Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material for the manuscript: "Spectroscopy of a rotating hydrogen molecule in carbon nanotubes"

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The first section of this supplementary material provides pictures showing the accuracy of the fittings to the potential model proposed in this work as well as the parameters and coefficients of the potential fit. In this section, the explicit transformation from Eq. (4) to Eq. (5) of the main text is also provided. The second section presents four tables with the complete list of calculated molecular energy levels for a rotating molecule of hydrogen inside and outside carbon nanotubes. Section S3 provides explicit expressions for the calculation of angular factors from the Hamiltonian matrix elements. Finally, details on the reasons why the $(n\ 1\ 0)$ and $(n\ 1\ 1a)$ levels are degenerate for wide carbon nanotubes are presented in section S4.

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S1 Fittings of model potentials

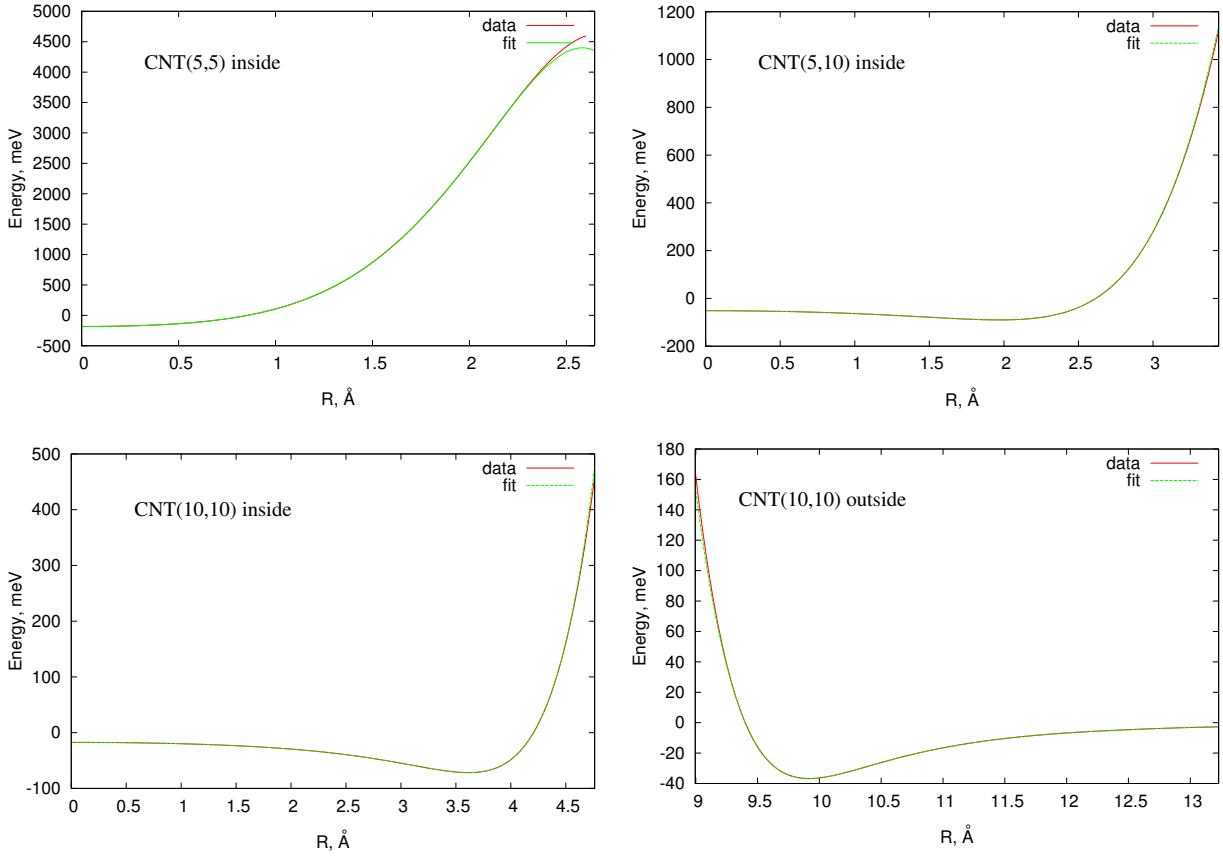

Figure S1: Pictures showing the accuracy of the fitting of H_2-nanotube interaction potentials to polynomial expansions for nanotubes of different helicity indexes (n,m), with H_2 both inside and outside of the nanotubes (see Eq. (4) of the main manuscript).

As discussed in the main text, the model H-CNT interaction potential $V_{\mathrm{H-CNT}}$ is expanded in a polynomial series

$$V_{\mathrm{H-CNT}}(\rho^2) = \sum_{L=0}^{n} V_L(\rho^2 - \rho_0^2)^L. \tag{S1}$$

Considering the expression of $\rho_{\pm}^2$ (see Eq. (2) of the main text), we can write

$$\left(\rho_{\pm}^2 - \rho_0^2\right)^L = \sum_{K=0}^{L} (\pm 1)^K \begin{pmatrix} L \\ K \end{pmatrix} \tag{S2}$$
$$\times \left(R^2 + \frac{r_0^2(1-x^2)}{4} - R_0^2\right)^{I-K} \left(r_0\, R\, \sqrt{1-x^2}\, \cos(\phi)\right)^K$$

