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

Electronic Supplementary Information

Optical spectroscopy of isolated flavins:

photodissociation of protonated lumichrome

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Figure S1. Structures of the H^+iso-LC(N5) and H^+iso-LC(O4) isomers calculated at the PBE0/cc-pVDZ level.

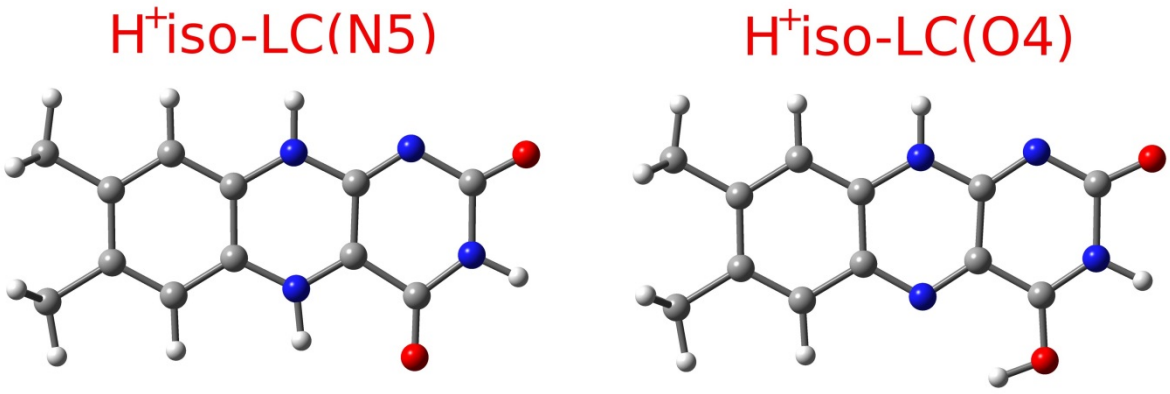


Figure S2. Photodissociation mass spectra of protonated lumichrome. Laser-on (solid line) and laser-off (dotted line) mass spectra of H^+LC (m/z 243) with the laser frequency tuned resonantly to the $S_1 \leftarrow S_0$ band origin at 19962 cm^{-1}. The difference between both spectra is given by the dashed line. Major photo-induced fragments are m/z 198 and m/z 172.

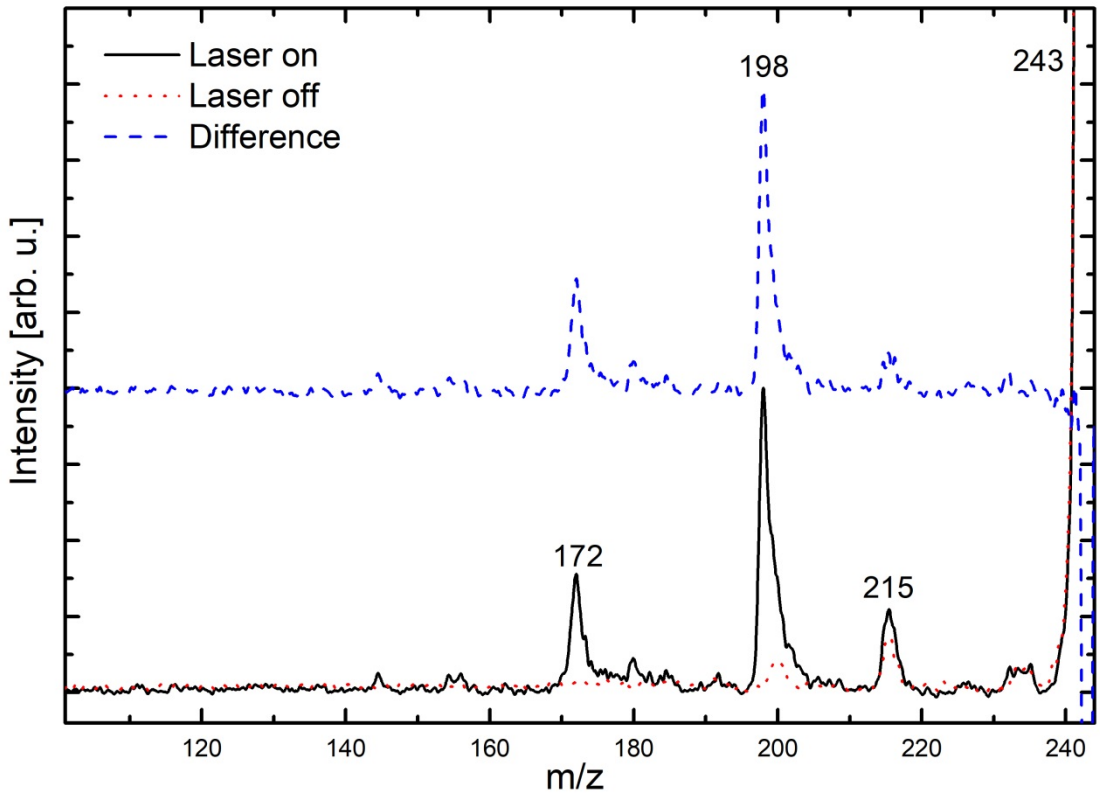


Figure S3. Overview of recorded VISPD spectrum of protonated lumichrome (H^+LC) obtained at an ion trap temperature of 25 K.

