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Coumarin 102 excitation in aqueous solution: contributions of vibronic coupling and hydration

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SUPPLEMENTARY MATERIAL

Functional choice

It is known that all three values of E_{vert}, E_{adia}, and E_{vibron} are largely determined by the X fraction of the "exact" Hartree-Fock exchange: with X increasing, as a rule, and the values of these three energies grow also [78,79]. The comparison with the experimental energy E_{max} should not be E_{vert} (as was for the C102 case in Refs. [35,43,45,47,49,57–60], but E_{vibron} [80]). It is known from the just-mentioned theoretical works on C102 that the absorption spectrum of its solutions in the visible range consists of one band due to the singlet HOMO→LUMO ($S_0 \rightarrow S_1$) transition of $\pi \rightarrow \pi^*$ type. As an initial approximation, we used the most popular B3LYP functional with X=20% [81]. However, it gave the E_{vibron}=2.95 eV value underestimated compared with the experimental E_{max}=3.16 eV energy (Table S1).

Table S1. Calculated energies and corresponding wavelengths (vertical, adiabatic and maxima of vibronic absorption spectra) for C102 absorption in aqueous media. The X portion of the exact Hartree-Fock exchange is shown in parentheses

Functional	λ_{vert} (nm)	E_{vert} (eV)	λ_{adia} (nm)	E_{adia} (eV)	λ_{vibron} (nm)	E_{vibron} (eV)
B3LYP (20)	381	3.25	414	3.00	420	2.95
BMK (42)	341	3.64	376	3.30	377	3.29
M05 (28)	364	3.41	391	3.17	394	3.15
MN15 (44)	348	3.56	385	3.22	385	3.22
PBE0 (25)	366	3.39	398	3.12	404	3.07

Therefore, after that, several functionals with X larger values were applied, of which the M05 functional [82] gave excellent agreement with the experiment (see Table 1). The vibronic absorption spectrum of C102, calculated at the M05/(6–31++G(d,p)/IEFPCM theory level, in its shape also coincides well with the experimental one (Fig. 2). Therefore, further analysis will be carried out at this theory level.

Table S2. Parameters of vibronic transitions of C102 excitation in an aqueous media

#	Transition	λ (nm)	E (eV)	v (cm^{-1})	I (cm^{-1}/(molecule·cm^{-2}))	p (atomic units)	Vibration definition
1	$0_0 \rightarrow 0^0$	404	3.07	0	14250	2.79	-
2	$0_0 \rightarrow 7^1$	402	3.09	168	483	0.0941	Flexural vibration of the chromophore perpendicular to its plane
3	$0_0 \rightarrow 14^1$	399	3.11	338	1631	0.315	Compression-stretching of a chromophore along its long (B-C-D) axis
4	$0_0 \rightarrow 21^1$	396	3.13	500	2663	0.511	Compression-stretching of a perpendicular to its long axis
5	$0_0 \rightarrow 22^1$	396	3.13	522	465	0.0892	Shear vibration of a chromophore along its long axis
6	$0_0 \rightarrow 25^1$	395	3.14	586	529	0.101	Shear vibrations of C and D rings
7	$0_0 \rightarrow 52^1$	386	3.21	1198	958	0.179	Pendulum vibrations of hydrogen atoms
8	$0_0 \rightarrow 83^1$	381	3.26	1558	775	0.143	Compression-stretching of C and D rings
9	$0_0 \rightarrow 85^1$	378	3.28	1724	1798	0.329	Compression-stretching of carbonyl C=O bond

λ is the wavelength, E is the energy of the vibronic transition, v is the vibration frequency, I is the line intensity, and p is the dipole strength

Table S3. Cartesian coordinates (Å) of C102 molecule

Atom	Ground state (S_0)			Equilibrium excited state (S_1)		
	X	*Y*	*Z*	*X*	*Y*	*Z*
O	–2.00626	–1.38851	0.022638	–2.00749	–1.39995	0.044042
C	–1.01206	–0.4495	0.018273	–1.02273	–0.45602	0.030233
C	–1.33107	0.920412	0.006721	–1.33006	0.932038	0.018384
C	–2.71662	1.3056	–0.01053	–2.7089	1.340524	–0.00541
C	–3.67387	0.327649	–0.00966	–3.67782	0.324405	–0.02389
C	–3.34357	–1.06967	0.008879	–3.37287	–1.05645	0.000013
C	0.292918	–0.93799	0.028063	0.27719	–0.93912	0.029652
C	1.357795	–0.00198	0.044033	1.361082	0.008428	0.05884
C	1.068181	1.399626	0.044762	1.08933	1.40794	0.050861
C	–0.24614	1.818693	0.015834	–0.23109	1.832319	0.021099
N	2.661009	–0.43879	0.036811	2.653014	–0.45075	0.084849
C	3.761896	0.493264	0.237512	3.771548	0.471438	0.226075
C	3.487887	1.82565	–0.42841	3.500582	1.799144	–0.44899
C	2.188735	2.407271	0.101712	2.21497	2.401704	0.08973
C	0.550334	–2.42254	0.027616	0.538551	–2.41616	0.029155
C	1.966178	–2.7416	–0.42211	1.944706	–2.73954	–0.44108
C	2.959095	–1.84191	0.283683	2.947776	–1.86343	0.276477
C	–3.10335	2.750485	–0.02921	–3.07634	2.784804	–0.02495
O	–4.13133	–2.00596	0.014267	–4.1489	–2.02181	–0.00559
H	–0.4443	2.886205	0.01068	–0.43001	2.898734	0.008549
H	–4.73047	0.567872	–0.02229	–4.73438	0.572007	–0.05141
H	2.957009	–2.04417	1.366487	2.944038	–2.08031	1.357694
H	3.972428	–2.03344	–0.07764	3.961826	–2.04101	–0.0852
H	2.059521	–2.5963	–1.50362	2.032492	–2.57809	–1.52041
H	2.207465	–3.7871	–0.21321	2.183603	–3.78775	–0.24673
H	0.381603	–2.82181	1.035949	0.39119	–2.80069	1.048086
H	–0.17564	–2.92388	–0.6173	–0.20671	–2.91994	–0.58971
H	1.907826	3.304668	–0.45663	1.936571	3.294679	–0.47664
H	2.335885	2.724974	1.141958	2.369745	2.730808	1.126145
H	3.424602	1.682248	–1.51255	3.425125	1.646685	–1.5308
H	4.322908	2.504773	–0.2374	4.348969	2.464228	–0.27184
H	4.660776	0.034625	–0.18283	4.653177	–0.01482	–0.19604
H	3.945499	0.636491	1.314138	3.965706	0.619134	1.301003
H	–4.1869	2.867801	–0.04601	–4.16041	2.912102	–0.04191
H	–2.71425	3.269593	0.851611	–2.69096	3.319654	0.854052
H	–2.68836	3.253923	–0.90725	–2.66552	3.301751	–0.90361

Table S4. Cartesian coordinates (Å) of the "C102+H_2O (A)" system

Atom	Ground state (S_0)		
	X	*Y*	*Z*
O	2.190727	–1.41242	–0.07434
C	1.230098	–0.44106	–0.10667
C	1.584932	0.914004	–0.01165
C	2.97924	1.254084	0.136484
C	3.899836	0.246012	0.171654
C	3.530333	–1.14	0.06273
C	–0.08676	–0.88478	–0.24229
C	–1.11182	0.086159	–0.29425
C	–0.78584	1.472847	–0.23131
C	0.536335	1.847938	–0.08104
N	–2.44681	–0.31583	–0.36249
C	–3.44519	0.669416	–0.7815
C	–3.24112	1.993408	–0.075
C	–1.85247	2.531106	–0.37369
C	–0.37112	–2.36015	–0.35828
C	–1.83869	–2.68238	–0.13049
C	–2.72239	–1.67356	–0.83287
C	3.403624	2.683262	0.24833
O	4.289	–2.09801	0.07949
O	–3.33662	–0.54846	2.521181
H	0.766284	2.907602	–0.02852
H	4.958721	0.448138	0.281956
H	–2.5785	–1.72874	–1.92328
H	–3.77642	–1.8812	–0.63244
H	–2.0663	–2.6783	0.940329
H	–2.06865	–3.68508	–0.49984
H	–0.06499	–2.69982	–1.35573
H	0.253473	–2.91369	0.347346
H	–1.61855	3.379988	0.274914
H	–1.8281	2.915356	–1.40116
H	–3.37426	1.855489	1.002908
H	–4.00602	2.700694	–0.40597
H	–4.42838	0.254539	–0.54467
H	–3.40306	0.80697	–1.87327
H	4.484335	2.764933	0.363337
H	3.107897	3.247673	–0.64096
H	2.927238	3.165149	1.107031
H	–2.95648	–0.47363	1.629625
H	–2.59942	–0.80191	3.084242

Table S5. Cartesian coordinates (Å) of "C102+H_2O (B)"

Atom	Ground state (S_0)			Equilibrium excited state (S_1)		
	X	*Y*	*Z*	*X*	*Y*	*Z*
C	–3.21584	–2.09788	–0.28401	–3.19518	–2.12401	–0.27952
N	–3.07238	–0.66946	–0.04142	–3.06148	–0.68709	–0.08571
C	–1.82644	–0.09296	–0.04726	–1.83055	–0.08464	–0.05826
C	–0.6649	–0.90669	–0.03118	–0.64659	–0.90452	–0.03314
C	–0.75731	–2.41038	–0.031	–0.73903	–2.40103	–0.03222
C	–2.12906	–2.88231	0.420972	–2.09966	–2.88194	0.43722
C	–1.69226	1.332853	–0.04803	–1.71832	1.335874	–0.04817
C	–0.43324	1.894521	–0.01854	–0.45387	1.90532	–0.02259
C	0.744407	1.120609	–0.0088	0.738613	1.135457	–0.02356
C	0.576537	–0.27608	–0.02044	0.590471	–0.27509	–0.03586
O	1.670117	–1.0994	–0.02362	1.676419	–1.10362	–0.05054
C	2.954055	–0.63342	–0.00787	2.982257	–0.60543	–0.01333
C	3.137188	0.786247	0.010123	3.139082	0.797179	0.008475
C	2.077304	1.654922	0.009471	2.065369	1.699121	–0.00357
C	–4.27281	0.135071	–0.22684	–4.27873	0.103193	–0.21378
C	–4.1406	1.490473	0.435711	–4.15468	1.45146	0.463485
C	–2.91742	2.20948	–0.10572	–2.94888	2.19645	–0.08105
C	2.304639	3.132781	0.027653	2.266267	3.175057	0.013859
O	3.841528	–1.48585	–0.01129	3.866916	–1.48416	–0.01015
O	6.54022	–0.68359	0.009729	6.536403	–0.70709	0.041142
H	4.161349	1.140674	0.023712	4.162291	1.15959	0.030957
H	3.368681	3.36814	0.044011	3.328663	3.425278	0.027252
H	1.83688	3.587562	0.905646	1.801295	3.642477	0.893273
H	1.860318	3.605461	–0.85311	1.819151	3.661248	–0.86426
H	–0.3538	2.977262	–0.01346	–0.3762	2.987355	–0.00894
H	–2.735	3.136621	0.444609	–2.77054	3.11459	0.485318
H	–3.10366	2.500469	–1.14747	–3.14503	2.506435	–1.11625
H	–4.05344	1.357453	1.519484	–4.05603	1.306133	1.544357
H	–5.04655	2.073385	0.250504	–5.07397	2.016509	0.292998
H	–4.48427	0.255371	–1.3009	–4.49711	0.230202	–1.28646
H	–5.10952	–0.42037	0.204851	–5.09578	–0.48125	0.213802
H	–4.20118	–2.39785	0.080513	–4.18267	–2.41521	0.08162
H	–3.19445	–2.30032	–1.36634	–3.16682	–2.33651	–1.361
H	–2.25439	–3.948	0.212802	–2.21792	–3.95003	0.241081
H	–2.23617	–2.74746	1.502504	–2.20518	–2.73319	1.516719
H	–0.54748	–2.78826	–1.03979	–0.54835	–2.7652	–1.05149
H	0.019983	–2.82912	0.613008	0.058215	–2.81776	0.586526
H	5.617951	–1.00101	0.000662	5.602861	–1.00183	0.023291
H	7.080848	–1.47664	–0.03537	7.056118	–1.51504	0.03964