Next, we notice that the total potential $V_{\mathrm{H_2-CNT}}$ is the sum of $V_{\mathrm{H-CNT}}(\rho_+^2)$ and $V_{\mathrm{H-CNT}}(\rho_-^2)$. Hence, it is clear that the terms with odd k cancel.Therefore, we will have

$$V(R,x,\phi) = 2\sum_{L=0}^{n} V_L \sum_{K=0}^{L/2} \begin{pmatrix} L \\ 2K \end{pmatrix} \tag{S3}$$
$$\times \left(R^2 + \frac{r_0^2(1-x^2)}{4} - R_0^2\right)^{L-2K} \left(r_0^2\, R^2 \left(1-x^2\right)\, \cos^2(\phi)\right)^K$$

which can be written in a simplified form as

$$V(R,x,\phi) = \sum_{I,L=0}^{n} \sum_{K=0}^{I} P_{JIK} (R^2 - R_0^2)^J \left(1-x^2\right)^I \cos^{2K}(\phi), \tag{S4}$$

with coefficients explicitly given as

$$P_{JIK} = \sum_{L=max(2K,I+J,I+K)}^{min(n,I+J+K)} V_L \begin{pmatrix} l \\ 2K \end{pmatrix} \begin{pmatrix} L-2K \\ I-K \end{pmatrix} \tag{S5}$$
$$\begin{pmatrix} K \\ I+J+K-L \end{pmatrix} \frac{\left(r_0^2\right)^I}{4^{I-K}} \left(R_0^2\right)^{L-I-J}$$

which corresponds to Eq. 5 of the main text. The coefficients of the polynomial fit are provided in Table S1.

Table S1: Parameters of potential fit, R_0^2 (in bohr^2) and V_l (in meV), see Eq. (5) of the main text. Powers of 10 are given in parentheses.

	(5,5)	(10,5)	(10,10)	(10,10)-ext
R_0^2	0	13.859	46.643	351.08
l	(5,5)	(10,5)	(10,10)	(10,10) ext
0	−182.815	−89.921	−71.713	−36.883
1	42.910	0	0	0
2	9.7137	0.4672	0.14339	0.01400
3	0.31236	0.02651	5.511(−3)	−2.908(−4)
4	−0.019169	5.401(−4)	9.052(−5)	3.100(−6)
5	0	−1.097(−6)	5.804(−7)	−1.930(−8)
6	0	−1.592(−7)	1.229(−10)	6.997(−11)
7	0	0	0	−1.362(−13)
8	0	0	0	1.099(−16)

S2 Energy levels (in cm^{-1}) of a rotating H_2 molecule inside and outside carbon nanotubes for $n, j, |m| \leq 3$ and $\Lambda \leq 6$.

Table S2: Energy levels (in cm^{-1}) of a rotating H_2 molecule inside nanotube of helicity index (5,5), for $n, j, |m| \leq 3$ and $\Lambda \leq 6$. The energies at the potential minima ($E_{\rm min}$, in cm^{-1}) and the zero-point energies ($E_{\rm zp}$, in cm^{-1}) are also collected. The energy values are relative to that of the ground state (0 0 0). The energy of the ground state (0 0 0) is given between parenthesis. For $\Lambda > 0$, $\Delta E_\Lambda = (E_\Lambda - E_{\Lambda-1})/((\Lambda-m)^2-(\Lambda-1-m)^2)$, to reflect the leading character of the $1/R^2$ term. The energies of the lowest bound states without including the rotation are presented in brackets.