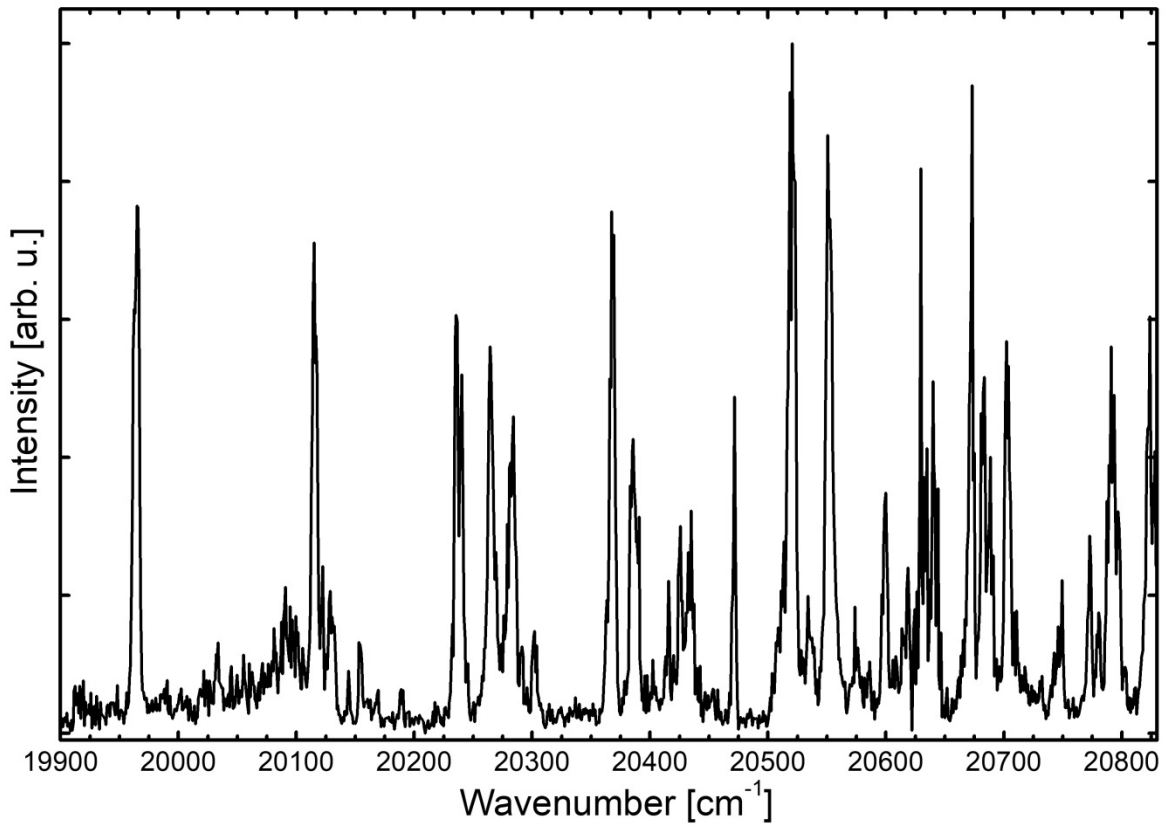


Figure S4. VISPD spectra of the $S_1 \leftarrow S_0$ electronic transition of H^+LC for a trap temperature of 25 K recorded in the m/z 172 and 198 fragment channels.

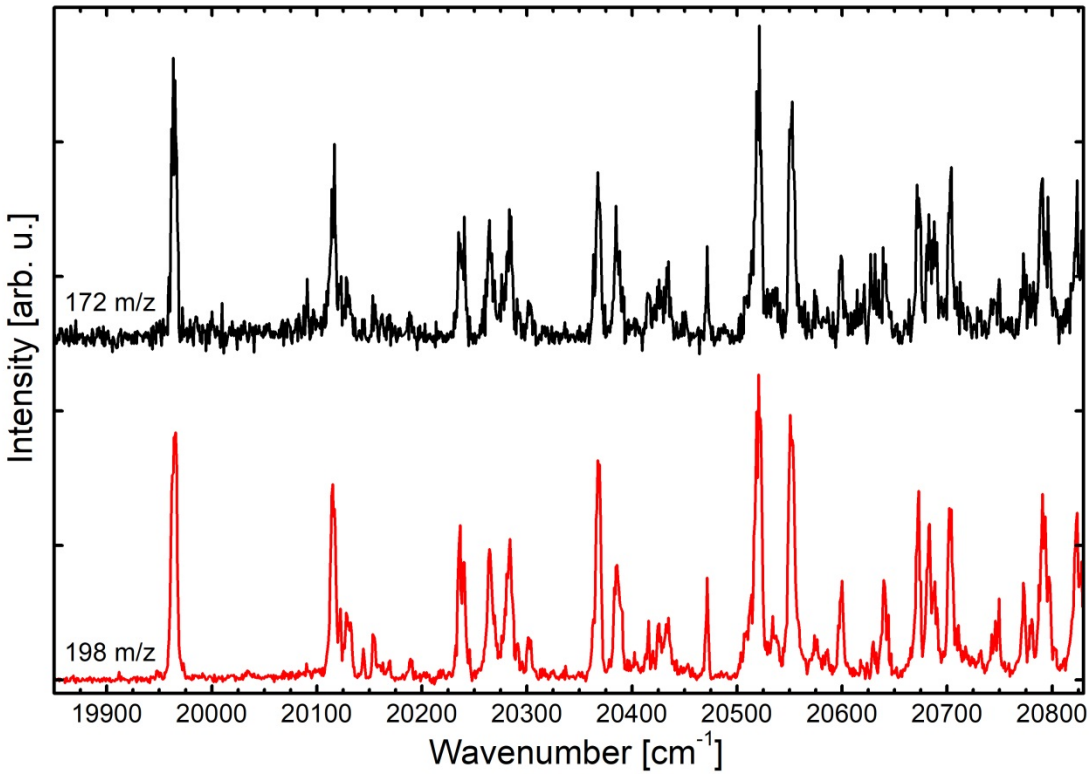


Figure S5. Comparison between experimental VISPD spectrum recorded for H^+LC and Franck-Condon simulations for the protonated iso-LC isomers shown in Figure S1 calculated at the PBE0/cc-pVDZ level using a convolution width of 6 cm^{-1}. Isomers are ordered from top to bottom according to their relative energy (Table 1). The energy scale of the simulated spectra is shifted by $\Delta\nu$ to match the frequencies of calculated and observed S_1 origins at 19965 cm^{-1}.

