΔE is the energy splitting due to tunneling.

v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE	v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE
0	0	0	+	-416.544	A_1	8.890	7	0	0	+	-0.737	A_1	105.986
				-407.655	B_2						105.249	B_2	
1	0	0	+	-274.754	A_1	17.728	8	0	0	+	-0.002	A_1	113.105
				-257.026	B_2						113.103	B_2	
2	0	0	+	-167.384	A_1	29.932	9	0	0	+	116.699	B_2	
				-137.451	B_2						117.965	B_2	
3	0	0	+	-91.617	A_1	45.057	0	2	0	+	80.143	A_1	278.809
				-46.560	B_2						358.952	B_2	
4	0	0	+	-43.271	A_1	62.073	1	2	0	+	175.051	A_1	299.037
				18.802	B_2						474.088	B_2	
5	0	0	+	-16.592	A_1	79.303	2	2	0	+	245.295	A_1	315.715
				62.711	B_2						561.009	B_2	
6	0	0	+	-4.684	A_1	94.605	3	2	0	+	293.600	A_1	328.931
				89.921	B_2						622.531	B_2	

Table S3: Lowest energy levels of $\text{Cl}^-(\text{D}_2)$ for $J = 0$ with their assigned vibrational quantum numbers v_1, v_2, l_2 whenever possible, parity p , representation Γ_{rovib} of the group G_4 . Energies are given in cm^{-1} with respect to the energy of separated monomers Cl^- and *ortho*- D_2 . For each set of quantum numbers (v_1, v_2, l_2, p) , we give the energies of the *para* and *ortho* states. ΔE is the energy splitting due to tunneling.

v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE	v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE
0	0	0	+	-521.704	A_1	0.394	11	0	0	+	-0.291	A_1	52.894
				-521.310	B_2						52.603	B_2	
1	0	0	+	-401.759	A_1	1.024	0	2	0	+	-74.073	A_1	76.724
				-400.736	B_2						2.651	B_2	
2	0	0	+	-299.431	A_1	2.207	1	2	0	+	-7.066	A_1	97.538
				-297.224	B_2						90.472	B_2	
3	0	0	+	-214.310	A_1	4.242	2	2	0	+	46.762	A_1	116.145
				-210.068	B_2						162.908	B_2	
4	0	0	+	-145.839	A_1	7.457	3	2	0	+	88.708	A_1	132.219
				-138.382	B_2						220.927	B_2	
5	0	0	+	-93.171	A_1	12.117	4	2	0	+	120.176	A_1	145.566
				-81.054	B_2						265.743	B_2	
6	0	0	+	-54.972	A_1	18.275	5	2	0	+	142.723	A_1	156.155
				-36.697	B_2						298.878	B_2	
7	0	0	+	-29.302	A_1	25.658	0	4	0	+	262.554	A_1	274.567
				-3.644	B_2						537.121	B_2	
8	0	0	+	-13.700	A_1	33.656	1	4	0	+	347.864	A_1	277.082
				19.956	B_2						624.946	B_2	
9	0	0	+	-5.403	A_1	41.385	2	4	0	+	417.217	A_1	280.081
				35.981	B_2						697.298	B_2	
10	0	0	+	-1.625	A_1	47.906	3	4	0	+	472.248	A_1	282.855
				46.281	B_2						755.103	B_2	

Table S4: Lowest energy levels of $\text{Cl}^-(\text{H}_2)$ for $J = 1$ with their assigned vibrational quantum numbers v_1, v_2, l_2 whenever possible, parity p , representation Γ_{rovib} of the group G_4 . Energies are given in cm^{-1} with respect to the energy of separated monomers Cl^- and *para*- H_2 . ΔE is the energy splitting due to tunneling.