CNT(5,5)									
$d_{\rm CNT}$, Å					6.7				
$E_{\rm min}$, cm^{-1}					−1474				
$E_{\rm zp}$, cm^{-1}					474				
n	j	m	$E_{\Lambda=0}$	$\Delta E_{\Lambda=1}$	$\Delta E_{\Lambda=2}$	$\Delta E_{\Lambda=3}$	$\Delta E_{\Lambda=4}$	$\Delta E_{\Lambda=5}$	$\Delta E_{\Lambda=6}$
0	0	0	0.000	154.088	78.937	52.695	38.218	30.608	31.370
			(−997.908)						
			[−1147.07]						
0	1	0	61.429	150.275	78.342	50.354	37.367	29.950	30.742
0	1	1	340.182	175.372	159.478	82.620	52.640	38.782	39.718
0	1	-1	309.649	87.381	51.542	38.849	31.274	26.285	26.885
0	2	0	338.445	154.303	81.558	52.003	38.760	31.111	31.961
0	2	1	510.758	166.231	154.749	80.522	51.679	38.295	39.412
0	2	-1	488.408	83.985	50.840	38.090	30.690	25.803	26.417
0	2	2	825.042	80.415	159.407	155.041	83.441	53.319	55.139
0	2	-2	835.032	54.831	40.083	31.939	26.774	23.139	23.570
0	3	0	689.682	152.101	81.405	51.414	38.362	30.822	31.676
0	3	1	859.625	169.543	158.271	81.161	51.939	38.527	39.693
0	3	-1	835.818	85.115	51.153	38.306	30.852	25.962	26.600
0	3	2	1126.917	79.799	160.623	157.678	81.982	52.602	54.554
0	3	-2	1130.289	54.551	39.403	31.094	26.229	22.746	23.227
0	3	3	1473.529	54.760	82.413	165.252	164.856	85.598	91.605
0	3	-3	1479.539	40.835	31.824	27.072	22.268	20.785	21.046
1	0	0	522.302	169.873	82.921	58.505	40.883	32.558	33.050
			[486.978]						
1	1	0	571.230	165.199	85.158	54.344	40.043	31.895	32.558
1	1	1	912.150	197.479	176.974	90.558	56.129	41.107	41.986
1	1	-1	857.645	96.142	53.824	41.170	33.063	27.710	28.260
1	2	0	877.251	151.240	89.038	55.716	41.378	33.049	33.789
1	2	1	1058.936	188.652	174.559	88.120	55.839	41.037	41.971
1	2	-1	1019.278	93.142	54.000	40.623	32.654	27.344	27.887
1	2	2	1390.569	81.314	168.072	161.582	90.185	57.178	58.772
1	2	-2	1414.431	59.326	42.845	33.718	28.143	24.188	
1	3	0	1220.591	148.815	89.525	55.416	41.169	32.947	179.729
1	3	1	1408.118	184.325	171.068	89.074	56.131	41.377	42.370
1	3	-1	1369.420	93.450	54.219	40.851	32.795	27.500	28.069
1	3	2	1689.711	82.611	180.917	175.201	89.208	56.789	58.442
1	3	-2	1698.469	59.295	42.722	32.828	27.710	23.990	24.425
1	3	3	2078.505	60.299	83.102	188.674	183.884	93.483	99.147
1	3	-3	2090.666	39.731	36.777	26.198	-25.520	65.408	
2	0	0	1087.333	183.886	85.637	63.805	42.870	35.047	34.793
			[1022.891]						
2	1	0	1123.970	177.651	90.716	57.671	42.262	33.491	34.026
2	1	1	1521.755	223.847	189.885	99.253	58.110	128.011	46.207
2	1	-1	1435.031	102.890	56.958	43.208			
2	2	0	1465.285	141.410	95.510	58.914	43.695	34.778	35.432
2	2	1	1646.533	206.788	191.429	94.239	59.332	43.396	44.209
2	2	-1	1592.477	100.678	56.764	42.869	34.402	28.722	29.209
2	2	2	1992.091	81.006	174.295	165.570	95.825	60.418	61.835
2	2	-2	2029.057	62.988	45.170	35.063			
2	3	0	1800.404	146.406	96.621	59.168	132.448	-38.760	
2	3	1	1997.280	191.823	177.582	95.590	59.650	43.804	44.689
2	3	-1	1943.296	101.201	56.907	43.142	34.531	28.887	29.403
2	3	2	2289.438	83.446	200.213	191.210	95.340	60.355	61.833
2	3	-2	2304.237	63.219	45.775	34.221	28.983	25.105	25.501
3	0	0	1687.142	197.185	324.850	-71.936	44.899	35.790	36.421
			[1599.650]						
3	0	0	1687.142	197.185	324.850	-71.936	44.899	35.790	36.421
3	1	0	1713.110	187.087	95.369	60.382	44.104	39.738	-39.013
3	1	1	2162.667	242.346	235.246	93.960			
3	1	-1	2048.142	120.272	52.397				
3	2	0	2089.220	131.882	101.186	61.720	45.755	36.323	
3	2	1	2267.823	222.087	205.927	99.427	62.383	45.483	46.210
3	2	-1	2201.894	107.058	59.273	44.880	35.975	29.967	30.408
3	2	2	2625.893	80.609	234.817	224.272	100.564	63.127	64.350

Table S3: Energy levels (in cm^{-1}) of a rotating H_2 molecule inside nanotube of helicity index (10,5), for $n, j, |m| \leq 3$ and $\Lambda \leq 6$. The energies at the potential minima ($E_{\rm min}$, in cm^{-1}) and the zero-point energies ($E_{\rm zp}$, in cm^{-1}) are also collected. The energy values are relative to that of the ground state (0 0 0). The energy of the ground state (0 0 0) is given between parenthesis. For $\Lambda > 0$, $\Delta E_\Lambda = (E - E_{\Lambda=0})/\Lambda^2$. The energies of the lowest bound states without including the rotation are presented in brackets.