Table S6. Cartesian coordinates (Å) of the "C102+2H_2O (A+B)" system

Atom	Ground state (S_0)		
	X	*Y*	*Z*
O	1.879565	–1.08685	–0.12962
C	0.812142	–0.23155	–0.13904
C	1.012761	1.154125	–0.03573
C	2.359736	1.648983	0.095105
C	3.390429	0.75062	0.104967
C	3.171364	–0.66212	–0.0122
C	–0.44556	–0.82323	–0.26115
C	–1.57541	0.025044	–0.29127
C	–1.40867	1.440175	–0.219
C	–0.13682	1.962993	–0.08199
N	–2.85526	–0.5252	–0.34866
C	–3.96617	0.342281	–0.74511
C	–3.90537	1.675177	–0.02884
C	–2.59101	2.370376	–0.33848
C	–0.56131	–2.32042	–0.38595
C	–1.97892	–2.80848	–0.13802
C	–2.98228	–1.90404	–0.82135
C	2.621839	3.115281	0.216626
O	4.035777	–1.53548	–0.01771
O	–3.70646	–0.85812	2.543282
O	6.760667	–0.84223	0.203397
H	5.830298	–1.12266	0.125868
H	7.271114	–1.65622	0.192733
H	–0.02796	3.041341	–0.0224
H	4.42136	1.071104	0.20081
H	–2.85047	–1.93847	–1.91398
H	–4.0026	–2.2304	–0.6059
H	–2.18802	–2.83536	0.936267
H	–2.09904	–3.82921	–0.50986
H	–0.23519	–2.6159	–1.39102
H	0.13335	–2.80423	0.305274
H	–2.44744	3.235137	0.315295
H	–2.62319	2.763045	–1.36253
H	–4.00833	1.514567	1.049198
H	–4.74988	2.293167	–0.34446
H	–4.89176	–0.18466	–0.49912
H	–3.95527	0.491588	–1.83596
H	3.688334	3.318458	0.311168
H	2.244308	3.65107	–0.65914
H	2.111666	3.529791	1.090902
H	–3.33274	–0.74653	1.653347
H	–2.9587	–1.09903	3.097887

Table S7. Cartesian coordinates (Å) of the "C102+3H_2O (A+2B)" system

Atom	Ground state (S_0)		
	X	*Y*	*Z*
O	2.175555	–1.41719	–0.08739
C	1.216693	–0.43911	–0.11669
C	1.576021	0.909871	–0.0142
C	2.963877	1.244445	0.137611
C	3.883331	0.237875	0.167127
C	3.508317	–1.13469	0.050872
C	–0.09474	–0.87676	–0.25456
C	–1.11437	0.096507	–0.30194
C	–0.78215	1.479239	–0.23478
C	0.535732	1.849283	–0.07938
N	–2.44177	–0.29758	–0.37683
C	–3.45092	0.689532	–0.74806
C	–3.22417	1.997794	–0.02202
C	–1.84757	2.536744	–0.36842
C	–0.38587	–2.34925	–0.37167
C	–1.85355	–2.65876	–0.12754
C	–2.73025	–1.651	–0.8386
C	3.388313	2.668908	0.259027
O	4.264633	–2.0979	0.062631
O	–3.16332	–0.55626	2.546252
O	7.099842	–1.60591	0.180367
H	6.153189	–1.82423	0.082518
H	7.560423	–2.34089	–0.2342
H	0.77317	2.906755	–0.0189
H	4.941301	0.440969	0.280881
H	–2.58559	–1.71938	–1.92811
H	–3.78652	–1.84524	–0.6365
H	–2.07218	–2.63054	0.94509
H	–2.09322	–3.66448	–0.48199
H	–0.09604	–2.68883	–1.37419
H	0.241424	–2.90684	0.32889
H	–1.58979	3.395912	0.257288
H	–1.85652	2.898789	–1.40456
H	–3.31076	1.83461	1.057714
H	–4.00149	2.71032	–0.30988
H	–4.42504	0.265871	–0.48991
H	–3.44241	0.853643	–1.83694
H	4.469432	2.744016	0.381721
H	3.095045	3.23629	–0.63004
H	2.902782	3.146819	1.115742
H	–2.88902	–0.46699	1.616671
H	–2.92915	–1.46162	2.772235
O	4.427679	–4.98172	–0.03415
H	4.253534	–4.02205	0.011642
H	3.558913	–5.39294	–0.01543

Table S8. Cartesian coordinates (Å) of "C102+2H_2O (2B)"

Atom	Ground state (S_0)			Equilibrium excited state (S_1)		
	X	*Y*	*Z*	*X*	*Y*	*Z*
O	1.571572	0.624336	–0.02396	1.576542	0.629696	–0.00238
C	0.376262	–0.04406	–0.00613	0.388842	–0.04679	0.007086
C	0.357844	–1.45093	0.001722	0.346695	–1.4615	0.017845
C	1.606211	–2.15683	–0.02258	1.588707	–2.19951	–0.00874
C	2.774186	–1.43638	–0.0481	2.770638	–1.44872	–0.05011
C	2.774523	–0.01002	–0.04603	2.795275	–0.0407	–0.04864
C	–0.76699	0.748846	0.004485	–0.75157	0.745885	0.000709
C	–2.02684	0.098301	0.046837	–2.03429	0.093629	0.054777
C	–2.08434	–1.33345	0.068781	–2.11423	–1.32861	0.071049
C	–0.91345	–2.05975	0.034381	–0.93775	–2.06293	0.042993
N	–3.18286	0.835734	0.047873	–3.17112	0.857831	0.088048
C	–4.48003	0.203132	0.250441	–4.48171	0.241458	0.247526
C	–4.53615	–1.16727	–0.39147	–4.55136	–1.12162	–0.40769
C	–3.41548	–2.03561	0.152858	–3.44893	–2.01485	0.13303
C	–0.65592	2.250944	–0.02567	–0.6397	2.240017	–0.0376
C	–1.95895	2.894382	–0.46942	–1.93028	2.890461	–0.50037
C	–3.13052	2.275053	0.263619	–3.10652	2.30391	0.248308
C	1.637559	–3.65152	–0.02174	1.589981	–3.68869	–0.00422
O	3.770864	0.722905	–0.06131	3.79442	0.717096	–0.07808
O	6.380736	–0.36833	–0.02953	6.385653	–0.32756	–0.06976
H	5.491702	0.029603	–0.01597	5.481432	0.043689	–0.0539
H	6.86223	0.068344	0.67827	6.849389	0.110312	0.648834
H	–0.98056	–3.14317	0.044558	–1.00642	–3.14564	0.048193
H	3.742343	–1.92237	–0.06722	3.737368	–1.94135	–0.08001
H	–3.06696	2.491366	1.341386	–3.03305	2.534446	1.323742
H	–4.07192	2.697589	–0.0952	–4.0511	2.717766	–0.10763
H	–2.09886	2.756385	–1.54672	–2.07191	2.733885	–1.57451
H	–1.93763	3.970611	–0.2801	–1.89985	3.968629	–0.32808
H	–0.37983	2.61663	0.971781	–0.38198	2.598468	0.969128
H	0.15898	2.548054	–0.69096	0.195485	2.528309	–0.67956
H	–3.36545	–2.98816	–0.38165	–3.40438	–2.95596	–0.42171
H	–3.62761	–2.28054	1.201464	–3.66977	–2.28185	1.17513
H	–4.44192	–1.06356	–1.4778	–4.45134	–1.00747	–1.49212
H	–5.51016	–1.62065	–0.19033	–5.53571	–1.55422	–0.21478
H	–5.23653	0.860227	–0.18622	–5.21917	0.924605	–0.1781
H	–4.69825	0.128954	1.327117	–4.69655	0.162368	1.325422
H	2.661311	–4.02449	–0.0435	2.609071	–4.07898	–0.02629
H	1.143731	–4.04983	0.869249	1.09391	–4.09689	0.887136
H	1.105536	–4.05176	–0.88956	1.054091	–4.10189	–0.87023
O	3.416701	3.536651	0.089842	3.440839	3.490075	0.127312
H	3.499974	2.566991	0.037832	3.518568	2.517777	0.056642
H	2.56338	3.686045	0.5062	2.597339	3.635973	0.563937

Table S9. Parameters of vibronic transitions of "C102+H_2O (B)" system excitation in an aqueous media

#	Transition	λ (nm)	E (eV)	v (cm^{-1})	I (cm^{-1}/ (molecule·cm^{-2}))	p (atomic units)	Vibration definition
1	$0_0 \rightarrow 0^0$	409	3.03	0	11670	2.31	-
2	$0_0 \rightarrow 2^1 5^1$	408	3.04	31.2 60.6	462	0.0912	Pendulum vibration of bound water in the plane of the chromophore; torsional vibration of B ring
3	$0_0 \rightarrow 18^1$	404	3.07	342	1435	0.280	Compression-stretching of the chromophore along its long axis
4	$0_0 \rightarrow 26^1$	401	3.09	501	2233	0.434	Compression-stretching of the chromophore perpendicular to its long axis
5	$0_0 \rightarrow 27^1$	401	3.10	523	464	0.0900	Shear vibration of a chromophore along its long axis
6	$0_0 \rightarrow 60^1$	390	3.18	1213	789	0.149	Compression-stretching of the C and D rings
7	$0_0 \rightarrow 92^1$	382	3.24	1712	1416	0.262	Compression-stretching of the carbonyl bond and the corresponding tracking oscillations of the angle of the bound water molecule

Table S10. Parameters of vibronic transitions of "C102+2H_2O (2B)" system photoexcitation in an aqueous media

#	Transition	λ (nm)	E (eV)	v (cm^{-1})	I (cm^{-1}/ (molecule·cm^{-2}))	p (atomic units)	Vibration definition
1	$0_0 \rightarrow 0^0$	414	2.99	0	12370	2.48	-
2	$0_0 \rightarrow 3^1$	414	3.00	27.2	708	0.142	Pendulum vibration of the water molecules in the plane of the chromophore
3	$0_0 \rightarrow 9^1$	412	3.01	108.9	554	0.111	Flexural vibration of the chromophore perpendicular to its plane
4	$0_0 \rightarrow 22^1$	408	3.04	343	1453	0.287	Compression-stretching of the chromophore along its long axis
5	$0_0 \rightarrow 31^1$	406	3.06	502	2511	0.493	Compression-stretching of the chromophore perpendicular to its long axis
6	$0_0 \rightarrow 32^1$	405	3.06	524	585	0.115	Sheared vibration of the chromophore along its long axis
7	$0_0 \rightarrow 66^1$	394	3.15	1214	847	0.162	Sheared vibrations of C and D rings
8	$0_0 \rightarrow 99^1$	387	3.21	1702	1440	0.270	Compression-stretching of the carbonyl group and the corresponding tracking vibrations of the angles of bound water molecules