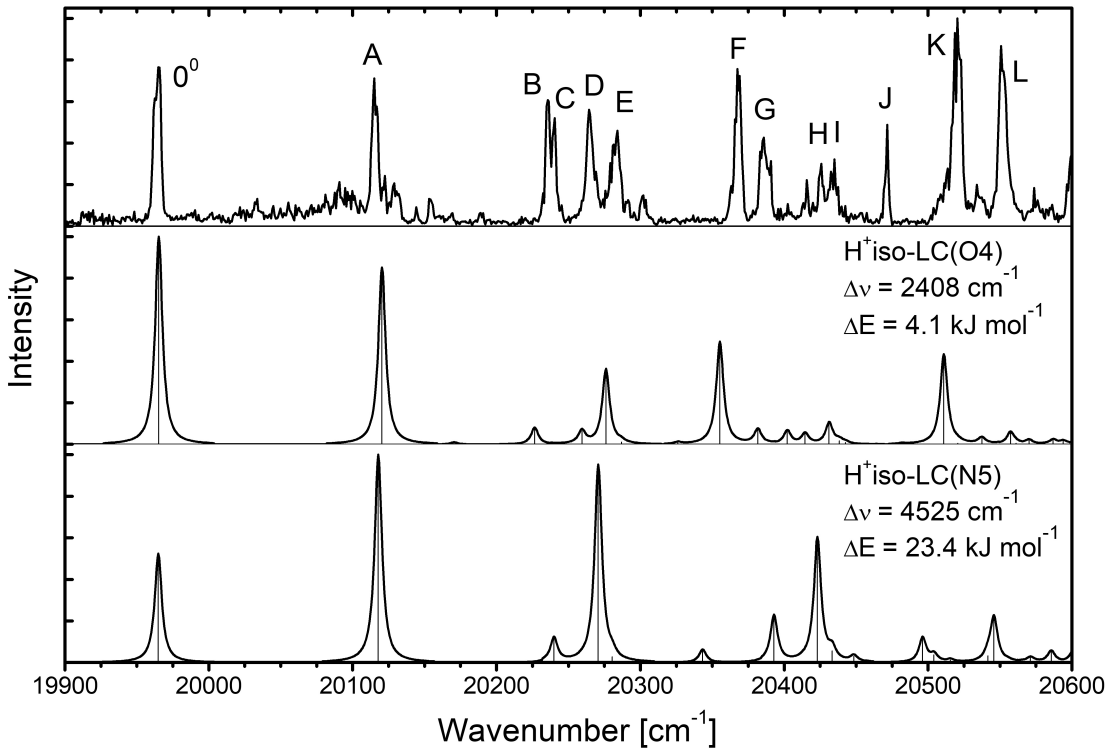
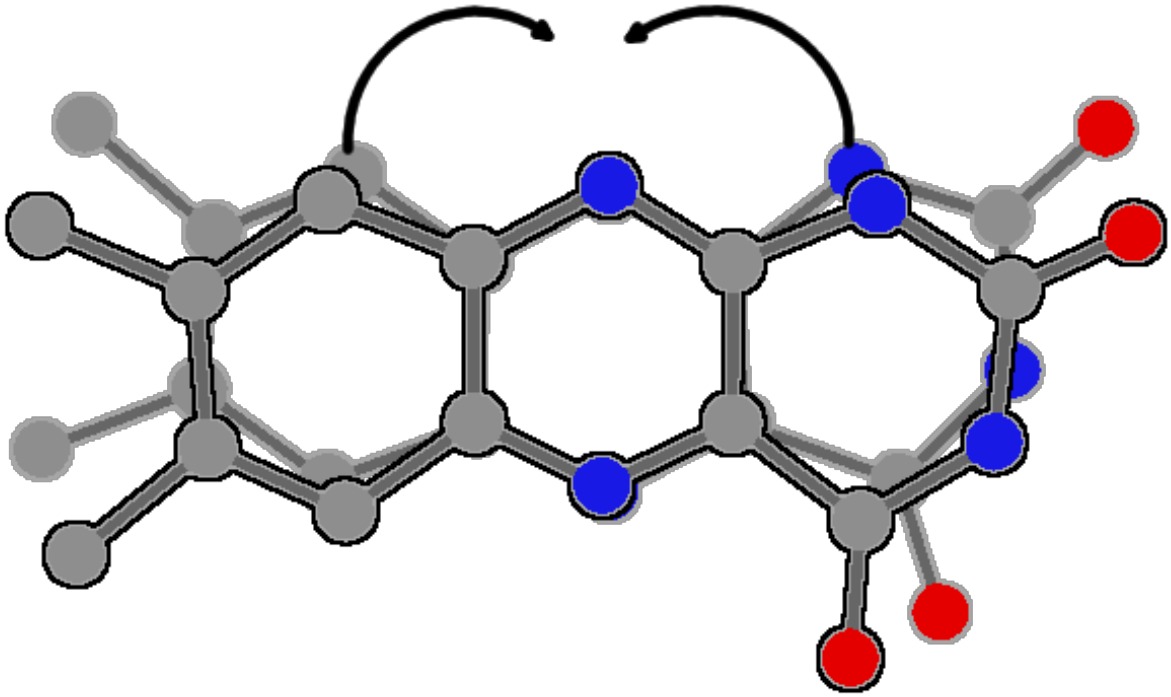
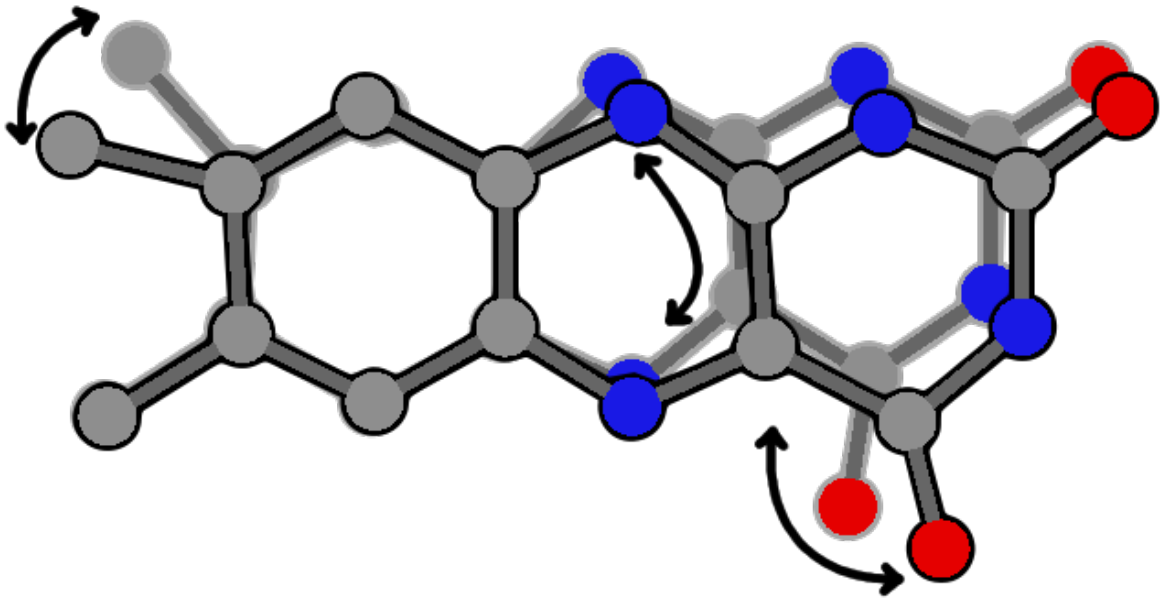


