Table S2 Equilibrium, ground and excited states rotational constants, harmonic and anharmonic frequencies of naphthalene from all performed calculations.[a]

	Experimental values	B971/ cc-pVTZ// ANO-DZP	B971/ cc-pVTZ// ANO-QZP	B3LYP/ 6-31G**	B971/ 6-31G**	B971/ ANO-DZP	B971/ cc-pVTZ	B971/ daVDZ	B971/ 3df2p	B971/ ANO-TZP	B971/ aVTZ	B971/ ANO-QZP	B971/ cc-pVQZ	MP2/ 6-31G**	MP2/ ANO-DZP	MP2/ cc-pVTZ
eq.																
A_e				0.104021	0.103539	0.104904	0.104332	0.103181	0.104311	0.106082	0.104304	0.104898	0.104377	0.104056	0.104692	0.104452
B_e				0.041042	0.040872	0.041389	0.041179	0.040752	0.041176	0.041865	0.041171	0.041403	0.041205	0.041134	0.041313	0.041324
C_e				0.029430	0.029304	0.029679	0.029526	0.029214	0.029522	0.030018	0.029519	0.029686	0.029543	0.029480	0.029623	0.029609
GS																
A_0	*0.104052*	0.104132	0.104126	0.103263	0.102784	0.104065	0.103552	0.102419	0.103501	0.105306	0.103527			0.103114	0.103859	
B_0	*0.041127*	0.041132	0.041146	0.040779	0.040612	0.041110	0.040917	0.040494	0.040941	0.041608	0.040910			0.040856	0.041037	
C_0	*0.029484*	0.029493	0.029500	0.029240	0.029115	0.029473	0.029334	0.029025	0.029342	0.029829	0.029328			0.029258	0.029420	
ν_{46}																
ω_e		777.832	772.477	803.656	800.011	836.701	799.957	795.067	798.734	825.050	803.013	830.935	797.976	764.493	823.058	794.956
ν_0	*782.331*	760.931	755.950	787.199	779.003	805.467	782.764	-3288	-295	796.868	562.354			896.394	800.038	
A_1	*0.103861*	0.103997	0.104001	0.103199	0.102720	0.104091	0.103488	0.102353	0.103435	0.105240	0.103462			0.103048	0.103789	
B_1	*0.041121*	0.041127	0.041142	0.040774	0.040606	0.041102	0.040911	0.040490	0.040936	0.041601	0.040904			0.040852	0.041029	
C_1	*0.029486*	0.029495	0.029502	0.029241	0.029117	0.029473	0.029335	0.029027	0.029344	0.029831	0.029330			0.029261	0.029420	
ν_{47}																
ω_e		470.240	468.148	491.096	486.372	504.234	484.877	489.318	483.712	496.424	485.809	493.960	483.470	442.162	497.236	477.588
ν_0	*473.740*	464.632	463.754	484.464	480.321	493.291	483.901	-1446	-239	491.181	3.752			584.215	486.374	
A_1	*0.104052*	0.104134	0.104129	0.103261	0.102783	0.104055	0.103551	0.102421	0.103500	0.105303	0.103525			0.103141	0.103851	
B_1	*0.041145*	0.041130	0.041145	0.040778	0.040610	0.041108	0.040915	0.040492	0.040941	0.041606	0.040909			0.040858	0.041036	
C_1	*0.029470*	0.029504	0.029511	0.029250	0.029126	0.029483	0.029345	0.029036	0.029354	0.029840	0.029339			0.029272	0.029430	
ν_{48}																
ω_e		156.776	155.661	175.675	173.963	179.586	171.881	175.067	171.261	175.111	171.833	175.256	170.774	165.914	176.984	169.615
ν_0	*166.658*	150.900	150.478	171.760	168.640	174.937	167.856	-5808	-1081	168.014	-429.970			179.296	173.461	
A_1	*0.103833*	0.103907	0.103901	0.103046	0.102567	0.103843	0.103333	0.102208	0.103282	0.105084	0.103308			0.102895	0.103636	
B_1	*0.041155*	0.041165	0.041180	0.040807	0.040640	0.041137	0.040946	0.040522	0.040971	0.041637	0.040940			0.040887	0.041065	
C_1	*0.029514*	0.029523	0.029530	0.029265	0.029141	0.029499	0.029361	0.029051	0.029369	0.029856	0.029355			0.029286	0.029446	
N basis functions				190	190	252	412	424	470	484	644	732	790			
CPU time /days	anharmonic			2.5	5	58	88	125	102	494	695			97	427	
	harmonic					0.1	0.1	0.2	0.2	1	0.3	3	4	0.2	2	36

All values are in cm^{-1}

3df2p = 6-311++G(3df,2p); daVDZ = d-aug-cc-pVDZ; aVTZ = aug-cc-pVTZ; ANO-XZP = ANO-RCC reduced to double-ζ (X=D), triple-ζ (X=T) and quadruple-ζ (X=Q) polarization

A_i, B_i, C_i = rotational constants at equilibrium (i=e), of the ground state (i=0) and of the excited state (i=1).

ω_e = harmonic frequency

ν_0 = anharmonic frequency