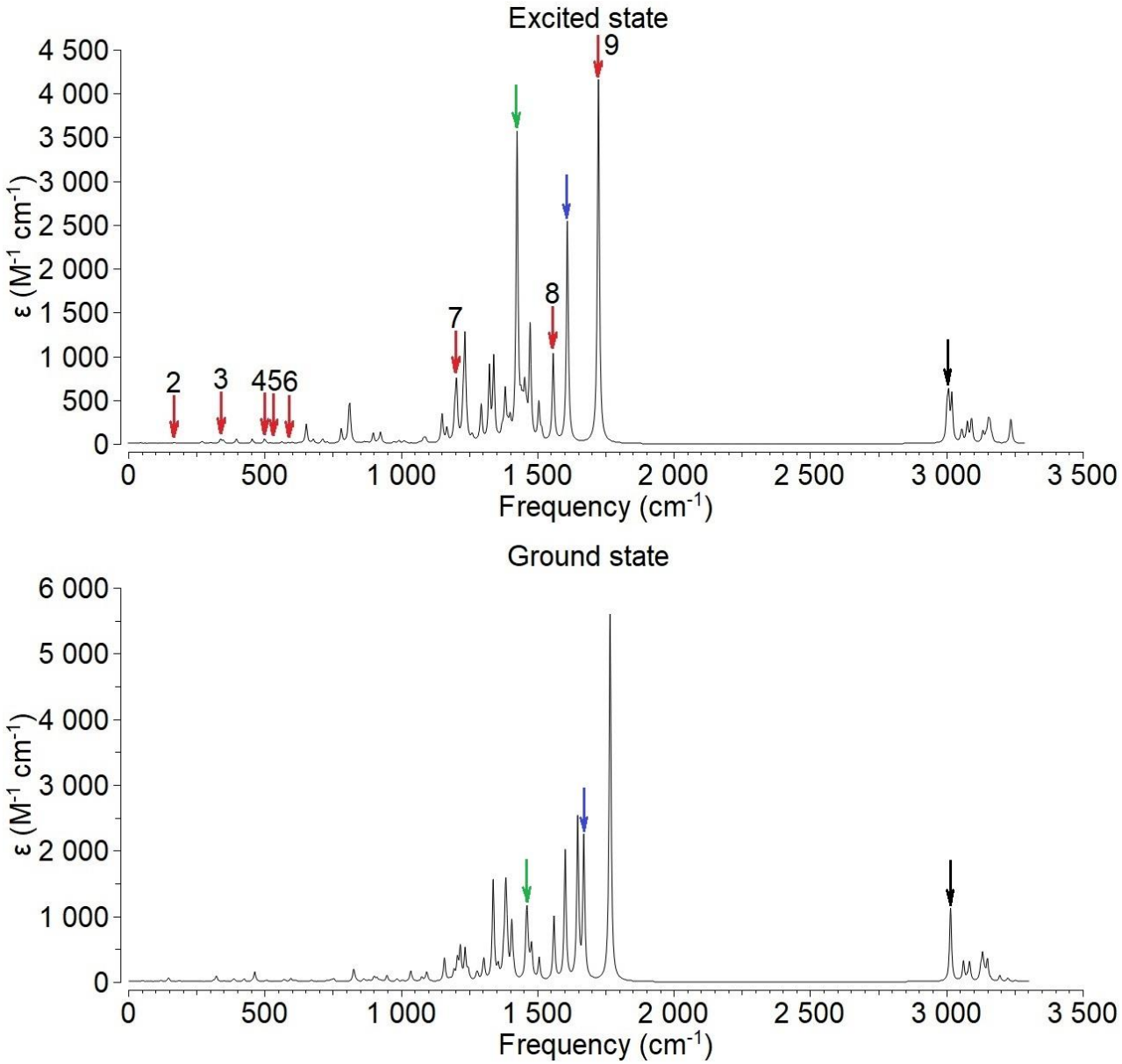


Fig. S1. IR spectra of C102 in aqueous media. Vibrations involved in vibronic transitions are shown with red arrows

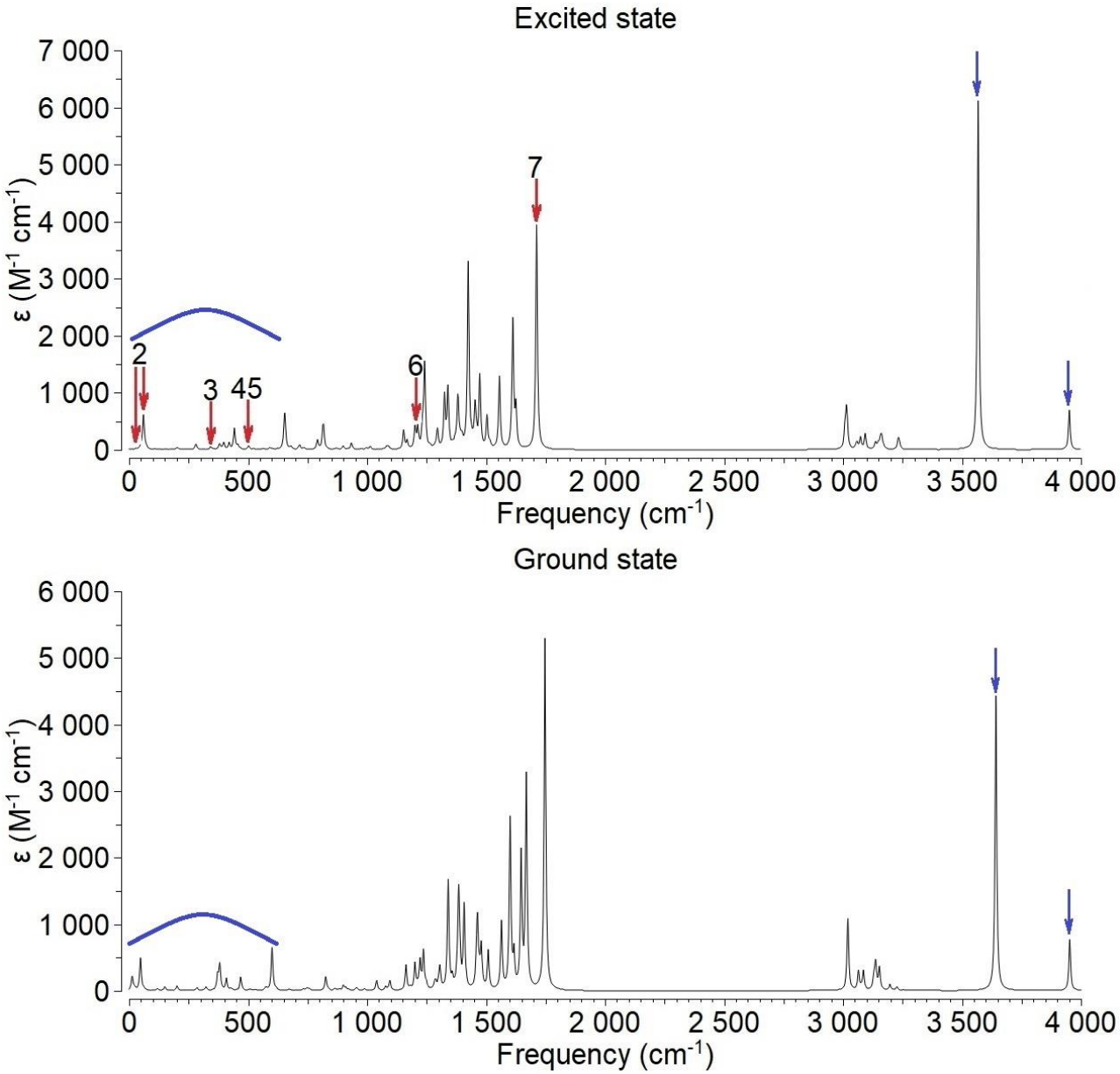


Fig. S2. IR spectra of the "C102+H_2O (B)" system in aqueous media. Here and in the following IR spectra, the region of pendulum vibrations of a water molecule relative to C102 and vibrations of its bond angle are shown by blue arcs. The compression-stretching of the O-H bonds of the water molecule is shown by blue arrows.