CNT(10,5)									
$d_{\rm CNT}$, Å					10.5				
$E_{\rm min}$, cm^{-1}					−725				
$E_{\rm zp}$, cm^{-1}					99				
n	j	m	$E_{\Lambda=0}$	$\Delta E_{\Lambda=1}$	$\Delta E_{\Lambda=2}$	$\Delta E_{\Lambda=3}$	$\Delta E_{\Lambda=4}$	$\Delta E_{\Lambda=5}$	$\Delta E_{\Lambda=6}$
0	0	0	0.000	2.905	2.875	2.834	2.787	2.737	2.686
			(−625.627)						
			[−650.433]						
0	1	0	110.148	2.778	2.754	2.720	2.680	2.637	2.593
0	1	1	140.229	4.183	4.003	3.804	3.620	3.459	3.319
0	1	-1	112.058	1.646	1.786	1.920	2.020	2.089	2.132
0	2	0	345.202	2.072	1.823	3.939	3.280	3.009	2.859
0	2	1	367.277	4.263	4.019	3.777	3.570	3.398	3.253
0	2	-1	345.509	1.360	1.568	1.751	1.883	1.972	2.030
0	2	2	382.259	11.179	7.617	-2.436	-0.676	0.192	0.686
0	2	-2	375.399	-4.388	-0.742	23.674	15.732		
0	3	0	699.621	1.536	6.118	3.923	3.301	3.026	2.867
0	3	1	720.212	4.155	4.464	3.915	3.640	3.440	3.282
0	3	-1	699.902	1.062	1.251	1.321	2.197	2.080	2.102
0	3	2	732.272	10.105	-6.821	-2.347	-0.692	0.148	0.647
0	3	-2	725.029	-3.349					
0	3	3	749.809	-14.283	-6.011	-2.687	-1.871	-0.769	-0.108
0	3	-3	748.891						
1	0	0	117.289	5.473	5.003	4.624	4.316	4.062	3.849
			[126.178]						
1	1	0	230.937	5.068	4.698	4.383	4.119	3.896	3.707
1	1	1	256.851	8.366	7.172	6.250	5.584	5.088	4.704
1	1	-1	234.331	0.745	2.081	2.686	2.930	3.014	3.023
1	2	0	467.850	3.594	33.766	4.997	4.496	4.171	3.932
1	2	1	486.606	8.764	7.203	6.181	5.488	4.987	4.604
1	2	-1	469.366	0.100	1.685	2.395	2.701	2.825	2.863
1	2	2	505.672	20.008	-7.441	-7.601	-2.414	-0.244	0.878
1	2	-2	500.797	-10.555					
1	3	0	823.155	2.693	6.391	5.037	4.515	4.156	3.904
1	3	1	841.438	8.763	7.211	6.195	5.505	4.997	4.598
1	3	-1	824.591	0.139	1.235	2.700	2.799	2.858	2.884
1	3	2	855.690	19.224	-23.721	-7.914	-2.681	-0.410	0.735
1	3	-2	851.769	-9.411					
1	3	3	881.676	-112.425	-21.985	-6.502	-2.495	-0.950	-0.013
2	0	0	205.702	14.606	10.592	8.512	7.238	6.370	5.750
			[220.287]						
2	1	0	321.341	13.555	10.000	8.120	6.955	6.155	5.568
2	1	1	353.967	18.234	12.968	10.239	8.560	7.430	6.618
2	1	-1	332.991	-6.195	2.597	4.423	4.722	4.649	4.477
2	2	0	560.816	9.167	39.823	8.425	7.211	6.386	5.801
2	2	1	584.240	19.849	13.255	10.242	8.489	7.339	6.523
2	2	-1	568.653	-7.433	1.909	3.946	4.368	4.372	4.251
2	2	2	614.377	33.948	-15.065	-14.486	-7.129	-3.602	-1.729
2	2	-2	612.508	-22.713					
2	3	0	916.083	9.809	10.692	8.332	7.183	6.337	5.720
2	3	2	963.536	33.846	-33.855	-14.261	-7.068	-3.638	-1.749
2	3	-2	963.445	-22.859					
3	0	0	292.642	26.942	17.391	13.156	10.562	8.953	7.848
			[303.638]						
3	1	0	407.076	26.215	17.094	12.813	10.375	8.804	7.706
3	1	1	457.826	28.894	18.729	14.197	11.517	9.759	8.520
3	1	-1	432.210	-14.127	3.930	6.744	6.889	6.534	6.106
3	2	0	649.395	22.263					
3	2	1	685.749	32.389	19.630	14.477	11.602	9.767	8.495
3	2	-1	666.994	-17.194	2.727	6.054	6.420	6.186	5.833
3	2	2	729.318						
3	2	-2	730.282	-38.239					
3	3	0	1005.246	20.454	17.328	12.880	10.475	8.913	7.814
3	3	2	1077.362						
3	3	-2	1079.862	-36.790					

Table S4: Energy levels (in cm^{-1}) of a rotating H_2 molecule inside nanotube of helicity index (10,10), for $n, j, |m| \leq 3$ and $\Lambda \leq 6$. The energies at the potential minima ($E_{\min}$, in cm^{-1}) and the zero-point energies (E_{zp}, in cm^{-1}) are also collected. The energy values are relative to that of the ground state (0 0 0). The energy of the ground state (0 0 0) is given between parenthesis. For $\Lambda > 0$, $\Delta E_\Lambda = (E - E_{\Lambda=0})/\Lambda^2$. The energies of the lowest bound states without including the rotation are presented in brackets.

