Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Thermal and Solvent Effects on the Triplet Formation in Cinnoline
Electronic Supplementary Information

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1 Figures

Figure 1: Duschinsky matrix related to the transition between the S_0 and $S_1(n\pi^*)$ states. In order to visualize the normal mode mixing, absolute values of the matrix elements J_{ij} are shown.

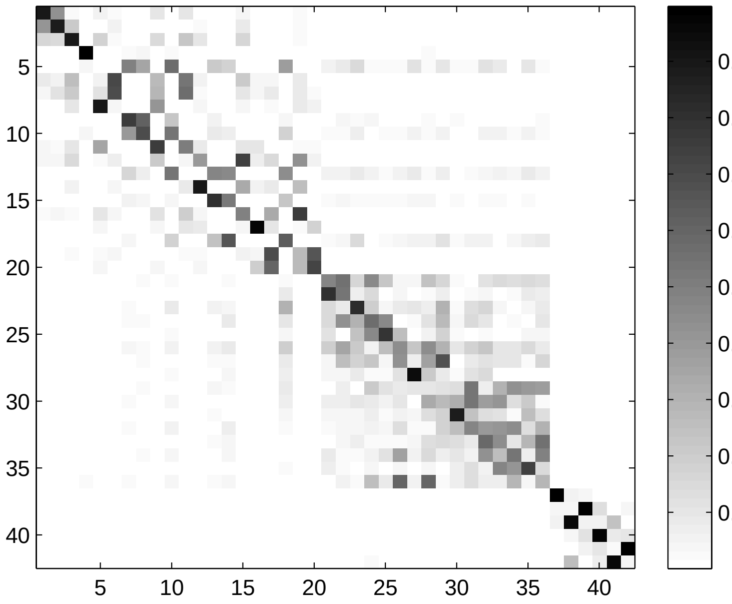


Figure 2: Duschinsky matrix related to the transition between the $T_1(n\pi^*)$ and S_0 states. In order to visualize the normal mode mixing, absolute values of the matrix elements J_{ij} are shown.

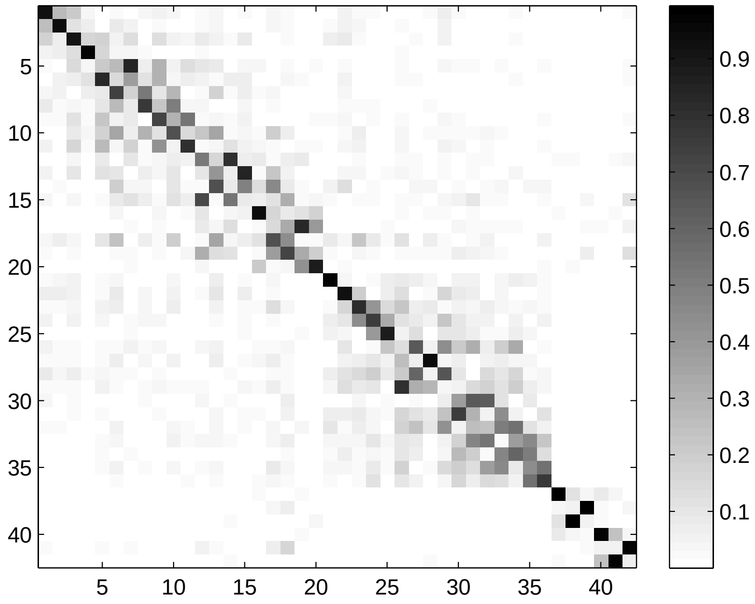


Figure 3: Duschinsky matrix related to the transition between the $S_2(\pi\pi^*)$ and S_0 states. In order to visualize the normal mode mixing, absolute values of the matrix elements J_{ij} are shown.