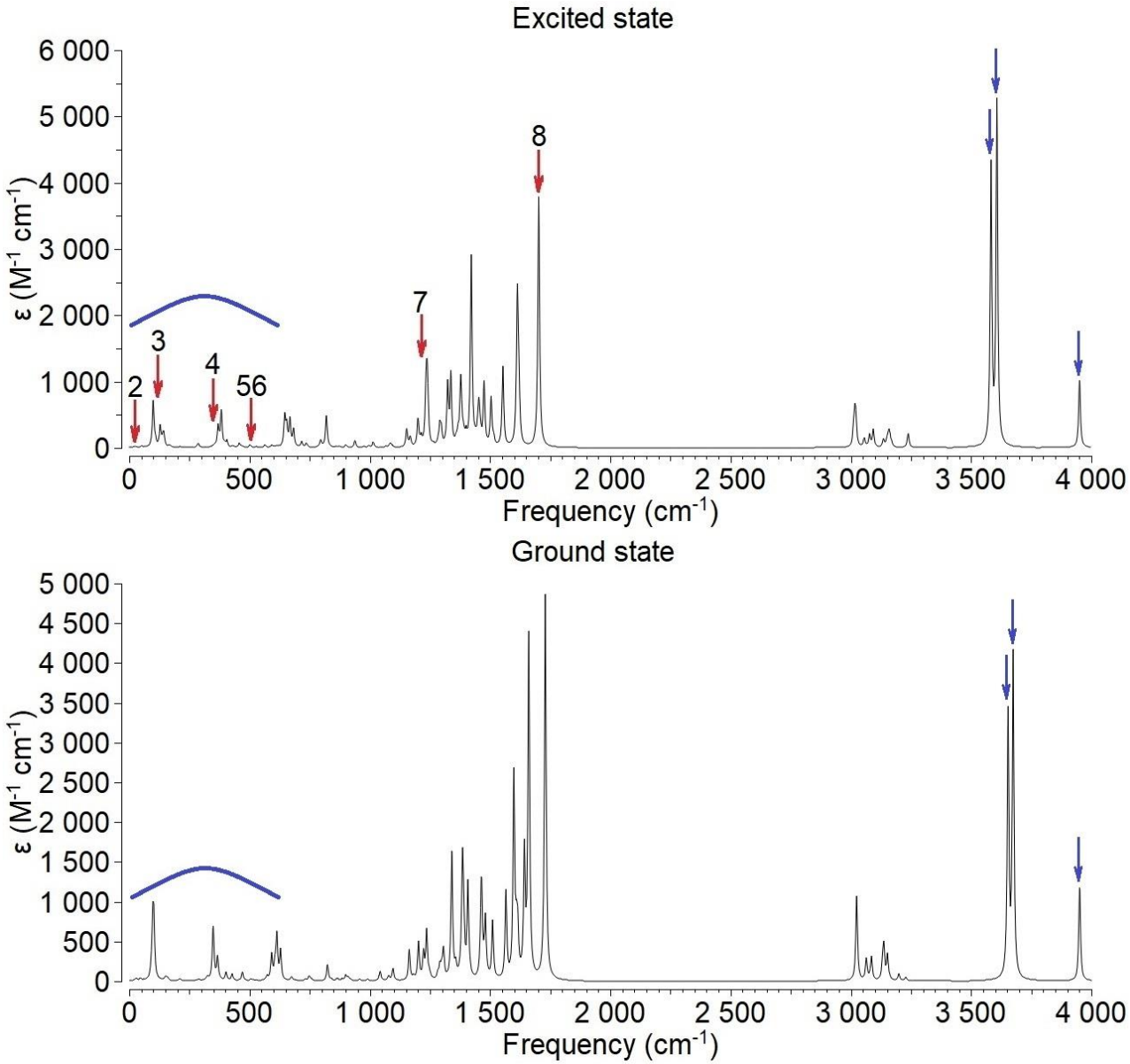


Fig. S3. IR spectra of "C102+2H_2O (2B)" system in aqueous media

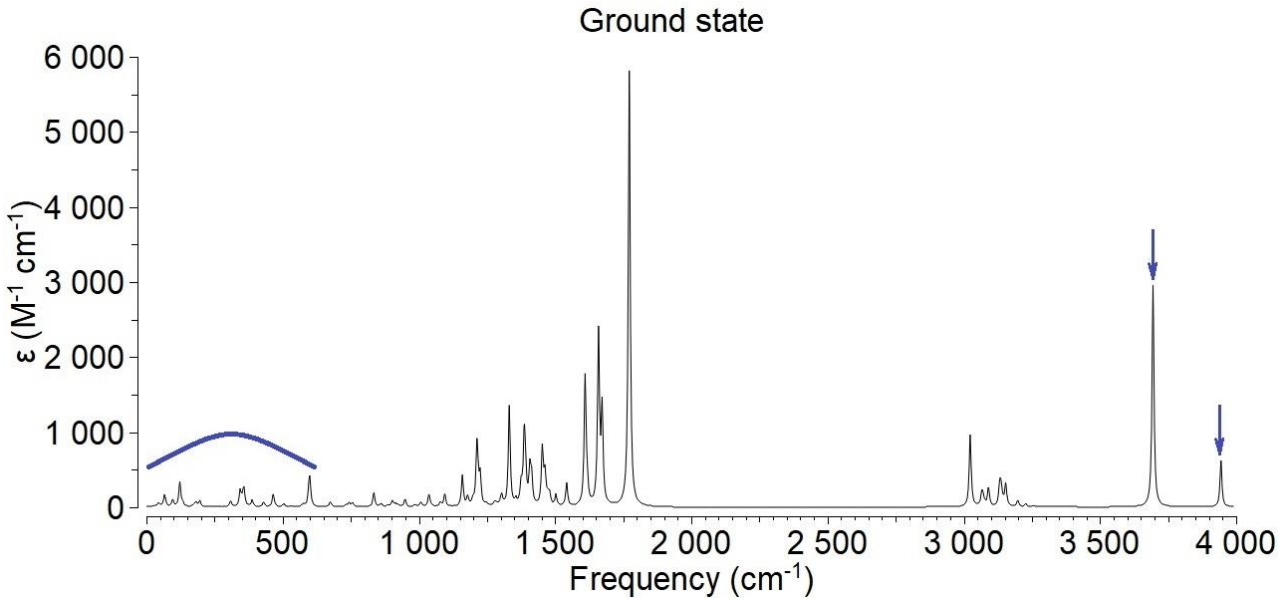


Fig. S4. IR spectra of "C102+H_2O (A)" system in aqueous media

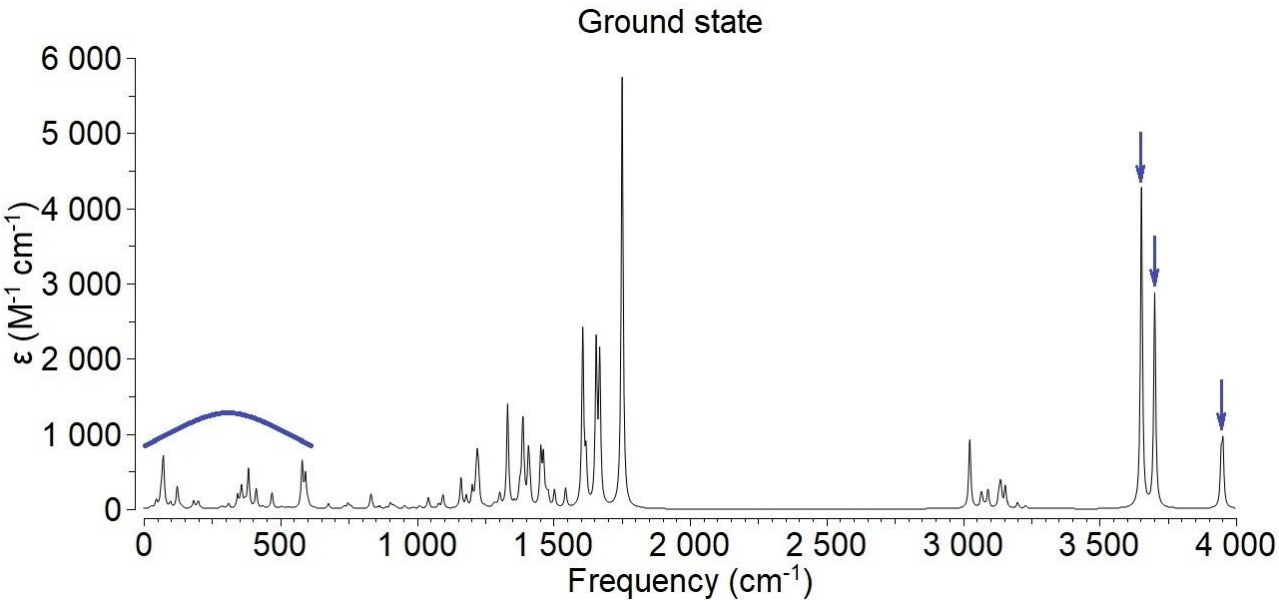


Fig. S5. IR spectra of "C102+2H_2O (A+B)" system in aqueous media

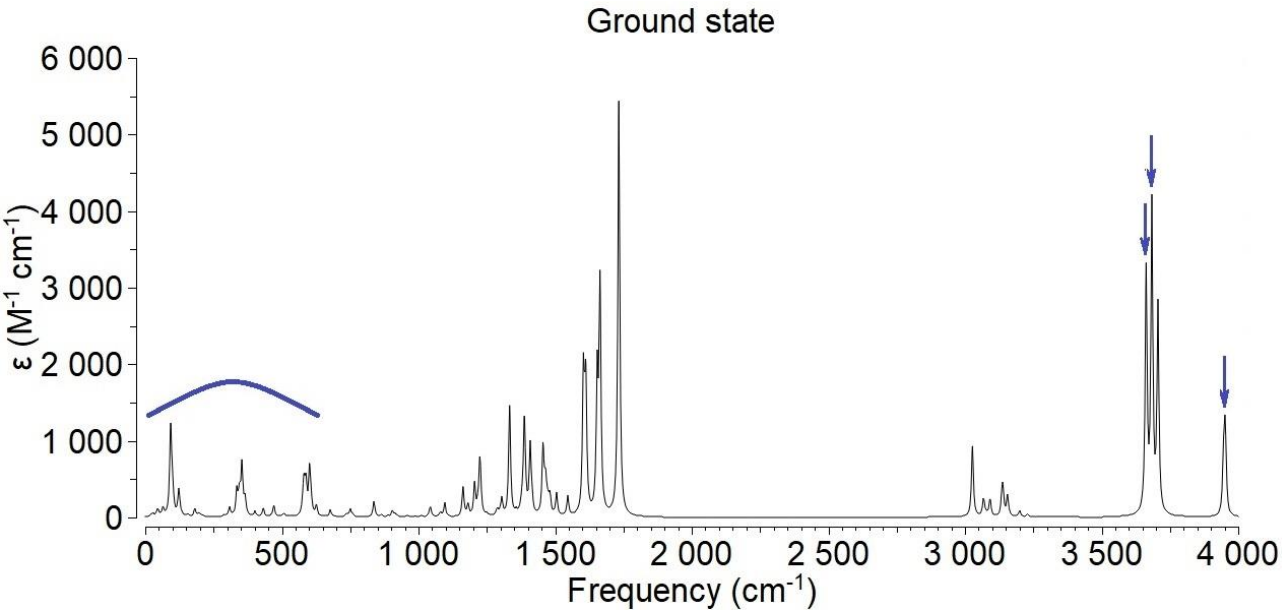


Fig. S6. IR spectra of "C102+3H_2O (A+2B)" system in aqueous media

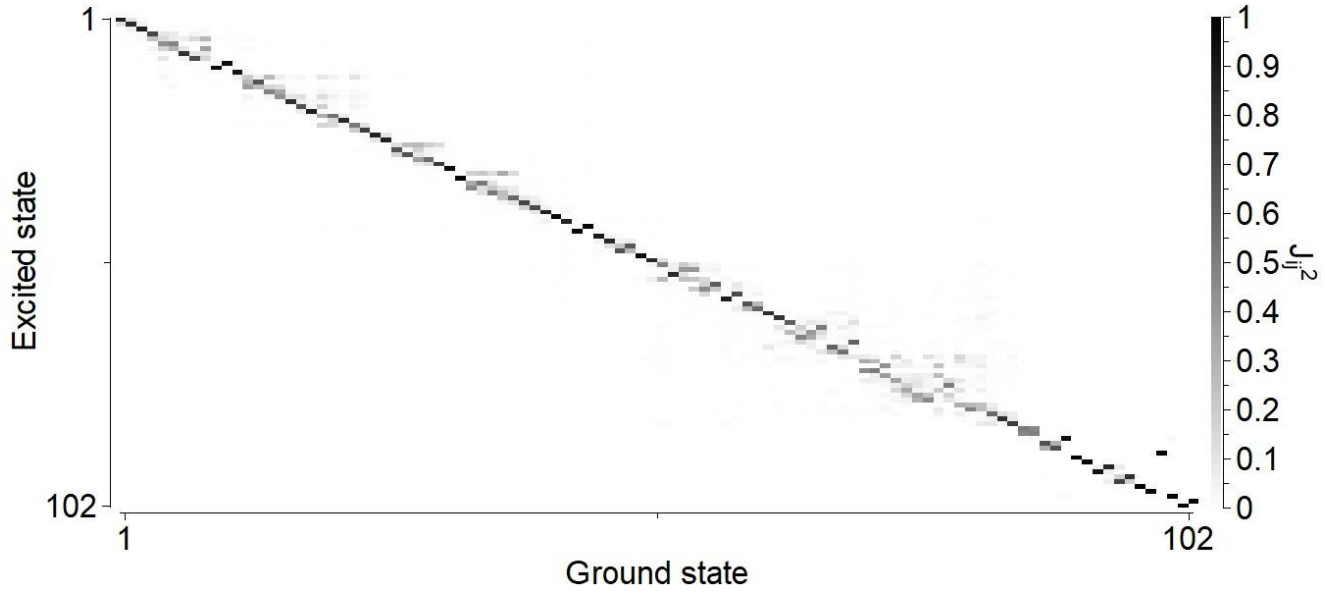


Fig. S7. Duschinsky rotation matrix of C102 in aqueous media

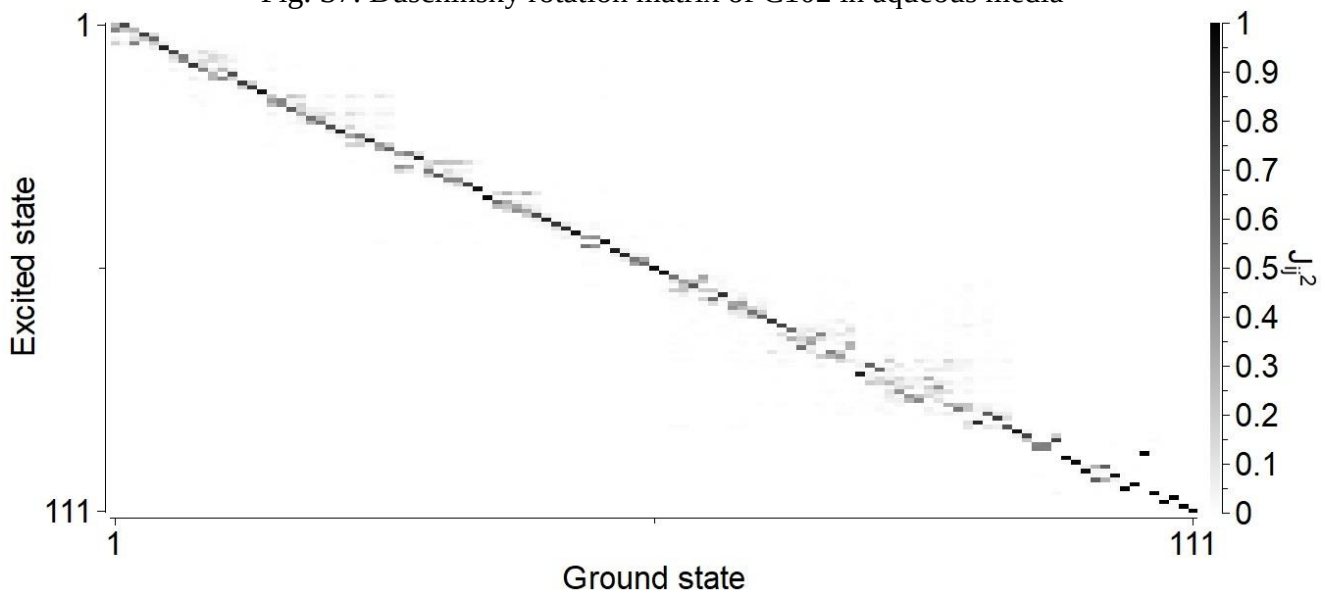


Fig. S8. Duschinsky rotation matrix of "C102+H_2O (B)" system in aqueous media

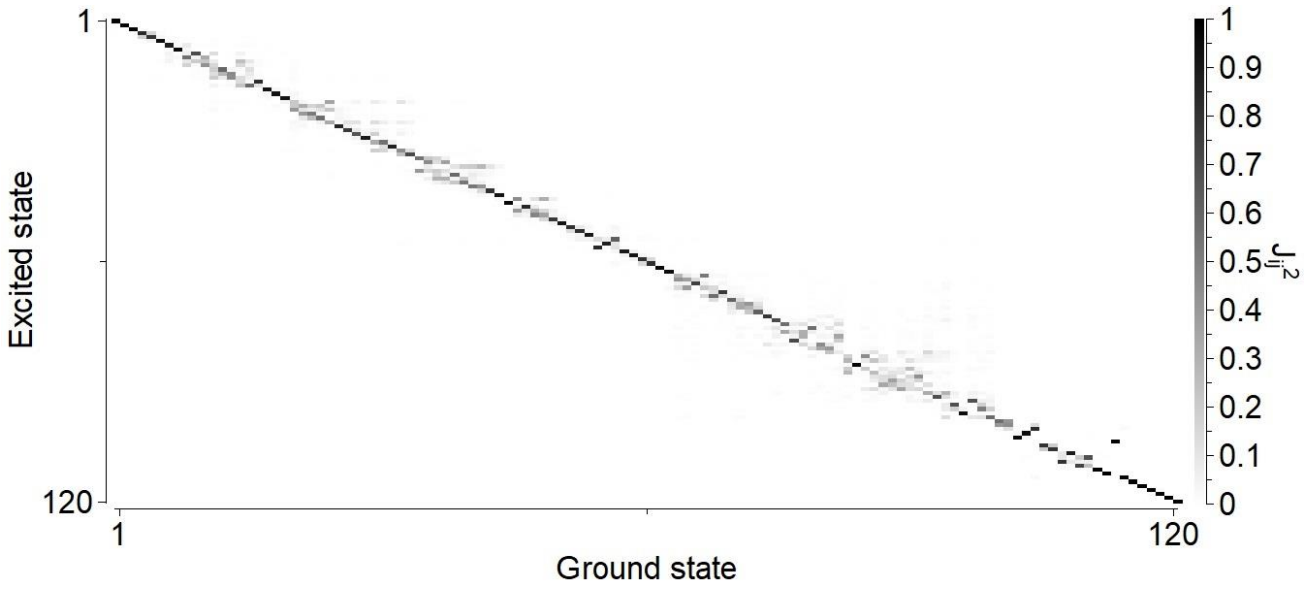
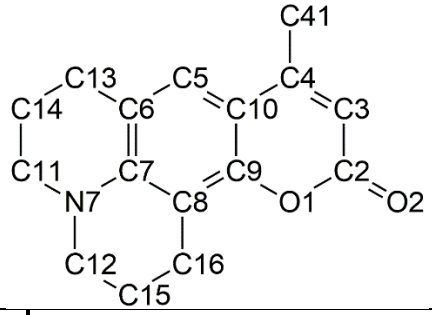


Fig. S9. Duschinsky rotation matrix of "C102+2H_2O (2B)" system in aqueous media

Table S11. Merz-Kollman charges (e) with hydrogens summed into heavy atoms for C102 molecule and its hydrated complexes in an aqueous media



Atom	C102			C102+H_2O (B)			C102+2H_2O (2B)		
	Ground state	Excited state		Ground state	Excited state		Ground state	Excited state	
		Franck–Condon	Equilibrium		Franck–Condon	Equilibrium		Franck–Condon	Equilibrium
O1	–0.537	–0.525	–0.511	–0.529	–0.526	–0.511	–0.331	–0.330	–0.378
C2	1.029	0.947	0.913	1.072	0.988	0.946	0.647	0.551	0.596
O2	–0.728	–0.772	–0.765	–0.739	–0.783	–0.771	–0.478	–0.514	–0.617
C3	–0.584	–0.594	–0.563	–0.594	–0.594	–0.554	–0.394	–0.382	–0.367
C4	0.656	0.463	0.433	0.645	0.454	0.404	0.518	0.330	0.323
C41	–0.055	–0.080	–0.070	–0.053	–0.086	–0.070	–0.042	–0.077	–0.063
C5	0.006	–0.106	–0.107	–0.016	–0.121	–0.124	–0.063	–0.151	–0.090
C6	–0.008	0.046	0.077	0.031	0.068	0.078	0.053	0.080	0.055
C7	0.088	0.049	–0.017	0.029	0.014	–0.021	0.059	0.035	0.005
N7	–0.044	0.063	0.121	–0.034	0.063	0.093	–0.033	0.074	0.117
C8	–0.197	–0.117	–0.080	–0.161	–0.087	–0.058	–0.238	–0.142	–0.112