			CNT(10,10)						
d_{CNT}, Å					13.6				
$E_{\min}$, cm^{-1}					−575				
E_{zp}, cm^{-1}					99				
n	j	m	$E_{\Lambda=0}$	$\Delta E_{\Lambda=1}$	$\Delta E_{\Lambda=2}$	$\Delta E_{\Lambda=3}$	$\Delta E_{\Lambda=4}$	$\Delta E_{\Lambda=5}$	$\Delta E_{\Lambda=6}$
0	0	0	0.000	0.727	0.727	0.726	0.726	0.725	0.724
			(−475.369)						
			[−502.037]						
0	1	0	109.371	0.714	0.714	0.713	0.712	0.712	0.711
0	1	1	138.983	0.828	0.826	0.824	0.821	0.818	0.814
0	1	-1	109.775	0.645	0.646	0.647	0.648	0.649	0.651
0	2	0	342.789	0.680	0.616	0.626	0.625	0.624	0.622
0	2	1	365.256	0.829	0.827	0.824	0.820	0.816	0.811
0	2	-1	342.748	0.619	0.620	0.622	0.624	0.627	0.630
0	2	2	377.855	-0.254	0.997	1.116	1.121	1.033	1.035
0	2	-2	367.170	0.129	0.241	0.401	0.379	0.444	0.492
0	3	0	696.437	0.564	0.568	0.568	0.567	6.426	4.711
0	3	1	716.105	0.649	0.589	1.434	1.082	0.951	0.899
0	3	-1	696.436	0.575	0.559	0.567	0.568	0.568	0.568
0	3	2	726.391	1.296	1.233	1.173	1.119	-0.631	-0.264
0	3	-2	716.485	0.316	0.374	0.435	0.486	0.529	0.563
1	0	0	123.191	0.895	0.894	0.892	0.889	0.885	0.881
			[130.899]						
1	1	0	235.674	0.876	0.875	0.873	0.870	0.867	0.863
1	1	1	258.877	1.070	1.064	1.056	1.045	1.034	1.021
1	1	-1	236.068	0.748	0.751	0.755	0.759	0.763	0.767
1	2	0	470.371	0.765	0.859	0.724	0.717	5.376	4.074
1	2	1	487.858	1.082	1.074	1.062	1.048	1.033	1.018
1	2	-1	470.381	0.698	0.704	0.711	0.720	0.728	0.735
1	2	2	499.811	0.215	1.511	1.562	1.407	-0.468	-0.112
1	2	-2	490.208	-0.112	0.183	0.278	0.455	0.559	
1	3	0	824.798	0.632	0.622	0.622	7.805	5.385	4.076
1	3	2	848.841	1.982	1.758	1.592	-0.881	-3.824	-2.365
1	3	-2	841.186	0.094	0.296	0.451	0.562		
2	0	0	218.204	1.247	1.238	1.224	1.207	1.188	1.169
			[231.836]						
2	1	0	332.906	1.211	1.203	1.190	1.176	1.159	1.142
2	1	1	350.725	1.632	1.595	1.547	1.496	1.447	1.401
2	1	-1	333.508	0.886	0.908	0.932	0.953	0.967	0.976
2	2	0	569.158	0.498	0.796	0.811	1.609	4.753	3.781
2	2	1	581.976	1.679	1.625	1.561	1.500	1.443	1.393
2	2	-1	568.833	0.771	0.810	0.852	0.886	0.910	0.927
2	2	2	592.094	4.737	2.766	2.420	-0.625	-2.323	-1.248
2	2	-2	585.367	-1.427	-0.105	0.434			
2	3	0	923.817	0.732	0.678	2.059			
2	3	2	942.996	3.652	2.832	-1.453	-4.411	-4.104	-2.653
2	3	-2	937.686	-0.736	0.091				
3	0	0	286.614	2.321	2.165	2.028	1.910	1.809	1.721
			[304.817]						
3	1	0	402.903	2.202	2.072	1.953	1.849	1.757	1.678
3	1	1	416.994	3.345	3.005	2.686	2.435	2.240	2.084
3	1	-1	404.416	0.712	1.084	1.278	1.360	1.387	1.387
3	2	0	639.756	1.701					
3	2	1	650.062	3.569	3.072	2.696	2.424	2.220	2.061
3	2	-1	640.480	0.400	0.888	1.138	1.252	1.300	1.314

Table S5: Energy levels (in cm^{-1}) of a rotating H_2 molecule outside the nanotube of helicity index (10,10), for $n, j, |m| \leq 3$ and $\Lambda \leq 6$. The energies at the potential minima ($E_{\rm min}$, in cm^{-1}) and the zero-point energies ($E_{\rm zp}$, in cm^{-1}) are also collected. The energy values are relative to that of the ground state (0 0 0). The energy of the ground state (0 0 0) is given between parenthesis. For $\Lambda > 0$, $\Delta E_\Lambda = (E - E_{\Lambda=0})/\Lambda^2$. The energies of the lowest bound states without including the rotation are presented in brackets.