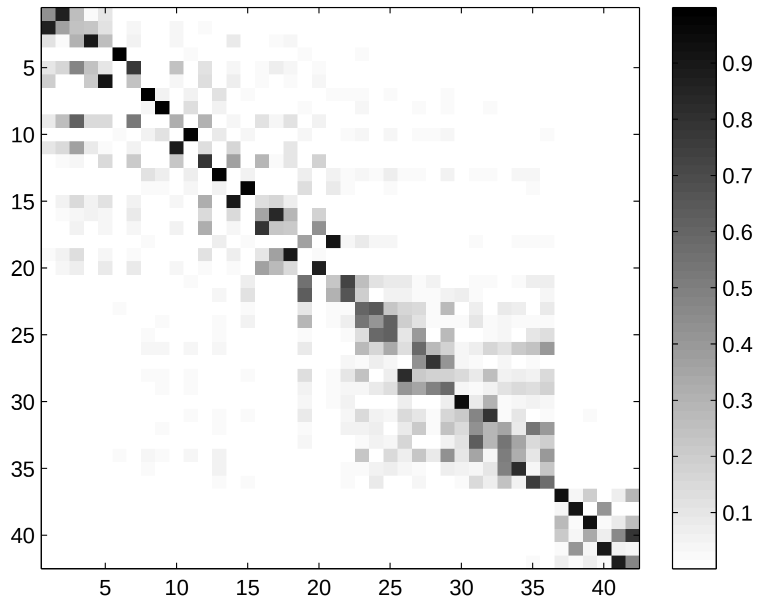


Figure 4: Duschinsky matrix related to the transition between the $S_1(n\pi^*)$ and $T_1(n\pi^*)$ states. In order to visualize the normal mode mixing, absolute values of the matrix elements J_{ij} are shown.

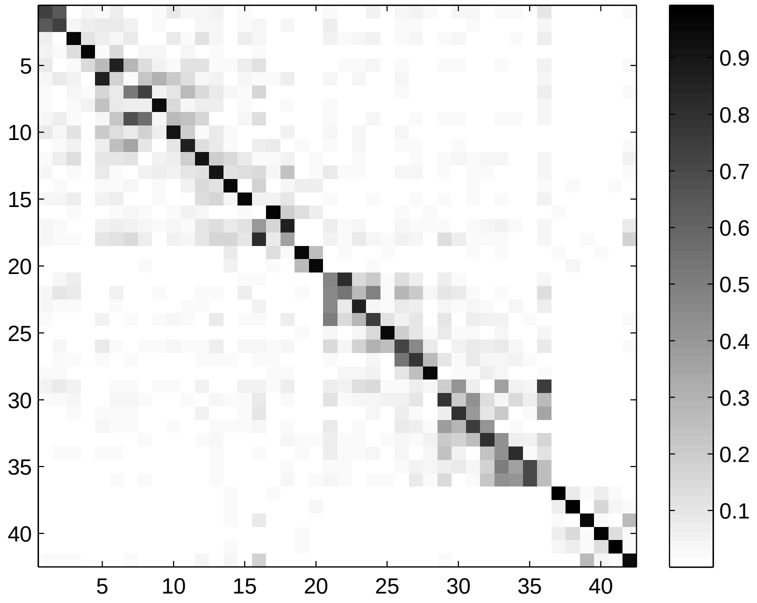


Figure 5: Duschinsky matrix related to the transition between the $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$ states. In order to visualize the normal mode mixing, absolute values of the matrix elements J_{ij} are shown.