C9	0.547	0.471	0.452	0.516	0.447	0.427	0.393	0.324	0.389
C10	–0.520	–0.300	–0.294	–0.461	–0.245	–0.223	–0.312	–0.114	–0.201
C11	0.043	0.071	0.041	0.023	0.057	0.057	0.043	0.069	0.064
C12	0.049	0.058	0.054	0.081	0.091	0.088	0.074	0.083	0.080
C13	0.044	0.055	0.030	0.024	0.037	0.030	0.036	0.048	0.038
C14	0.071	0.093	0.117	0.099	0.117	0.118	0.082	0.105	0.112
C15	0.076	0.110	0.111	0.068	0.101	0.104	0.021	0.057	0.078
C16	0.065	0.067	0.059	0.062	0.068	0.060	0.160	0.156	0.130
OB1*	–	–	–	–0.062	–0.064	–0.071	–0.081	–0.085	–0.059
OB2*	–	–	–	–	–	–	–0.116	–0.117	–0.101

*Oxygen atom of a water molecule bound

Table S11 (continued)

Atom	C102+H_2O (A)		C102+2H_2O (A+B)		C102+3H_2O (A+2B)	
	Ground state	Franck–Condon excited state	Ground state	Franck–Condon excited state	Ground state	Franck–Condon excited state
O1	–0.502	–0.494	–0.521	–0.522	–0.388	–0.387
C2	1.004	0.926	1.068	0.985	0.745	0.647
O2	–0.719	–0.758	–0.727	–0.765	–0.546	–0.578
C3	–0.519	–0.541	–0.567	–0.583	–0.425	–0.425
C4	0.541	0.363	0.617	0.440	0.548	0.368
C41	–0.034	–0.058	–0.042	–0.071	–0.040	–0.074
C5	–0.031	–0.139	–0.018	–0.118	–0.012	–0.101
C6	0.128	0.155	0.148	0.174	0.114	0.136
C7	–0.377	–0.262	–0.359	–0.271	–0.274	–0.206
N7	0.561	0.453	0.522	0.458	0.473	0.432
C8	–0.030	–0.025	–0.030	–0.016	–0.194	–0.150
C9	0.434	0.385	0.483	0.444	0.464	0.412
C10	–0.345	–0.142	–0.407	–0.215	–0.349	–0.164
C11	–0.073	–0.008	–0.091	–0.031	–0.088	–0.031
C12	–0.130	–0.061	–0.103	–0.046	–0.047	0.001
C13	–0.078	–0.049	–0.106	–0.080	–0.086	–0.063
C14	0.171	0.183	0.207	0.220	0.193	0.209
C15	0.149	0.159	0.145	0.159	0.049	0.071
C16	–0.002	0.024	–0.009	0.017	0.138	0.153
OA*	–0.149	–0.112	–0.143	–0.111	–0.121	–0.091
OB1*	-	-	–0.064	–0.067	–0.067	–0.072
OB2*	-	-	-	-	–0.086	–0.088

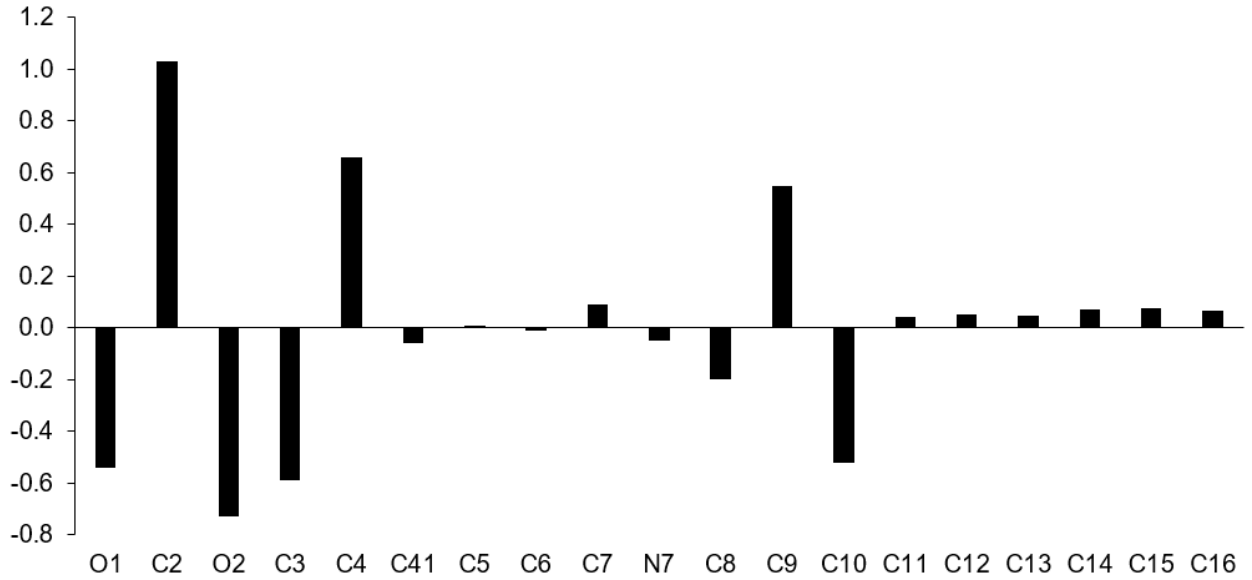


Fig. S10. Merz-Kollman charges (*e*) with hydrogens summed into heavy atoms of C102 in its ground state