v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE	v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE
0	0	0	-	-414.871	A_2	8.899	2	1	-1	-	69.379	B_1	145.339
				-405.972	B_1							214.718	
1	0	0	-	-273.282	A_2	17.754	2	1	1	+	69.367	B_2	145.432
				-255.527	B_1							214.799	
2	0	0	-	-166.130	A_2	29.984	3	1	-1	-	102.909	B_1	174.266
				-136.146	B_1							277.174	
3	0	0	-	-90.599	A_2	45.144	3	1	1	+	102.898	B_2	174.351
				-45.455	B_1							277.249	
4	0	0	-	-42.500	A_2	62.202	4	1	-1	-	116.501	B_1	200.261
				19.702	B_1							316.762	
5	0	0	-	-16.068	A_2	79.478	4	1	1	+	116.493	B_2	200.348
				63.410	B_1							316.841	
6	0	0	-	-4.383	A_2	94.814	0	2	0	-	81.632	A_2	278.323
				90.432	B_1							359.955	
7	0	0	-	-0.609	A_2	106.204	1	2	0	-	176.333	A_2	298.600
				105.595	B_1							474.932	
0	1	-1	-	-79.796	B_1	85.677	2	2	0	-	246.360	A_2	315.347
				5.881	A_2							561.707	
0	1	1	+	-79.811	B_2	85.801	3	2	0	-	294.449	A_2	328.592
				5.989	A_1							623.041	
1	1	-1	-	9.710	B_1	115.551	0	3	1	+	404.326	B_2	
				125.262	A_2							404.742	
1	1	1	+	9.697	B_2	115.657	1	3	1	+	511.251	B_2	
				125.354	A_1							511.706	

Table S5: Lowest energy levels of $\text{Cl}^- (\text{D}_2)$ for $J = 1$ with their assigned vibrational quantum numbers v_1, v_2, l_2 whenever possible, parity p , representation Γ_{rovib} of the group G_4 . Energies are given in cm^{-1} with respect to the energy of separated monomers Cl^- and *ortho*- D_2 . ΔE is the energy splitting due to tunneling.

v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE	v_1	v_2	l_2	p	Energy	Γ_{rovib}	ΔE
0	0	0	-	-520.792	A_2	0.395	2	1	-1	-	-69.079	B_1	28.570
				-520.398	B_1						-40.508	A_2	
1	0	0	-	-400.916	A_2	1.025	2	1	1	+	-69.081	B_2	28.591
				-399.892	B_1						-40.490	A_1	
2	0	0	-	-298.660	A_2	2.210	3	1	-1	-	-16.262	B_1	41.969
				-296.450	B_1						25.707	A_2	
3	0	0	-	-213.616	A_2	4.248	3	1	1	+	-16.264	B_2	41.998
				-209.368	B_1						25.734	A_1	
4	0	0	-	-145.227	A_2	7.469	4	1	-1	-	20.427	B_1	56.631
				-137.758	B_1						77.058	A_2	
5	0	0	-	-92.645	A_2	12.138	4	1	1	+	20.425	B_2	56.676
				-80.507	B_1						77.101	A_1	
6	0	0	-	-54.537	A_2	18.309	5	1	-1	-	43.264	B_1	71.788
				-36.228	B_1						115.052	A_2	
7	0	0	-	-28.960	A_2	25.708	5	1	1	+	43.261	B_2	71.866
				-3.252	B_1						115.127	A_1	
8	0	0	-	-13.450	A_2	33.722	6	1	-1	-	55.123	B_1	86.388
				20.273	B_1						141.511	A_2	
9	0	0	-	-5.237	A_2	41.466	6	1	1	+	55.121	B_2	86.590
				36.229	B_1						141.711	A_1	
10	0	0	-	-1.527	A_2	47.994	0	2	0	-	-73.299	A_2	76.716
				46.467	B_1						3.416	B_1	
11	0	0	-	-0.250	A_2	52.987	1	2	0	-	-6.370	A_2	97.587
				52.737	B_1						91.217	B_1	
12	0	0	-	56.392	B_1		2	2	0	-	47.381	A_2	116.232
				58.337	B_1						163.613	B_1	
0	1	-1	-	-230.373	B_1	8.350	3	2	0	-	89.257	A_2	132.331
				-222.023	A_2						221.588	B_1	
0	1	1	+	-230.374	B_2	8.359	4	2	0	-	120.675	A_2	145.704
				-222.015	A_1						266.379	B_1	
1	1	-1	-	-139.901	B_1	17.131	0	3	-1	-	82.887	B_1	176.337
				-122.771	A_2						259.224	A_2	
1	1	1	+	-139.903	B_2	17.145	0	3	1	+	82.879	B_2	178.788
				-122.758	A_1						261.667	A_1	