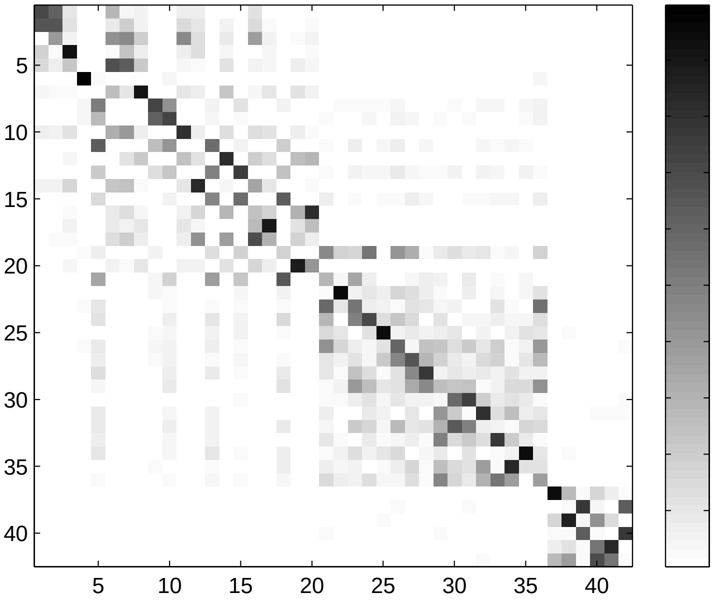
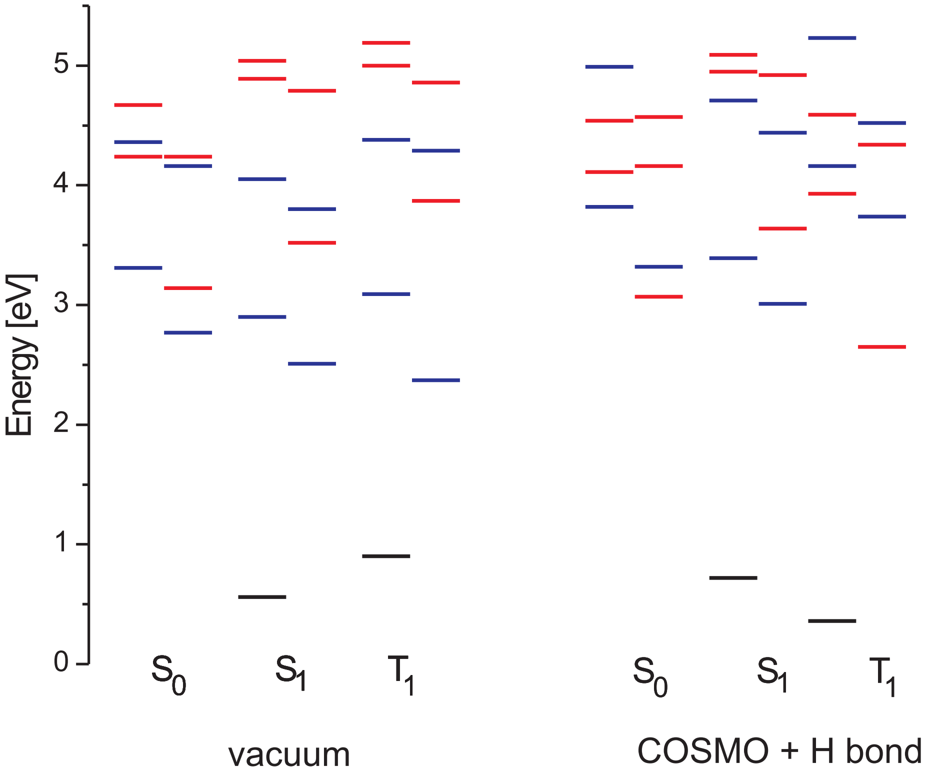


Figure 6: Energy level scheme of cinnoline at various minimum nuclear arrangements *in vacuo* (left) and in hydroxylic solution (right). For each nuclear arrangement, singlet levels are displayed on the left, triplet levels on the right side. Color code: blue $n\pi^*$ states, red $\pi\pi^*$ states.



2 Tables

Table 1: Calculated S_0 state harmonic frequencies (in cm^{-1}) and intensities (in km/mol) for cinnoline at the RI-CC2/cc-pVDZ level. Description: ip = in-plane, oop = out-of-plane, s = symmetric, a = antisymmetric