Figure S6. Schematic representation of various normal coordinates in the S_1 state of H^+LC(N5) calculated at the PBE0/cc-pVDZ level. Hydrogen atoms are omitted for the sake of simplicity. Shown are the structures for maximum positive and maximum negative elongation. The arrows indicate major movements.

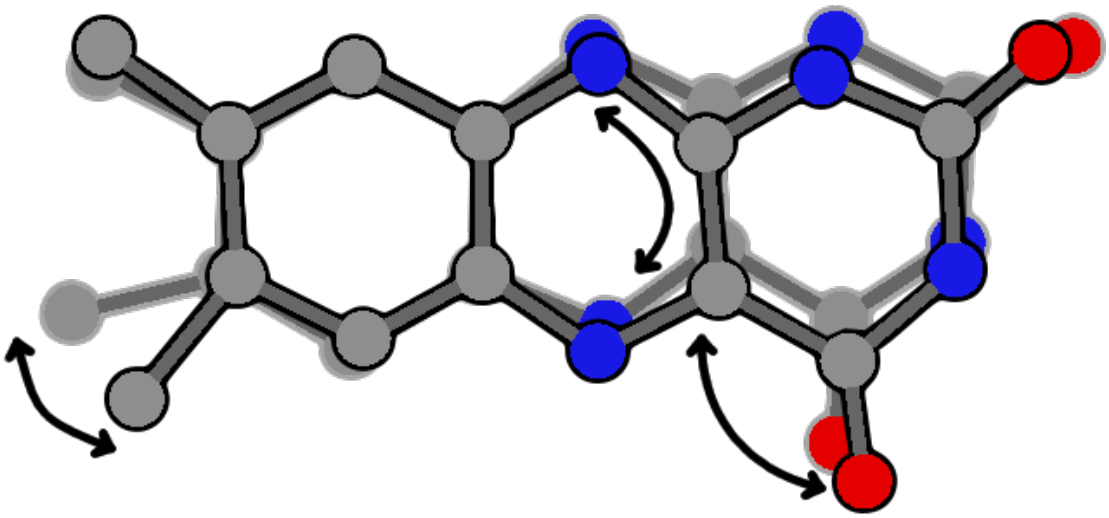
(a) mode 53



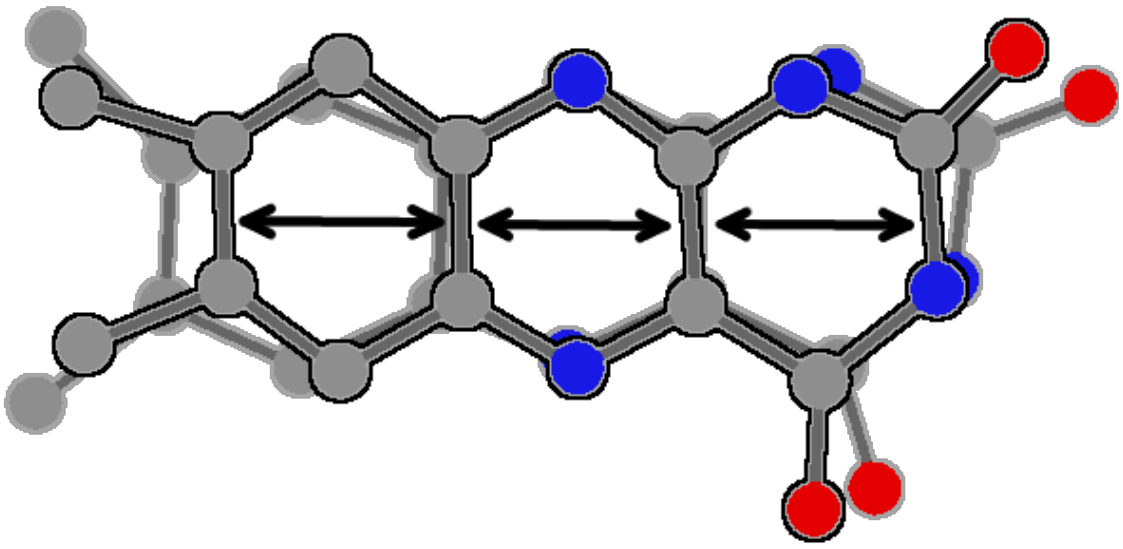
(b) mode 52



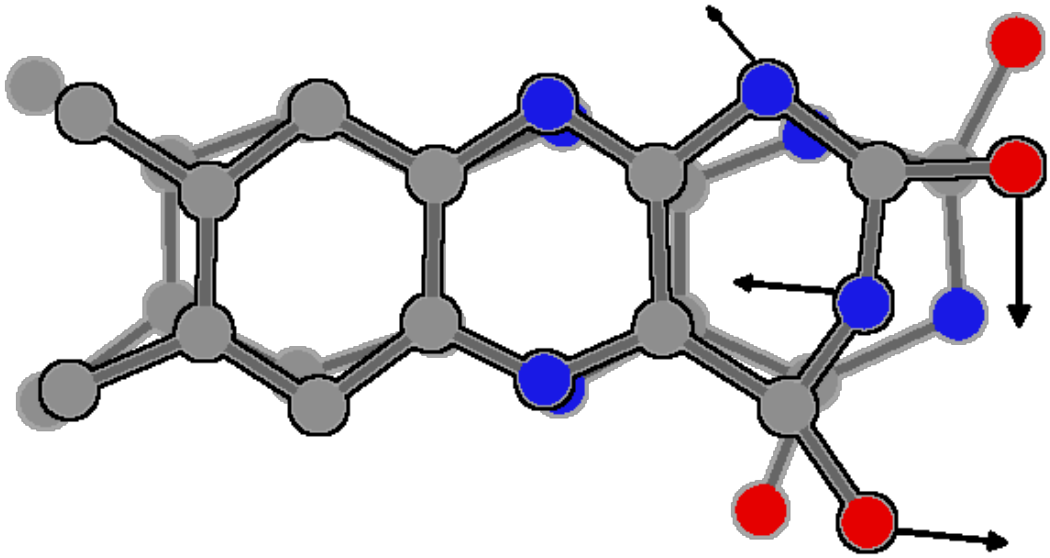
(c) mode 51



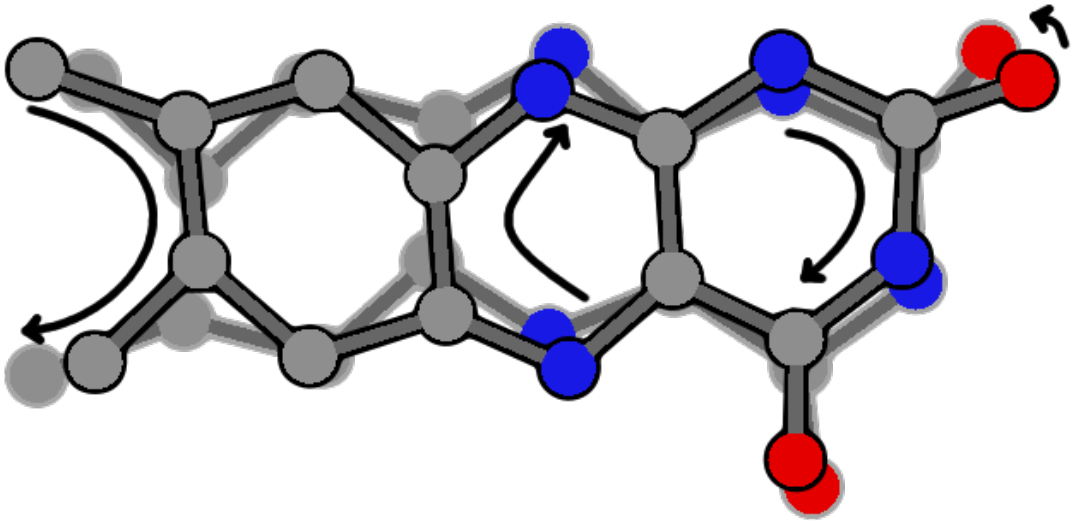
(d) mode 50



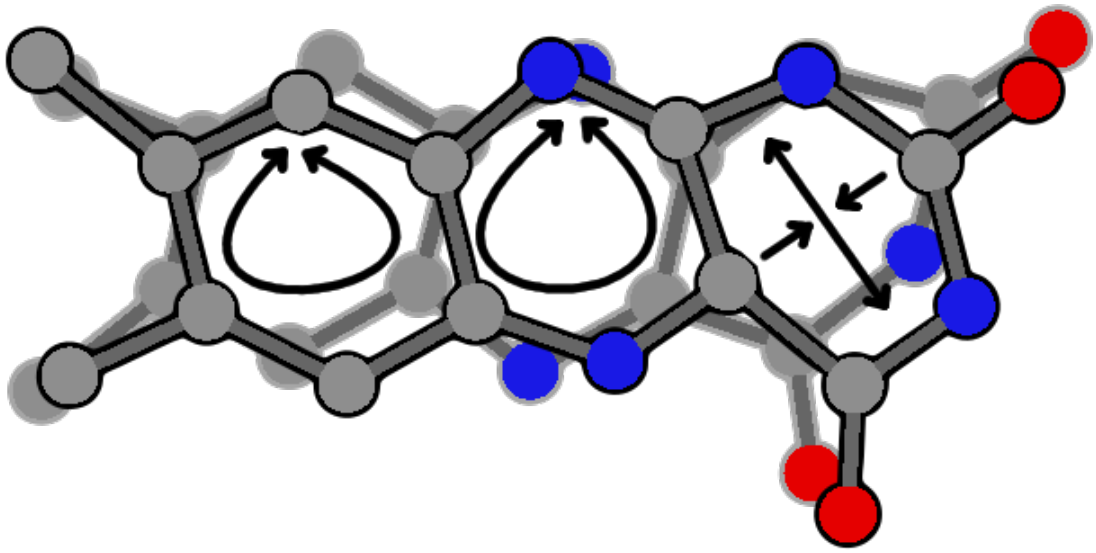
(e) mode 49



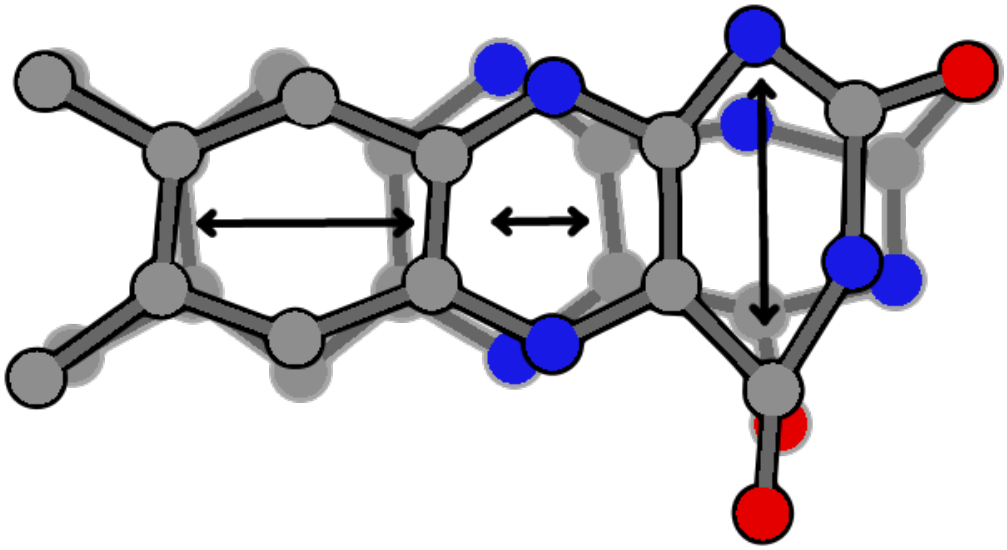