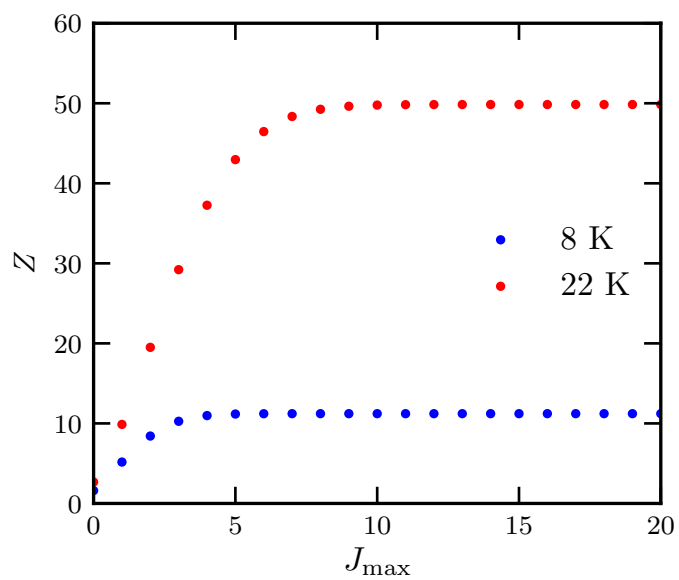


Figure S2: Partition functions for $^{35}\text{Cl}^-(\text{H}_2)$ at 8 or 22 K, including both *ortho* and *para* species in a 3:1 ratio, versus the maximal value of the total angular momentum.

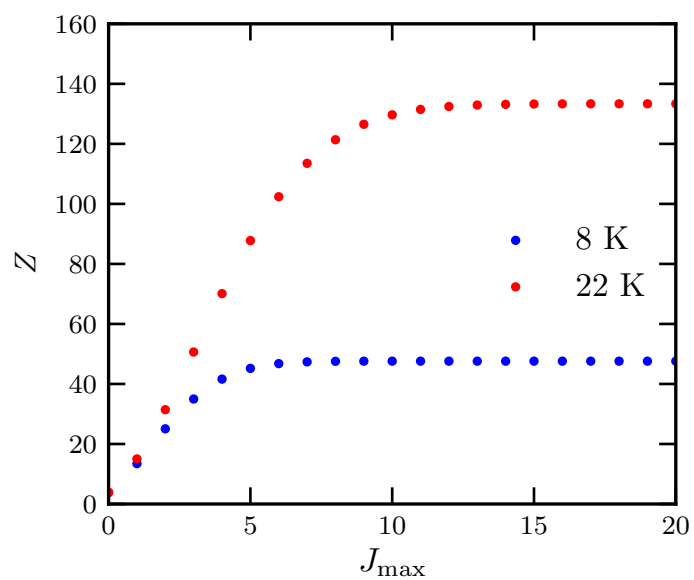


Figure S3: Partition functions for $^{35}\text{Cl}^-(\text{D}_2)$ at 8 or 22 K, including both *ortho* and *para* species in a 2:1 ratio, versus the maximal value of the total angular momentum.