ν	I	Assign.	Exp.[a]	ν	I	Assign.	Exp.[a]	ν	I	Assign.	Exp.[a]
168	4.35	oop ring bend.		846	40.46	oop C-H bend. + oop ring bend.	844 vs	1291	8.99	C-N str. + ip C-H bend.	1392 s
174	1.69	oop ring bend.		860	0.02	oop C-H bend. + oop ring bend.	875 m	1429	4.01	ring str. + ip C-H bend.	1416 m-s
363	0.71	oop ring bend.		945	0.53	oop C-H bend. + oop ring bend.	962 m	1442	1.93	ring str. + ip C-H bend.	1440 m-s
363	2.40	ip ring bend.	373 s	953	1.39	ip ring bend.	1007 w-m	1476	9.88	ring str.+ ip C-H bend.	1491 s
455	1.10	oop ring bend.		958	0.01	oop C-H bend. + oop ring bend.	1030 w	1518	5.67	ring str. + ip C-H bend.	1538 w-m
460	4.80	oop ring bend.	470 s	963	0.33	oop C-H bend. + oop ring bend.	1070 vw	1568	1.44	ring str. ip C-H bend.	1550 w-m
503	1.41	ip ring bend.	512 m	1028	2.46	C-C str.	1090 vs	1606	12.54	ring str. + ip C-H bend.	1580 vs
526	0.54	ip ring bend.	530 m	1034	0.80	C-N str.	1117 vw	1661	2.55	ring str. + ip C-H bend.	1620 m
602	0.40	oop ring bend.	633 m-s	1133	4.00	ip ring bend.	1138 m-s	3203	1.29	C-H str. a	2925
629	2.13	ip ring bend.	650 m-s	1155	2.33	N-N str.	1158 w-m	3206	3.17	C-H str. a	2966 sh.
706	1.86	oop ring bend.	716 vw	1160	1.68	ring str. + ip C-H bend.	1170 w?	3218	7.44	C-H str. a	2990 sh.
757	31.8	oop C-H bend. + oop ring bend.	748 vs	1240	14.33	ring str.	1179 m-s	3230	9.09	C-H str. a	3016 sh.
773	1.8	ring breath.	774 m	1260	2.60	ring str. + ip C-H bend.	1258 m	3231	15.94	C-H str. s	3054
820	2.55	ip ring bend.	821 m	1284	2.51	N-N str. + C-N str.	1291 m-s	3241	7.54	C-H str. s	

[a] liquid phase IR spectrum, s = strong, m = medium, w = weak, v = very, sh = shoulder [1]

Table 2: Energies relative to the ground state minimum (eV), oscillator strengths for transtions to the ground state (in parentheses), and characters of the electronic states of cinnoline calculated at excited-state minimum geometries using the RI-CC2/aug-cc-pVDZ level of theory. Geometries were optimized at RI-CC2/cc-pVDZ level.

State	$S_1(n\pi^*)$ geo	$T_1(n\pi^*)$ geo	$S_2(n\pi^*)$ geo	$S_2(\pi\pi^*)$ geo
S_0	0.56	0.90	0.78	0.17
S_1	2.90 (0.0012) $n\pi^*$	3.09 (0.0072) $n\pi^*$	3.30 (0.0013) $n\pi^*$	3.59 (0.0029) $n\pi^*$
S_2	4.05 (0.0006) $n\pi^*$	4.38 (0.0034) $n\pi^*$	3.63 (0.0003) $n\pi^*$	4.03 (0.0372) $\pi\pi^*$
S_3	4.89 (0.0215) $\pi\pi^*$	5.00 (0.0592) $\pi\pi^*$	5.07 (0.0073) $\pi\pi^*$	4.59 (0.0367) $\pi\pi^*$
S_4	5.04 (0.0468) $\pi\pi^*$	5.19 (0.0554) $\pi\pi^*$	5.23 (0.0084) $n\sigma^*$	4.76 (0.0002) $n\pi^*$
T_1	2.51 $n\pi^*$	2.37 $n\pi^*$	2.86 $n\pi^*$	2.95 $\pi\pi^*$
T_2	3.52 $\pi\pi^*$	3.87 $\pi\pi^*$	3.46 $n\pi^*$	3.07 $n\pi^*$
T_3	3.80 $n\pi^*$	4.29 $n\pi^*$	4.21 $\pi\pi^*$	4.17 $\pi\pi^*$
T_4	4.79 $\pi\pi^*$	4.86 $\pi\pi^*$	4.97 $\pi\pi^*$	4.53 $\pi\pi^*$

Table 3: Calculated $S_1(n\pi^*)$ state harmonic frequencies (in cm^{-1}) and intensities (in km/mol) for cinnoline at the RI-CC2/cc-pVDZ level. Description: ip = in-plane, oop = out-of-plane, s = symmetric, a = antisymmetric. Displacement of the S_1 normal modes relative to the S_0 modes in dimensionless harmonic oscillator coordinates