(f) mode 48



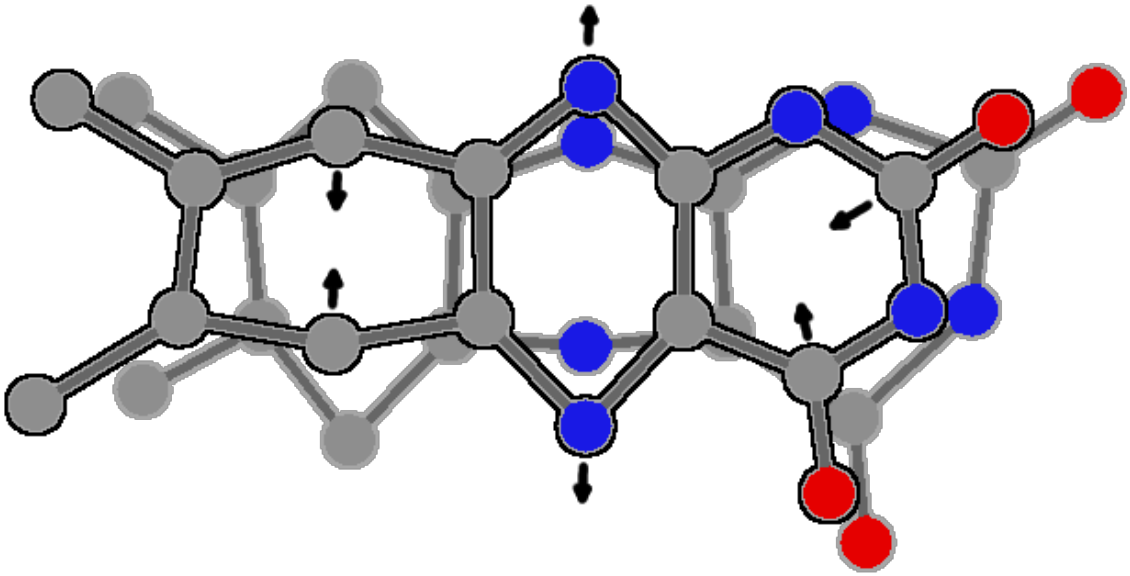
(g) mode 47



(h) mode 46



(i) mode 45



(k) mode 44

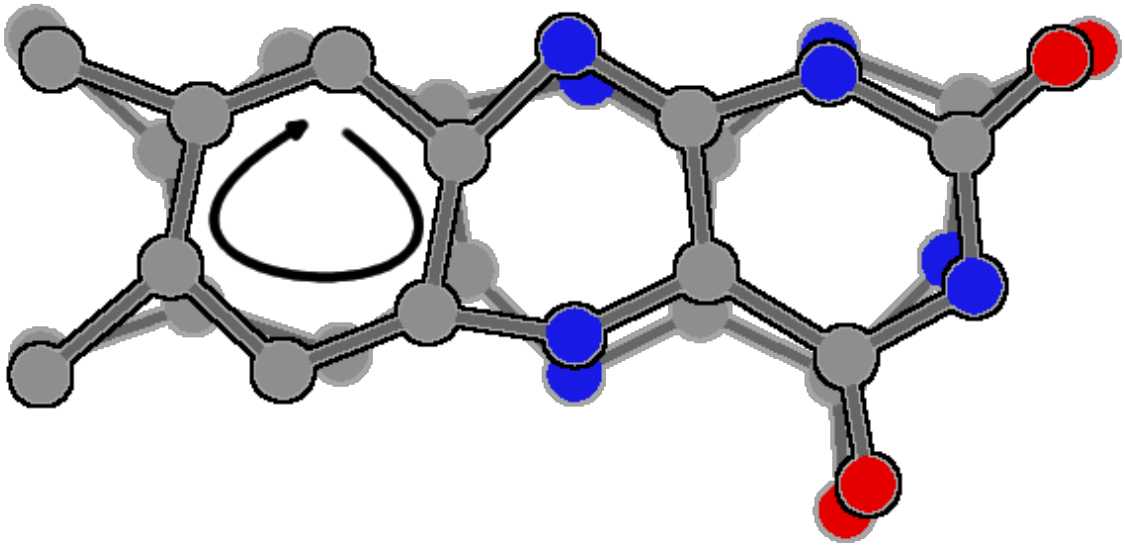


Figure S7. Ground state S_0 (top, absolute distances) and S_1 excited state geometry (bottom, relative distances relative to S_0) of neutral lumichrome