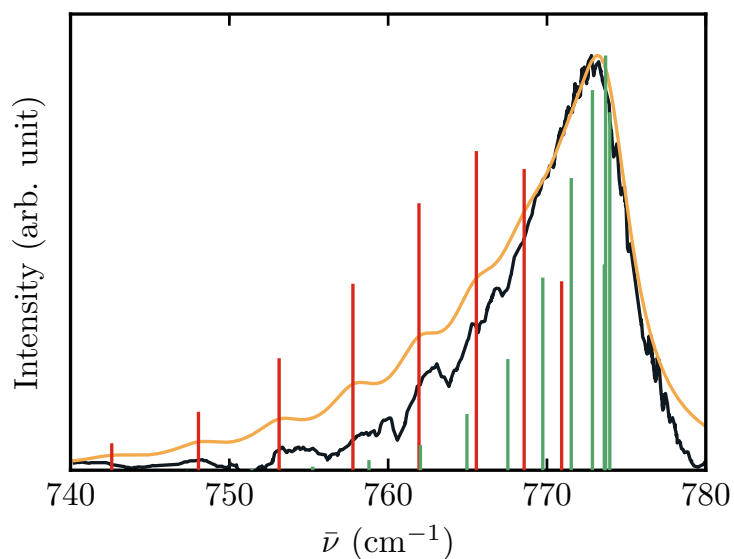


Figure S4: Comparison between the experimental (black) and the convolved theoretical predissociation spectra (orange) of Cl⁻(H₂) at 22 K, assuming a linewidth broadening of about 1 cm⁻¹. The theoretical stick spectrum is also shown, in red for the P band and green for the R band. The theoretical spectra are shifted to the blue by 8 cm⁻¹. All spectra are normalized to unity at the maximum.

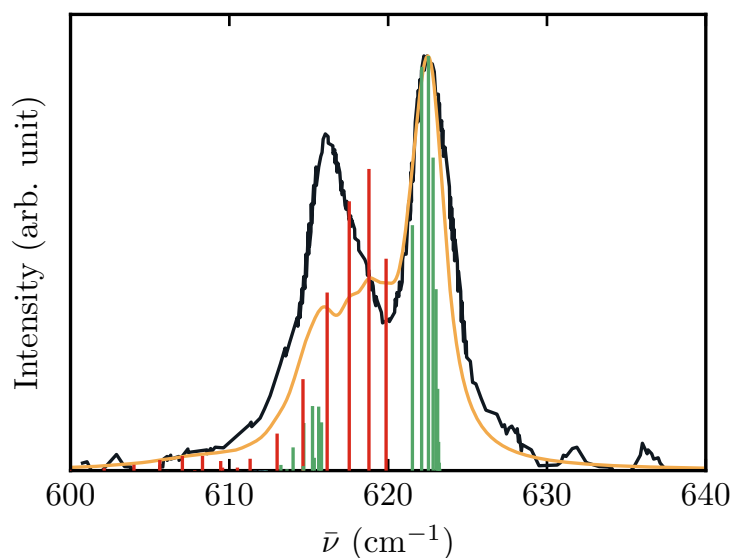


Figure S5: Comparison between the experimental (black) and the convolved theoretical predissociation spectra (orange) of Cl⁻(D₂) at 8 K, assuming a linewidth broadening of about 1 cm⁻¹. The theoretical stick spectrum is also shown, in red for the P band and green for the R band. The theoretical spectra are shifted to the blue by 8 cm⁻¹. All spectra are normalized to unity at the maximum.

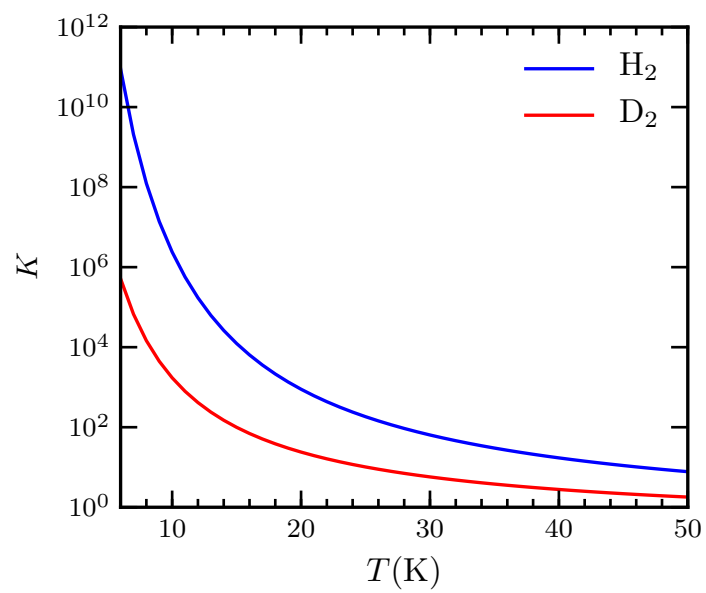


Figure S6: Calculated equilibrium constant for the ligand exchange reactions.