			CNT(10,10)						
$d_{\rm CNT}$, Å					13.6				
$R_{\rm min}$, Å					9.914				
$E_{\rm min}$, cm^{-1}					−296				
$E_{\rm zp}$, cm^{-1}					81				
n	j	m	$E_{\Lambda=0}$	$\Delta E_{\Lambda=1}$	$\Delta E_{\Lambda=2}$	$\Delta E_{\Lambda=3}$	$\Delta E_{\Lambda=4}$	$\Delta E_{\Lambda=5}$	$\Delta E_{\Lambda=6}$
0	0	0	0.000	0.081	0.081	0.081	0.081	0.081	0.081
			(−215.516)						
			[−233.840]						
0	1	0	112.222	0.082	0.082	0.082	0.082	0.082	0.082
0	1	1	130.974	0.082	0.082	0.082	0.082	0.082	0.082
0	1	-1	112.313	0.081	0.081	0.081	0.081	0.081	0.081
0	2	0	346.558	0.081	0.081	0.081	0.081	0.080	0.080
0	2	1	361.193	0.083	0.083	0.083	0.083	0.083	0.083
0	2	-1	346.560	0.080	0.080	0.080	0.080	0.080	0.080
0	2	2	367.951	0.092	0.092	0.092	0.091	0.091	0.091
0	2	-2	361.452	0.071	0.071	0.071	0.071	0.072	0.072
0	3	0	700.804	0.079	0.079	0.079	0.079	0.079	0.079
0	3	1	713.022	0.077	0.076	0.076	0.076	0.076	0.076
0	3	-1	700.804	0.079	0.079	0.079	0.079	0.079	0.079
0	3	2	719.869	0.090	0.090	0.090	0.090	0.090	0.090
0	3	-2	713.036	0.075	0.075	0.075	0.075	0.075	0.075
1	0	0	93.195	0.076	0.076	0.076	0.076	0.076	0.076
			[100.079]						
1	1	0	208.018	0.076	0.076	0.076	0.076	0.076	0.076
1	1	1	220.864	0.076	0.076	0.076	0.076	0.076	0.076
1	1	-1	208.069	0.075	0.075	0.075	0.075	0.075	0.075
1	2	0	443.506	0.074	0.074	0.074	0.074	0.074	0.074
1	2	1	453.361	0.077	0.077	0.077	0.077	0.077	0.077
1	2	-1	443.503	0.074	0.074	0.074	0.074	0.074	0.074
1	2	2	458.592	0.088	0.088	0.087	0.087	0.087	0.087
1	2	-2	453.576	0.064	0.064	0.064	0.065	0.065	0.065
1	3	0	798.412	0.073	0.073	0.073	0.073	0.073	0.073
1	3	2	811.418	0.087	0.087	0.087	0.087	0.086	0.086
1	3	-2	806.638	0.068	0.068	0.068	0.068	0.068	0.068
2	0	0	155.322	0.069	0.069	0.069	0.069	0.069	0.069
			[166.508]						
2	1	0	271.706	0.069	0.069	0.069	0.069	0.069	0.069
2	1	1	279.919	0.069	0.069	0.069	0.069	0.069	0.069
2	1	-1	271.743	0.067	0.067	0.067	0.067	0.067	0.067
2	2	0	507.901	0.067	0.067	0.067	0.067	0.067	0.067
2	2	1	514.236	0.071	0.071	0.071	0.071	0.071	0.071
2	2	-1	507.907	0.067	0.067	0.067	0.067	0.067	0.067
2	2	2	518.548	0.078	0.078	0.078	0.078	0.078	0.078
2	2	-2	514.422	0.063	0.063	0.063	0.064	0.064	0.064
2	3	0	863.236	0.065	0.065	0.065	0.065	0.065	0.065
2	3	2	871.662	0.083	0.083	0.082	0.082	0.082	0.081
2	3	-2	868.585	0.058	0.058	0.059	0.059	0.059	0.060
3	0	0	195.549	0.063	0.063	0.063	0.063	0.063	0.063
			[208.683]						
3	1	0	312.511	0.063	0.063	0.063	0.063	0.063	0.063
3	1	1	319.371	0.065	0.065	0.065	0.065	0.065	0.065
3	1	-1	312.522	0.061	0.061	0.061	0.061	0.061	0.061
3	2	0	549.010	0.060	0.060	0.060	0.060	0.060	0.060
3	2	1	554.048	0.066	0.066	0.066	0.066	0.066	0.066
3	2	-1	549.010	0.060	0.060	0.060	0.060	0.060	0.060

S3 Calculation of angular factors

In practice, we used the following functions as angular basis in our computer codes:

$$\Theta_{j|m|}(x)\frac{\exp(\imath m\phi)}{\sqrt{(2\pi)}}$$

where $x = \cos\theta$ and $\Theta_{j|m|}(x)$ are the associated Legendre functions. These basis functions only differ from spherical harmonics Y_{jm} by a phase factor for $m < 0$. The angular factors (cf. Eq. (7) of the main text) can be expressed as:

$$\langle j'm'|(1-x^2)^I\cos^{2K}(\phi)|jm\rangle = \langle\Theta_{j'|m'|}(x)|(1-x^2)^I|\Theta_{j|m|}(x)\rangle\langle m'|\cos^{2K}(\phi)|m\rangle$$

where the factors depending on ϕ can easily be evaluated from

$$\cos^2(\phi) = \frac{2+\exp(2\imath\phi)+\exp(-2\imath\phi)}{4}$$

and

$$\langle m'|\exp(\imath M\phi)|m\rangle = \delta_{m',m+M}$$

In order to perform the integrals over x, the following relation can be used recursively:

$$\left(1-x^2\right)\Theta_{jK} = -a_{j-2,-K}a_{j-1,-(K+1)}\Theta_{j-2K} - a_{jK}a_{j+1,-(K+1)}\Theta_{j+2K} + \left(a^2_{j-1,-(K+1)} + a^2_{jK}\right)\Theta_{jK}$$

with

$$a_{jK} = \sqrt{\frac{(j+K+1)(j+K+2)}{(2j+1)(2j+3)}}$$

S4 On the degeneracy of $(n\ 1\ 0)$ and $(n\ 1\ 1a)$ levels

From the results presented in the main text and above, we can see that, apart from (5,5) nanotube, the energy levels $(n\ 1\ 0)$ and $(n\ 1\ 1a)$ are almost degenerate while the levels $(n\ 1\ 1s)$ and $(n\ 1\ 1a)$ have different energies. Looking at the decomposition in Table 3 of the main text, it can be observed that the difference comes mainly from the potential term and, to a lesser extent, from the kinetic R-dependent $K(R)$ term. To understand better the origin of this degeneracy, we provide in Table S6 the list of the main contributions to the potential for the $(n\ 1\ m)$ levels associated to a H_2 molecule rotating outside the nanotube of helicity index (10,10) and inside the nanotube of helicity index (5,5). These contributions are given as a function of indexes I and K, see Eq. (5) of the main text (in cm^{-1}).

Table S6: Contributions from different p_{JIK} terms of the potential to the $(n = 0\ j = 1)$ levels of a single H_2 molecule rotating outside of the nanotube of helicity index (10,10) and inside the nanotube of helicity index (5,5) (in cm^{-1}). The different kinetic energy contributions are also provided.