ν	I	Assign.	Displ.	ν	I	Assign.	Displ.	ν	I	Assign.	Displ.
159	2.48	oop ring bend.	0.000	767	27.85	ip ring bend.	-0.962	1338	27.45	C-C str.	0.914
169	2.13	oop ring bend.	0.000	781	27.59	oop C-H bend. + oop ring bend.	0.001	1373	4.54	ring str.	0.144
279	0.04	oop ring bend.	0.000	795	0.06	oop C-H bend. + oop ring bend.	0.000	1408	3.91	ring str.	0.299
367	2.63	ip ring bend.	0.461	826	2.40	ip ring bend.	0.272	1438	1.00	ring str.	0.087
394	7.20	ip ring bend.	0.273	859	1.32	oop C-H bend. + oop ring bend.	-0.001	1522	32.29	ring str.	0.415
408	0.90	oop ring bend.	0.001	914	0.08	oop C-H bend. + oop ring bend.	0.000	1547	61.82	ring str.	-0.498
475	3.61	oop ring bend.	-0.001	1015	43.19	C-C str.	-0.019	1579	63.52	ring str.	0.110
497	0.01	oop ring bend.	0.004	1038	2.05	ring str.	-0.050	1656	95.97	N-N str.	-0.528
506	2.00	ip ring bend.	1.874	1075	29.51	ring str.	-0.309	3198	4.42	C-H str. a	0.000
540	1.48	ip ring bend.	0.549	1118	35.45	ring str.	0.642	3214	7.15	C-H str. a	-0.002
561	1.54	oop ring bend.	0.000	1162	1.93	C-C str.	-0.114	3223	1.91	C-H str.	0.037
610	24.24	oop C-H bend. + oop ring bend.	0.000	1203	41.48	ring str.	0.591	3226	16.21	C-H str. a	0.001
702	10.09	ip ring bend.	1.153	1212	13.32	ring str.	0.307	3238	6.01	C-H str. s	-0.004
729	56.72	oop C-H bend. + oop ring bend.	0.001	1257	16.25	ring str.	-0.023	3273	0.23	C-H str.	-0.034

Table 4: Calculated $S_2(n\pi^*)$ state harmonic frequencies (in cm^{-1}) and intensities (in km/mol) for cinnoline at the RI-CC2/cc-pVDZ level. Description: ip = in-plane, oop = out-of-plane, s = symmetric, a = antisymmetric

ν	I	Assign.	ν	I	Assign.	ν	I	Assign.
146	2.06	oop ring bend.	734	28.30	ip ring bend.	1327	13.64	ring str.
158	0.01	oop ring bend.	770	0.02	oop C-H bend. + oop ring bend.	1381	10.54	ring str.
264	2.48	oop ring bend.	861	8.08	oop C-H bend. + oop ring bend.	1415	0.68	ring str.
310	5.92	oop ring bend.	870	28.34	ip ring bend.	1479	2.41	ring str.
344	0.70	ip ring bend.	895	0.02	oop C-H bend. + oop ring bend.	1569	11.74	C-C str.
363	24.45	oop ring bend.	908	22.04	C-N str.	1602	12.15	C-C str.
408	2.20	oop ring bend.	909	0.82	oop C-H bend. + oop ring bend.	1676	373.41	N-N str.
468	12.36	ip ring bend.	971	16.92	C-C str.	2481	200.34	ring str.
490	2.65	oop ring bend.	1103	11.70	ip ring bend.	3186	1.98	C-H str. a
506	6.99	ip ring bend.	1150	1.03	ring str.	3189	12.96	C-H str. a
542	16.31	oop C-H bend. + oop ring bend.	1162	1.12	ring str.	3215	3.04	C-H str. a
589	45.55	ip ring bend.	1202	2.05	ring str.	3224	11.65	C-H str. a
704	51.63	oop C-H bend. + oop ring bend.	1238	19.62	ring str.	3236	10.03	C-H str. s
705	20.28	ip ring bend.	1306	5.71	ring str.	3329	8.18	C-H str.