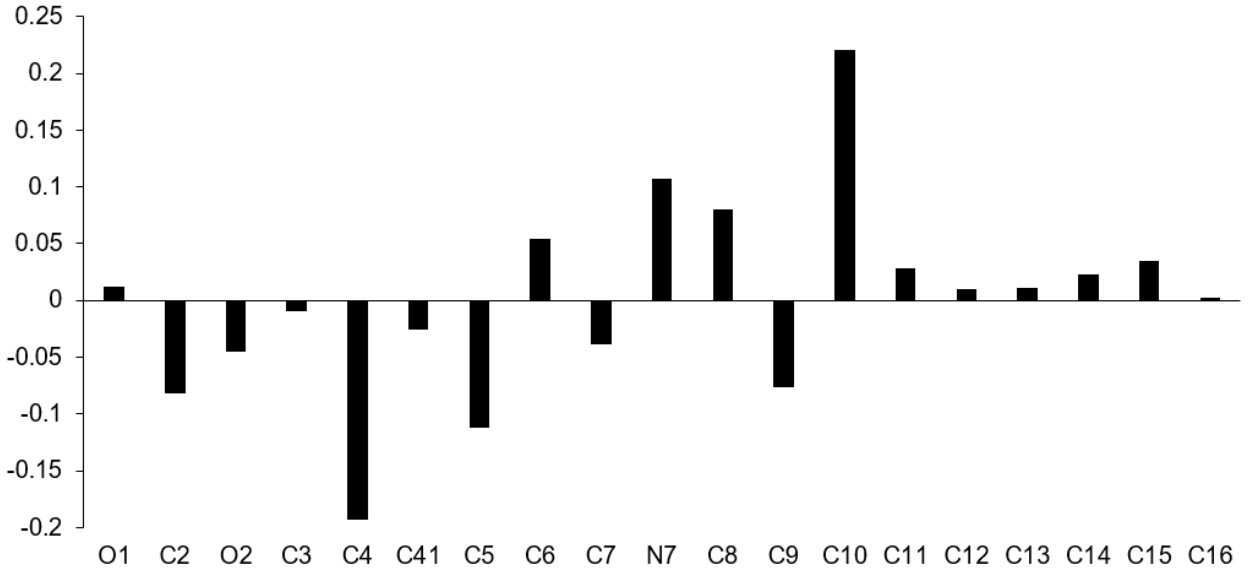


Fig. S11. Difference (*e*) of Merz-Kollman charges summed into heavy atoms of C102 between its Franck-Condon and ground states

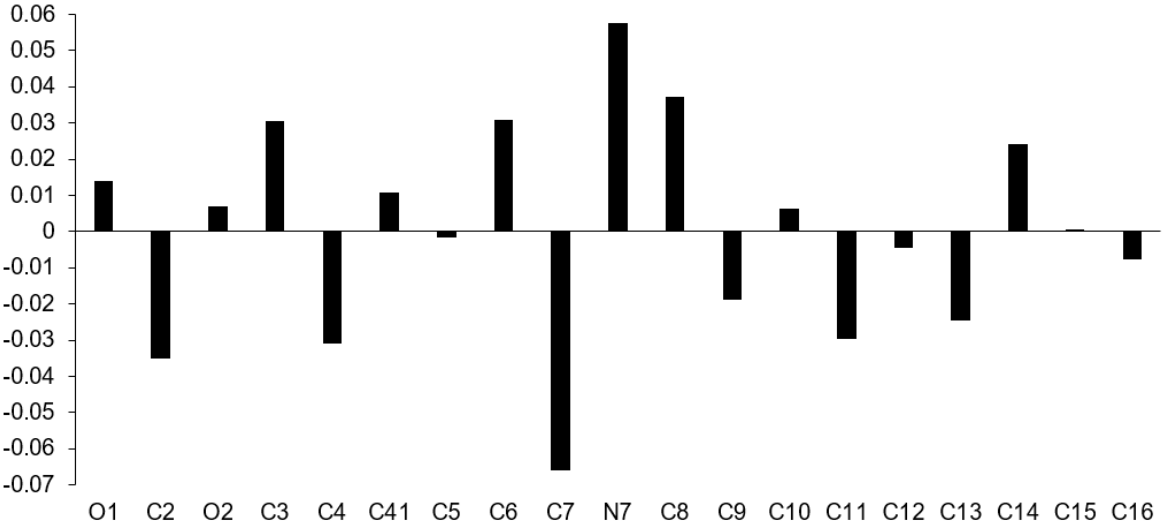


Fig. S12. Difference (*e*) of Merz-Kollman charges summed into heavy atoms of C102 between its equilibrium and Franck-Condon states

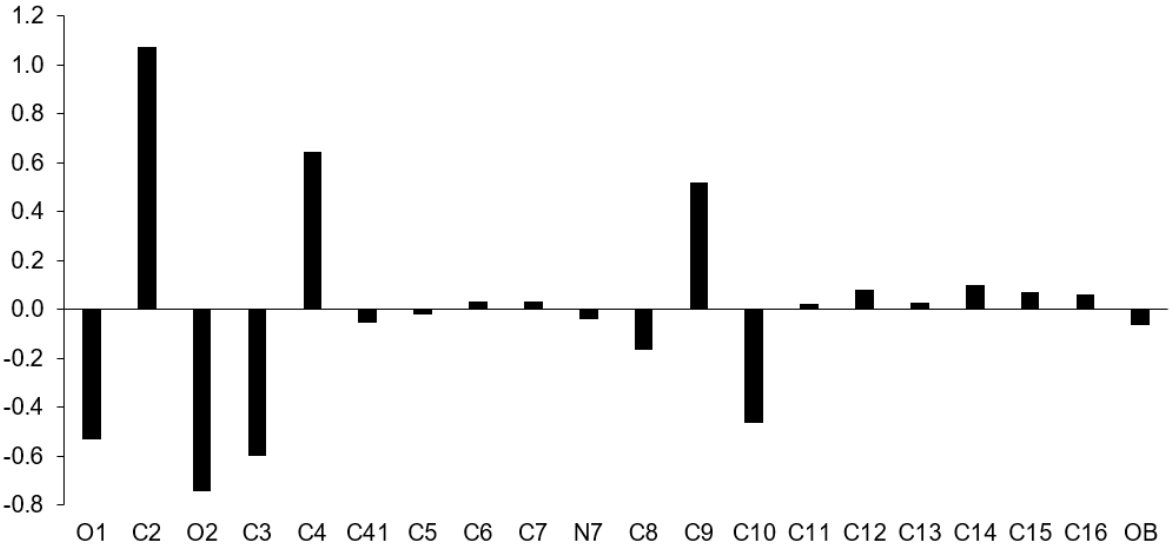


Fig. S13. Merz-Kollman charges (*e*) of "C102+H_2O (B)" system in its ground state

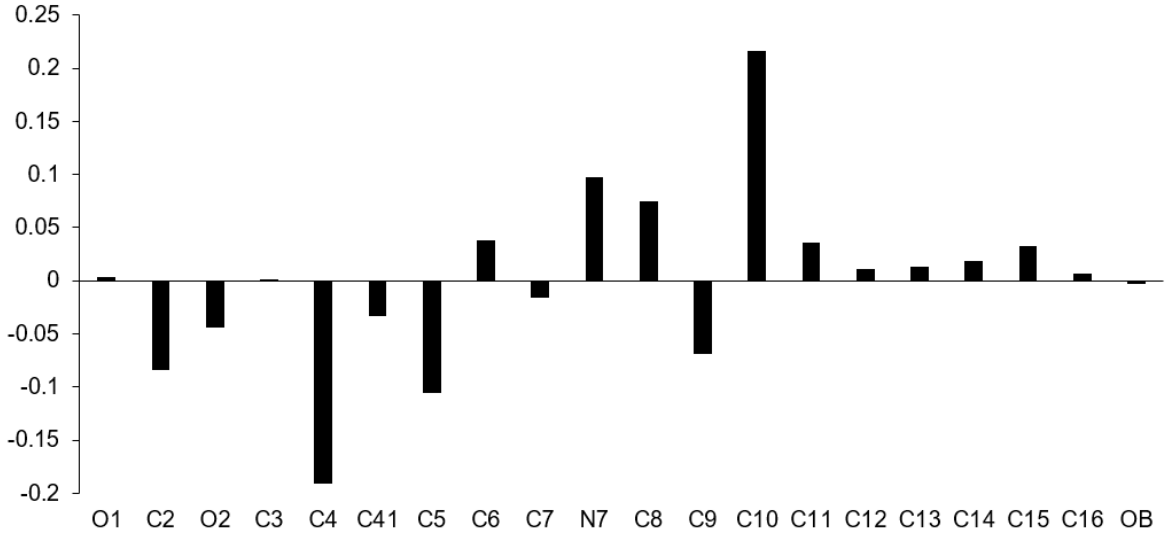


Fig. S14. Difference (*e*) of Merz-Kollman charges of "C102+H_2O (B)" system between its Franck-Condon and ground states

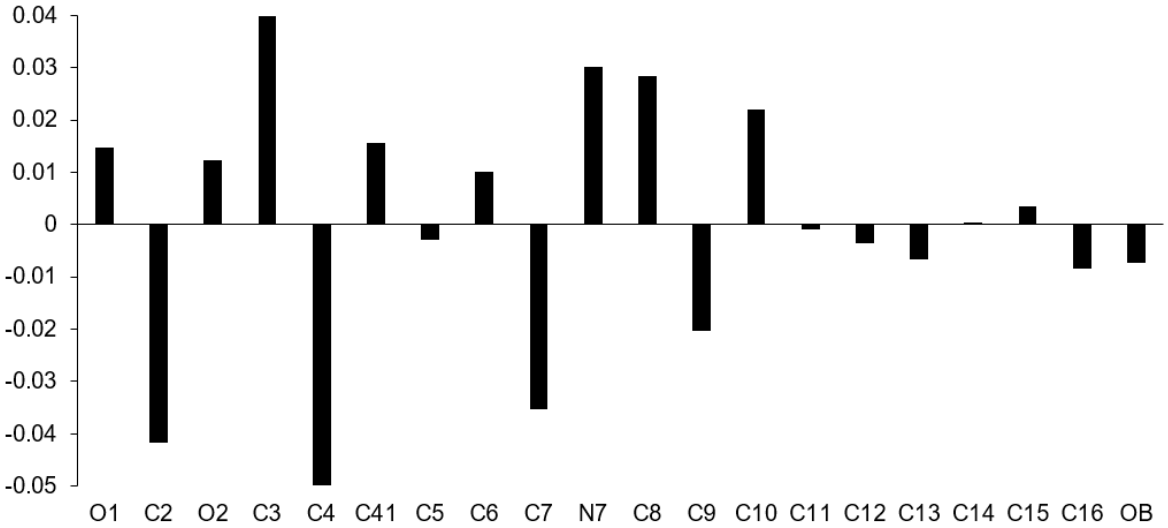


Fig. S15. Difference (*e*) of Merz-Kollman charges of "C102+H_2O (B)" system between its equilibrium excited and Franck-Condon states