	(10,10)-ext			(5,5)		
I,K	$(0\ 1\ 0)$	$(0\ 1\ 1a)$	$(0\ 1\ 1s)$	$(0\ 1\ 0)$	$(0\ 1\ 1a)$	$(0\ 1\ 1s)$
0,0	−260.698	−260.800	−251.257	-1330.062	-1276.432	-1287.344
1,0	0.111	0.199	0.547	70.376	160.881	157.534
1,1	9.592	9.708	18.242	10.123	14.710	42.554
2,1	−0.181	−0.278	−0.621	0.208	0.460	1.338
2,2	0.714	0.718	3.021	-0.0086	-0.015	-0.072
Total (pot)	−250.456	−250.440	−230.048	-1245.622	-1087.390	-1073.291
$K(R)$	28.068	28.055	26.349	183.653	160.341	168.339
K(int)	119.093	119.100	119.078	125.463	125.577	127.997
K(ext)	0.00016	0.082	0.080	0.026	113.214	119.229

From the expression of the angular factor given in section S3, it is clear that the $K = 0$ term gives no splitting of $j = 1$ levels. For $K = I = 1$, the θ-dependent factor is equal to $2/5$ (for $m = 0$) and $4/5$ (for $m = 1$) while the ϕ-dependent factor is equal to $1/2$ for $\Delta m = 0$ and $1/4$ for $\Delta m = 2$. It is easy to notice that the contribution of ϕ-factors f to $1a/1s$ term is $\langle 1|f|1\rangle \mp \langle 1|f|-1\rangle$ and, then, f results in $1/2 \mp 1/4 = 1/4, 3/4$ for $K = 1$. Therefore, it turns out that the total θ, ϕ factor for $I = K = 1$ is exactly the same (i.e., $1/5$) for $(n\ 1\ 0)$ and $(n\ 1\ 1a)$ levels, but three times larger for

the $(n\ 1\ 1s)$ level.

From Eq. (5) of the main text and section S1, it can be shown that the $I = K = 1$ term comes from potential expansion terms V_L [Eq. (4)] for which $L \geq I + K = 2$, with the term V_2 being the most important. The splitting of $(n\ 1\ 0)$ and $(n\ 1\ 1a)$ levels would arise from $I = 2$ and $K = 1$ factors which are related to the, much smaller, V_3 coefficient (see Table S1).

The difference in potential contributions to $(n\ 1\ 0)$ and $(n\ 1\ 1s)$ levels clearly leads to modification of radial factors as shown in Figure S2. Therefore, although the expected contribution of the term $I = K = 1$ is three times larger for $(n\ 1\ 1s)$ levels than for $(n\ 1\ 0)$ levels, in practice it is only two times larger for the particular case of the $(n = 0\ j = 1)$ levels of a H_2 molecule rotating in the outside of the (10,10) nanotube (see Table S6). Also, it leads to the modification of the $K(R)$ contributions noticed above.