calculated at the PBE0/cc-pVDZ level. All values are given in pm. Positive values correspond to elongations, negative values indicate contractions upon S_1 excitation.

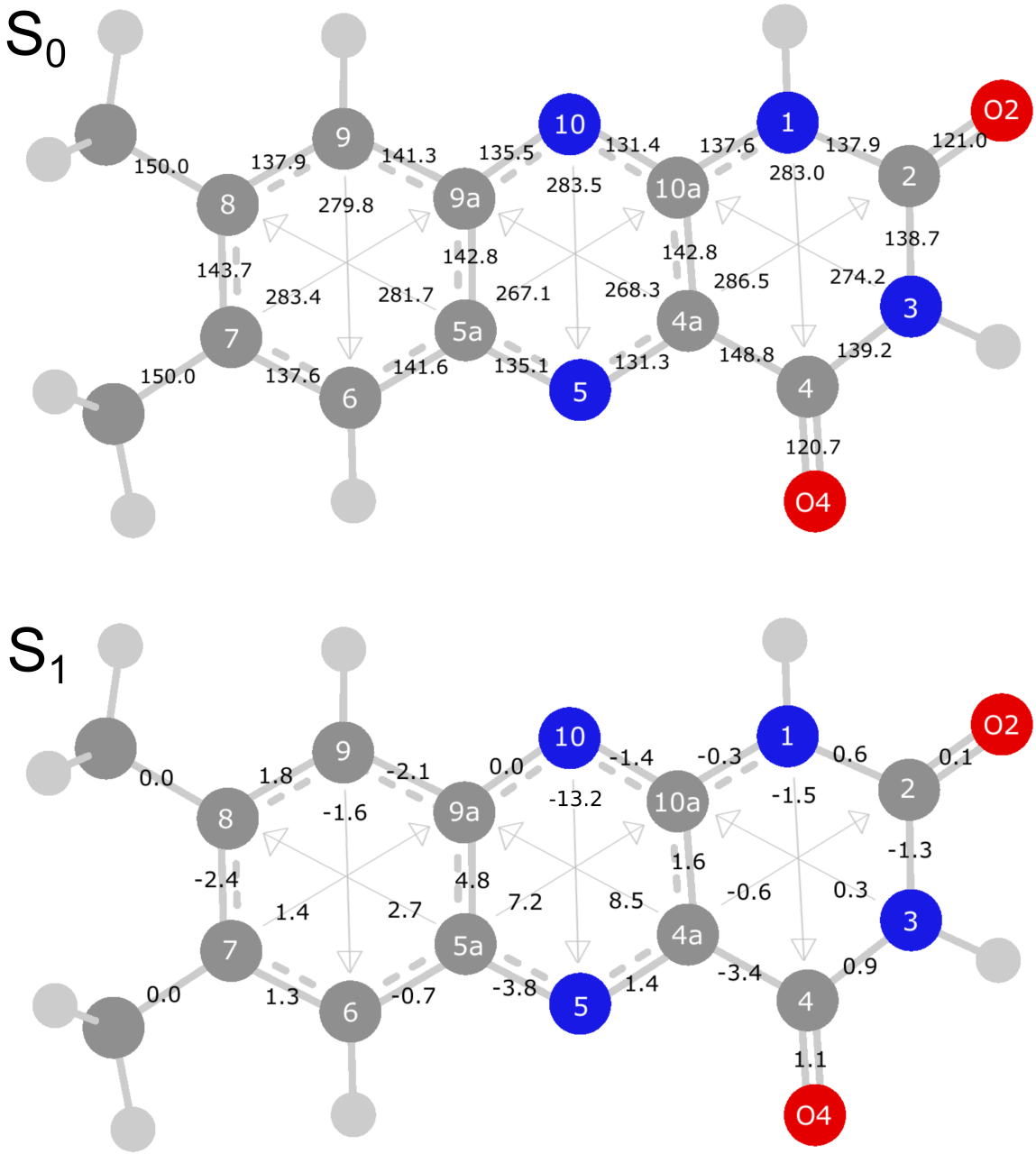


Figure S8. Geometry (in pm) of of H^+LC(N5) in the S_0 state calculated at the PBE0/cc-pVDZ level.