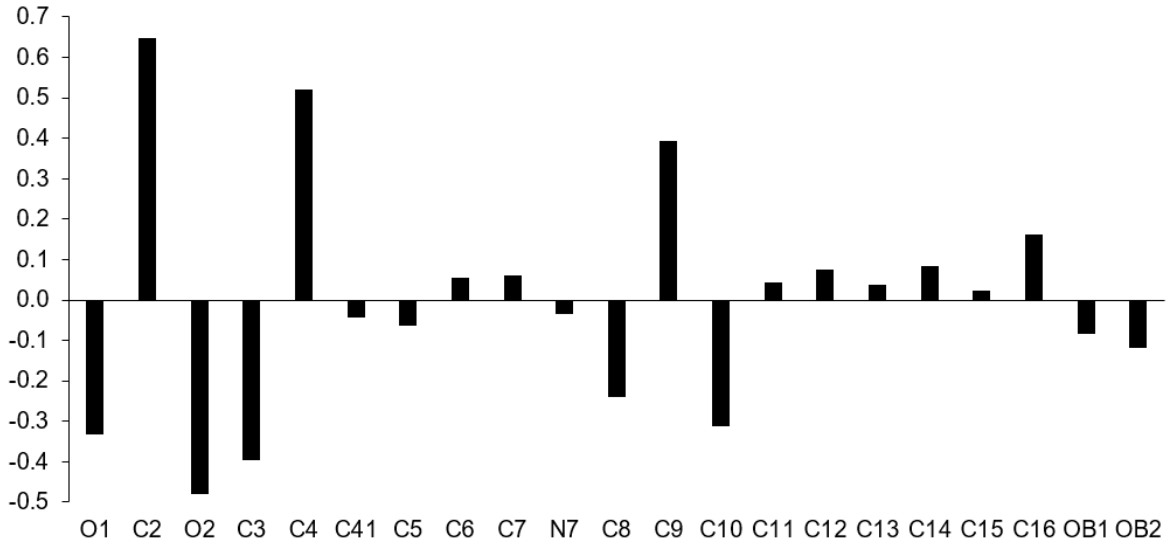


Fig. S16. Merz-Kollman charges (*e*) of "C102+2H_2O (2B)" system in its ground state

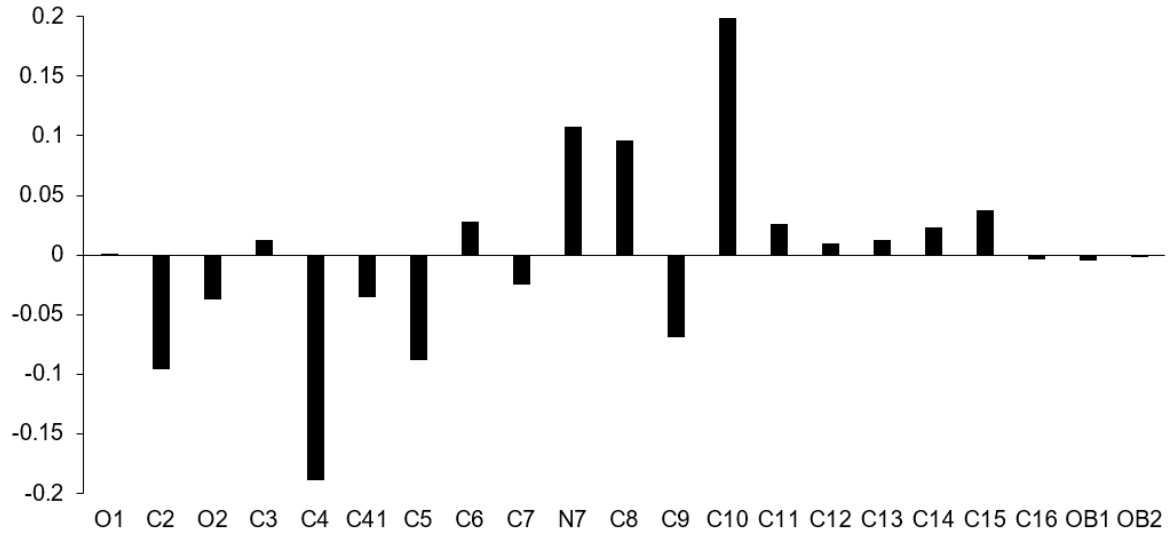


Fig. S17. Difference (*e*) of Merz-Kollman charges of "C102+2H_2O (2B)" system between its Franck-Condon and ground states

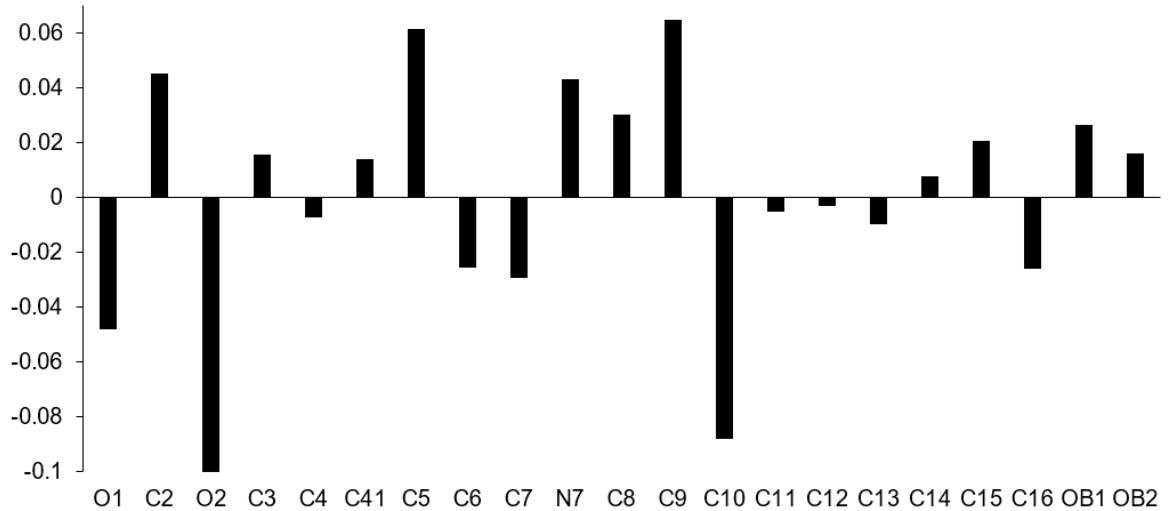


Fig. S18. Difference (*e*) of Merz-Kollman charges of "C102+2H_2O (2B)" system between its equilibrium and Franck-Condon states

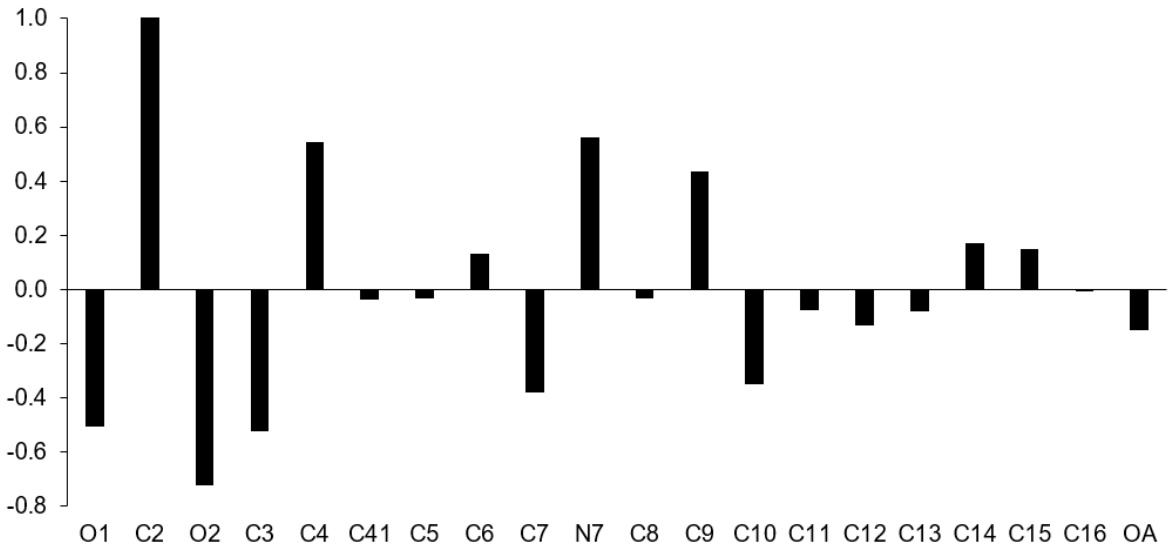


Fig. S19. Merz-Kollman charges (*e*) of "C102+H_2O (A)" system in its ground state

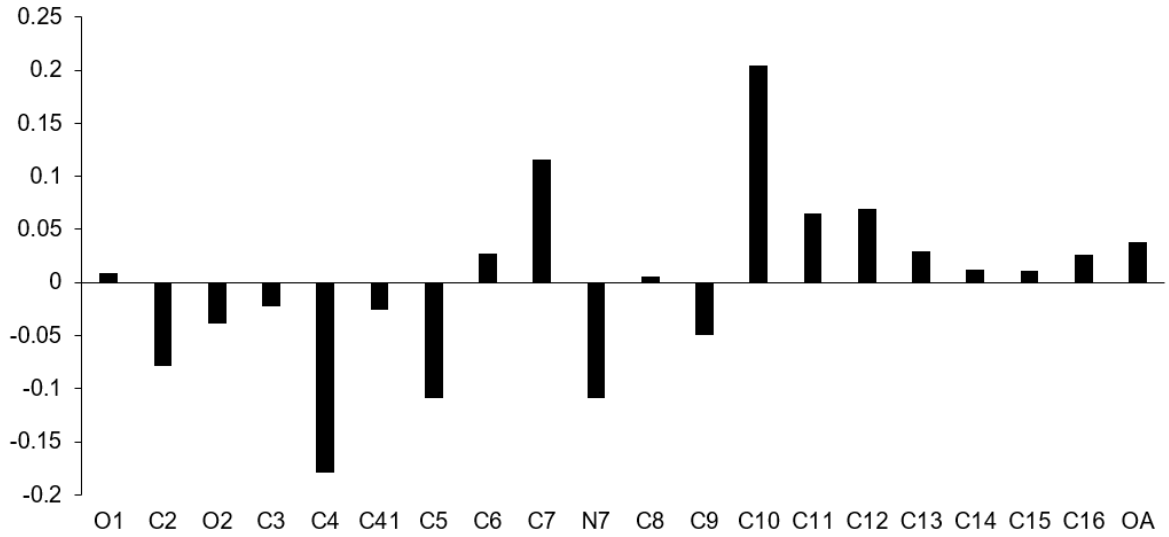


Fig. S20. Difference (*e*) of Merz-Kollman charges of "C102+H_2O (A)" system between its Franck-Condon and ground states

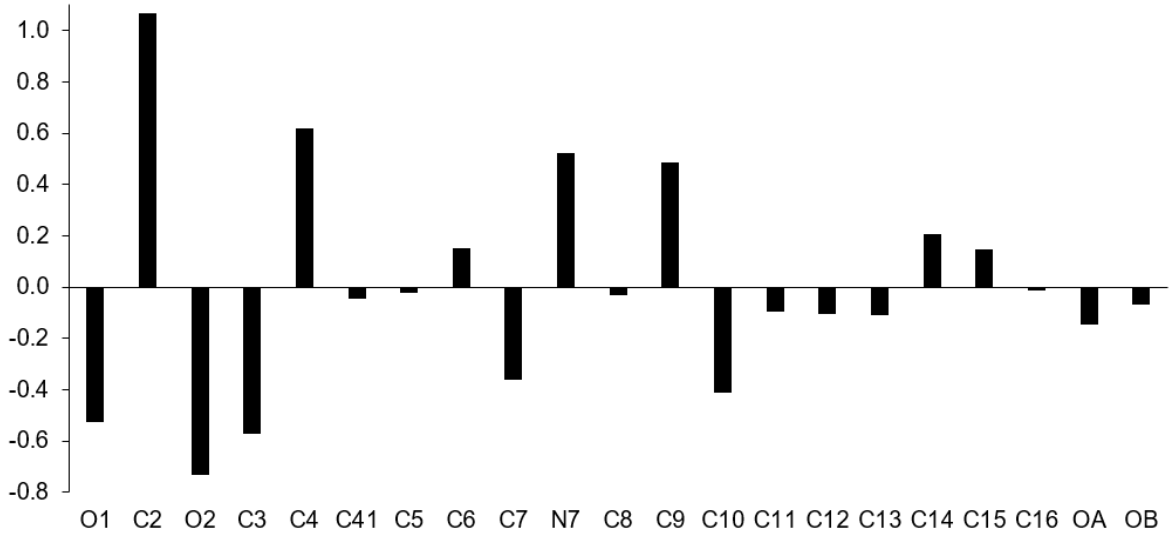


Fig. S21. Merz-Kollman charges (*e*) of "C102+2H_2O (A+B)" system in its ground state