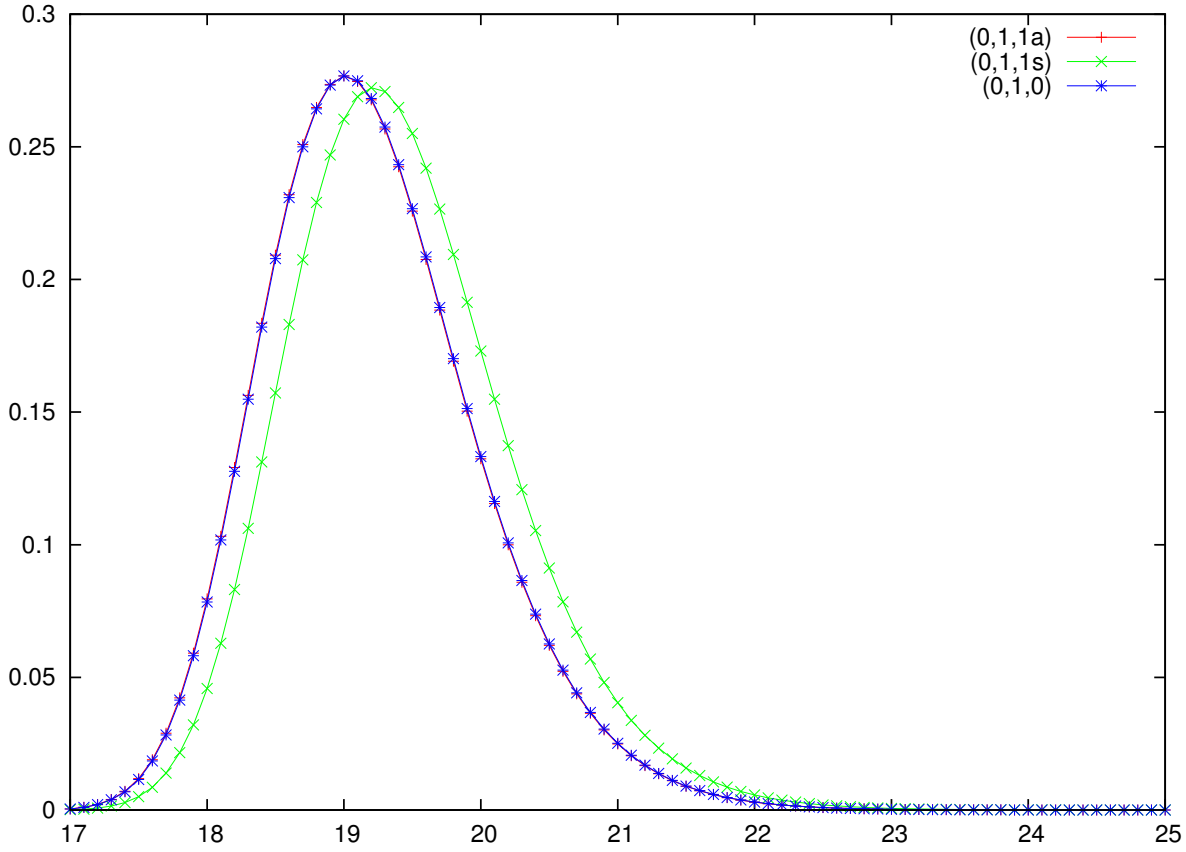

Figure S2: Picture showing the modification of the radial factor for the $(0\ 1\ 0)$ and $(0\ 1\ 1s)$ levels of a H_2 molecule rotating outside the (10,10) nanotube.

The situation is quite different for a H_2 molecule rotating inside the narrow nanotube of helicity index (5,5). In this case, the term K_{ext} containing the factor $1/R^2$ becomes much more important, causing the splitting of $(0\ 1\ 0)$ and $(0\ 1\ 1)$ levels. The radial factors are similar for $(0\ 1\ 1a)$ and $(0\ 1\ 1s)$ states and different from that of the $(0\ 1\ 0)$ state, as shown in Figure S3. Finally, the combination of different contribution to total energy leads to a smaller splitting (as compared with the $m = 0 - m = 1$ splitting) of $(0\ 1\ 1a)$ and $(0\ 1\ 1s)$ levels, as can be seen in Tables S2 and S6.

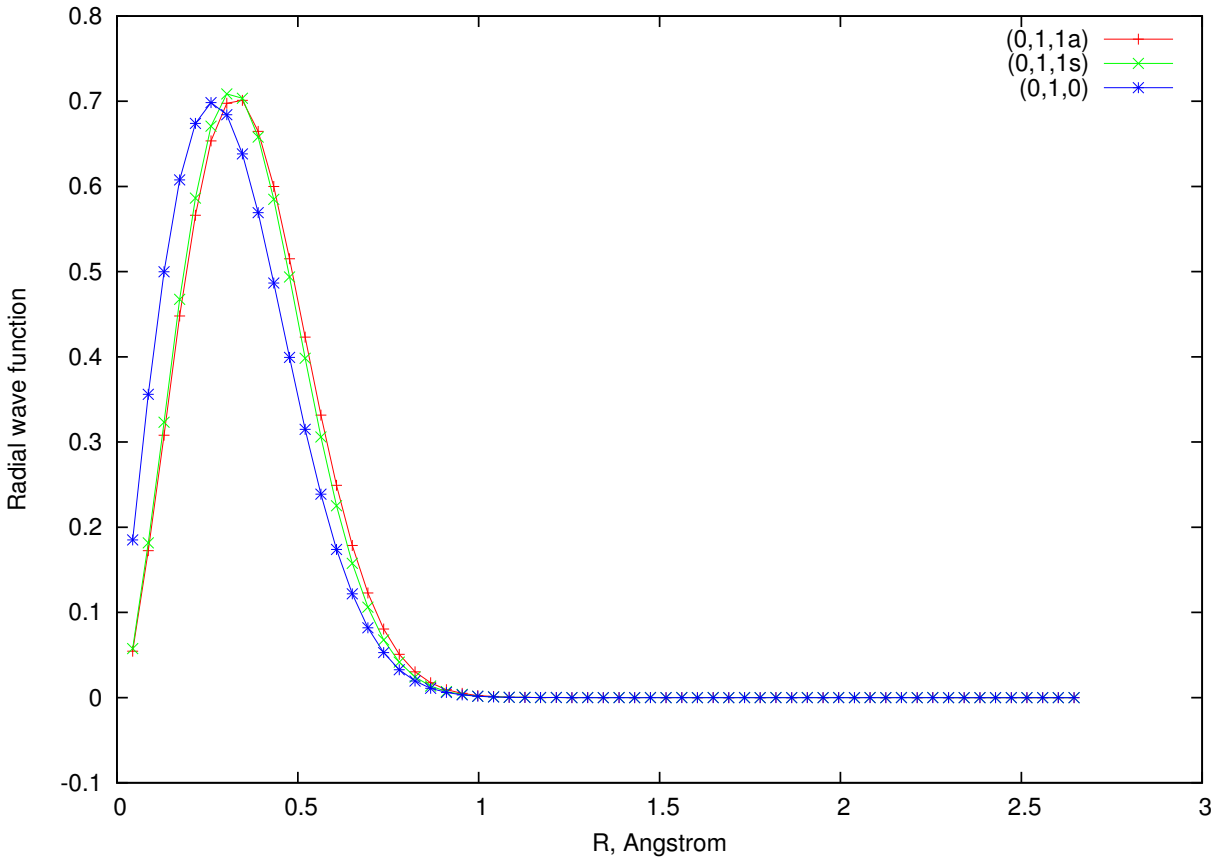

Figure S3: Picture showing the modification of the radial factor for $n = 0, j = 1$ levels of a H_2 molecule rotating inside the (5,5) nanotube.