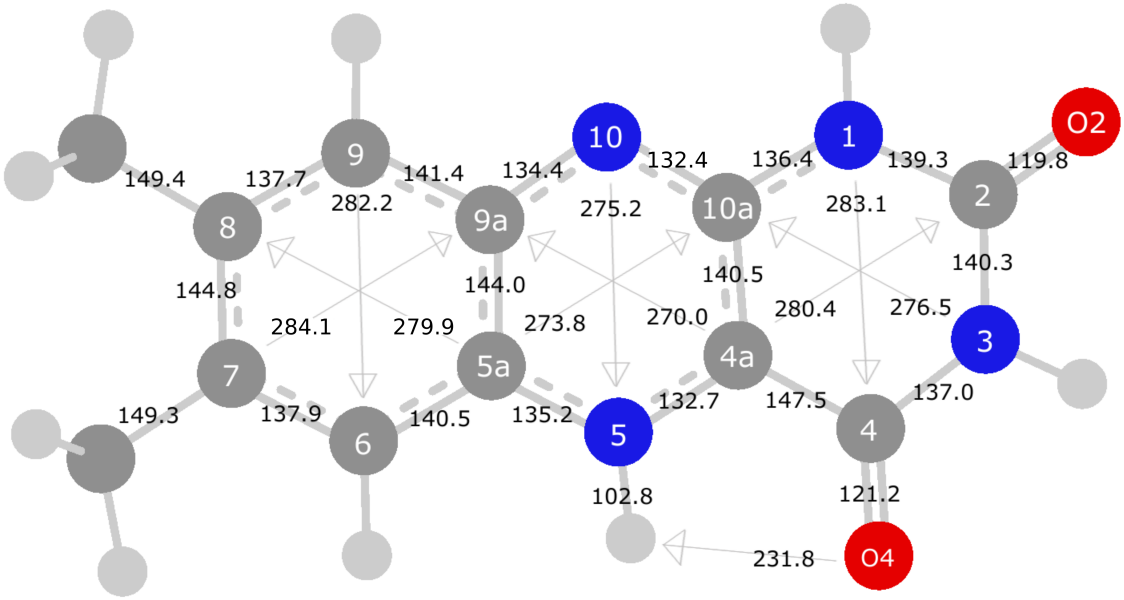


Table S1. Calculated vibrations (in cm^{-1}) for the S_0 and S_1 states of the H^+LC(N5) isomer.

S_0				S_1			
v	sym(a')	v	sym(a'')	v	sym(a')	v	sym(a'')
152.8	53	56.8	81	153.1	53	53.4	81
282.6	52	68.3	80	273.9	52	67.3	80
304.5	51	121.5	79	289.0	51	104.7	79
329.7	50	134.8	78	314.7	50	121.7	78
412.9	49	158.1	77	411.7	49	142.2	77
431.6	48	169.0	76	430.8	48	155.1	76
473.6	47	200.1	75	471.5	47	172.7	75
525.3	46	246.5	74	519.9	46	220.1	74
572.8	45	314.2	73	569.8	45	287.3	73
609.5	44	391.1	72	598.6	44	329.6	72
651.4	43	439.7	71	649.2	43	369.2	71
694.8	42	489.6	70	690.9	42	424.1	70
749.0	41	612.9	69	759.5	41	585.6	69
798.0	40	635.4	68	800.5	40	617.2	68
847.4	39	664.5	67	850.4	39	632.9	67
898.7	38	720.0	66	895.4	38	672.6	66
1003.8	37	768.0	65	999.7	37	687.4	65
1013.7	36	773.4	64	1010.0	36	719.5	64
1025.0	35	815.6	63	1013.2	35	762.8	63
1151.5	34	861.4	62	1142.9	34	767.3	62
1175.9	33	910.2	61	1165.9	33	877.5	61
1210.7	32	929.0	60	1212.7	32	903.9	60
1257.2	31	1029.6	59	1227.2	31	1006.1	59
1265.8	30	1049.0	58	1269.1	30	1035.4	58
1310.2	29	1436.3	57	1287.5	29	1429.6	57
1341.1	28	1452.1	56	1301.1	28	1444.1	56
1375.4	27	3137.6	55	1342.7	27	3116.6	55
1385.3	26	3137.8	54	1353.6	26	3127.9	54
1386.8	25			1377.6	25		
1398.6	24			1381.1	24		
1406.2	23			1387.9	23		
1428.4	22			1418.2	22		
1438.0	21			1426.7	21		
1448.1	20			1443.9	20		
1462.2	19			1463.7	19		
1492.9	18			1480.6	18		
1531.3	17			1492.2	17		
1557.6	16			1545.0	16		
1602.8	15			1576.6	15		
1639.3	14			1601.1	14		
1693.1	13			1649.8	13		
1712.8	12			1726.7	12		
1846.5	11			1806.1	11		
1905.1	10			1863.7	10		
3063.9	9			3050.1	9		
3064.5	8			3056.1	8		
3183.3	7			3182.4	7		
3185.9	6			3184.8	6		
3214.9	5			3210.0	5		
3239.5	4			3228.0	4		
3455.3	3			3554.6	3		
3593.6	2			3600.2	2		
3615.4	1			3612.6	1		