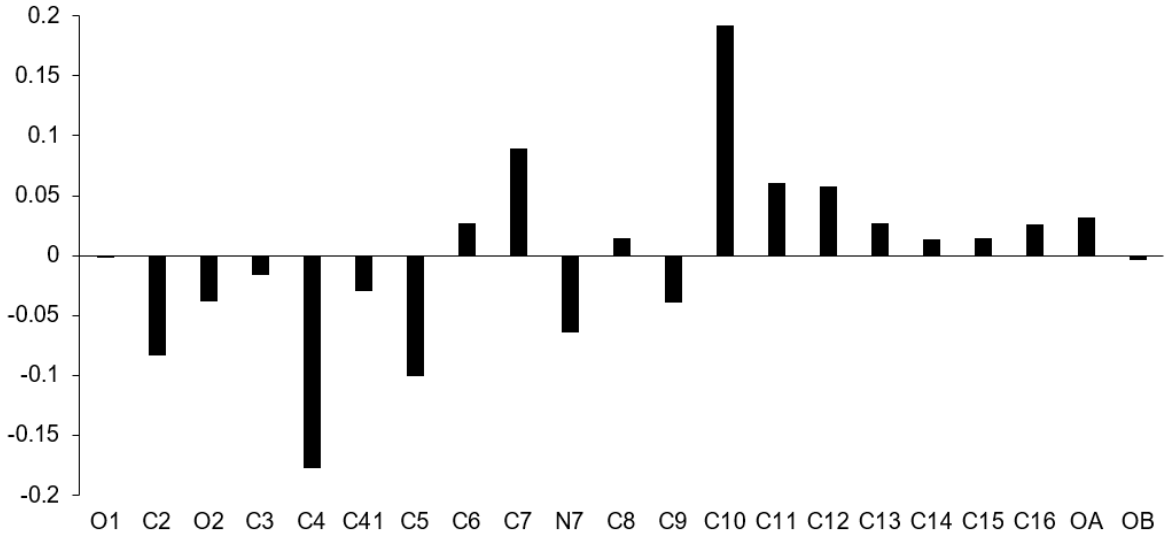


Fig. S22. Difference (*e*) of Merz-Kollman charges of "C102+2H_2O (A+B)" system between its Franck-Condon and ground states

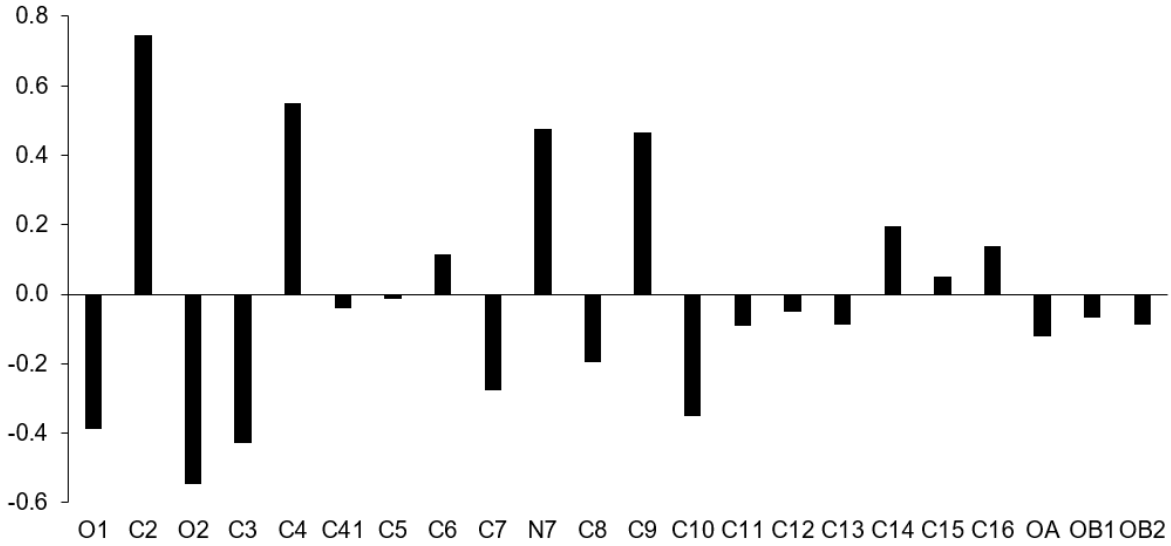


Fig. S23. Merz-Kollman charges (*e*) of "C102+3H_2O (A+2B)" system in its ground state

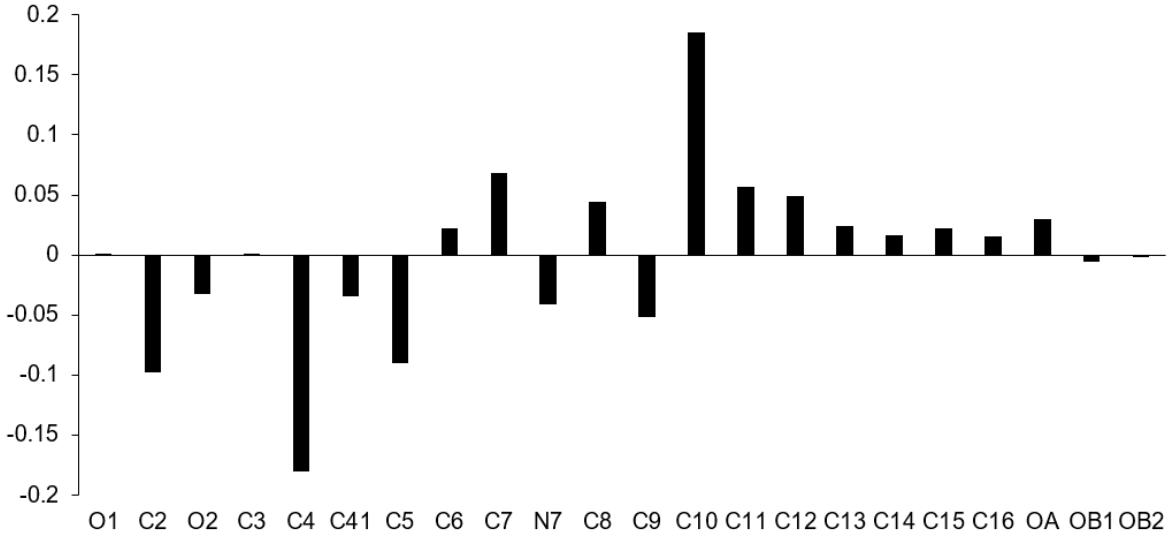


Fig. S24. Difference (*e*) of Merz-Kollman charges of "C102+3H_2O (A+2B)" system between its Franck-Condon and ground states

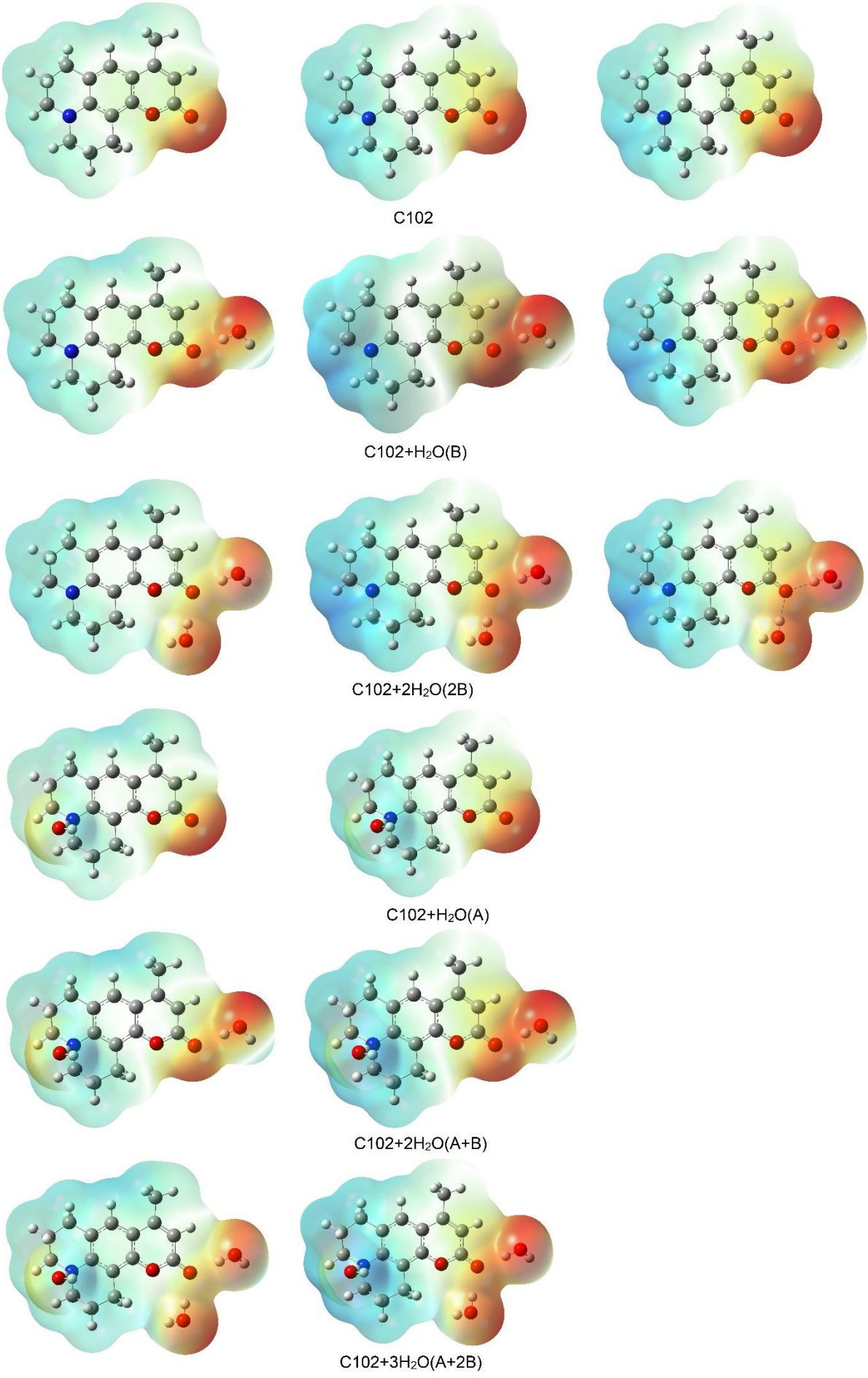


Fig. S25. Electrostatic potential maps of the ground state (left), Franck-Condon point (center), and equilibrium excited states (right). Positive potential surfaces are colored by blue and negative potential surfaces are colored by red