Table 5: Calculated $S_2(\pi\pi^*)$ state harmonic frequencies (in cm^{-1}) and intensities (in km/mol) for cinnoline at the RI-CC2/cc-pVDZ level. Description: ip = in-plane, oop = out-of-plane, s = symmetric, a = antisymmetric. Displacement of the $S_2(\pi\pi^*)$ normal modes relative to the $S_1(n\pi^*)$ modes in dimensionless harmonic oscillator coordinates

ν	I	Assign.	Displ.	ν	I	Assign.	Displ.	ν	I	Assign.	Displ.
86	6.94	oop ring bend.	0.000	788	6.50	ip ring bend.	-1.400	1268	148.77	ring str. + ip C-H bend.	0.722
151	0.20	oop ring bend.	0.000	814	2.37	oop C-H bend. + oop ring bend.	0.002	1394	53.52	ring str. + ip C-H bend.	-0.266
214	8.82	oop ring bend.	0.000	842	0.25	oop C-H bend. + oop ring bend.	0.002	1426	44.81	ring str. + ip C-H bend.	-0.248
286	0.29	oop ring bend.	0.000	882	2.38	oop C-H bend. + oop ring bend.	-0.001	1435	25.70	ring str. + ip C-H bend.	0.096
350	0.35	oop ring bend.	-0.001	896	16.42	ip ring bend.	-1.033	1486	46.55	ring str. + ip C-H bend.	0.473
356	4.39	ip ring bend.	0.361	903	3.57	oop C-H bend. + + oop ring bend.	-0.003	1509	52.16	ring str. + ip C-H bend.	0.446
395	5.04	oop ring bend.	0.000	930	0.43	ip ring bend.	1.035	1580	15.36	ring str. + ip C-H bend.	0.453
467	23.03	ip ring bend.	-1.854	998	19.32	C-C str.	-0.772	1682	97.19	ring str. + ip C-H bend.	-0.357
506	17.21	ip ring bend.	1.494	1043	100.54	N-N str.	-0.894	3196	5.27	C-H str. a	0.007
576	0.16	oop ring bend.	0.015	1098	3.50	ring str.	0.394	3201	15.57	C-H str. a	0.040
577	49.00	ip ring bend.	1.388	1133	89.38	ring str. + ip C-H bend.	-0.066	3213	4.36	C-H str. a	0.012
677	45.22	oop C-H bend. + oop ring bend.	0.000	1204	18.06	ring str.	0.452	3217	26.37	C-H str. s	0.062
705	22.83	ring breath.	1.158	1238	99.42	ring str. + ip C-H bend.	0.426	3229	3.23	C-H str. a	0.002
737	10.75	oop C-H bend. + oop ring bend.	0.000	1245	34.99	ring str. + ip C-H bend.	0.111	3249	3.68	C-H str. s	0.032

Table 6: Calculated $T_1(n\pi^*)$ state harmonic frequencies (in cm^{-1}) and intensities (in km/mol) for cinnoline at the RI-CC2/cc-pVDZ level. Description: ip = in-plane, oop = out-of-plane, s = symmetric, a = antisymmetric. Displacement of the $T_1(n\pi^*)$ normal modes relative to the $S_1(n\pi^*)$ modes in dimensionless harmonic oscillator coordinates

ν	I	Assign.	Displ.	ν	I	Assign.	Displ.	ν	I	Assign.	Displ.
147	6.35	oop ring bend.	2.338	768	32.32	ring breath.	0.493	1310	26.72	N-N str.	0.414
170	1.33	oop ring bend.	0.601	836	0.36	oop C-H bend + oop ring bend.	0.138	1380	26.63	ring str.	-0.595
311	8.42	oop ring bend.	1.937	851	6.91	ip ring bend.	0.111	1400	14.60	ring str.	0.068
361	1.28	ip ring bend.	0.124	894	10.29	oop C-H bend + oop ring bend.	0.184	1431	2.25	ring str.	0.188
412	22.45	oop ring bend.	-1.356	897	1.91	oop C-H bend + oop ring bend.	0.027	1469	1.43	ring str.	-0.197
448	10.84	ip ring bend.	-0.240	930	0.08	oop C-H bend + oop ring bend.	0.011	1523	34.47	ring str.	0.115
477	1.97	oop ring bend.	-0.192	1037	18.41	ring str.	0.352	1587	4.92	ring str.	0.054
503	8.72	ip ring bend.	-0.302	1046	41.85	ring str.	-0.713	1594	12.30	ring str.	-0.055
535	5.26	oop ring bend.	0.612	1089	14.44	ring str.	-0.286	3200	3.92	C-H str. a	-0.016
557	8.33	ip ring bend.	-0.532	1111	4.46	ring str.	0.506	3215	4.75	C-H str. a	0.004
633	6.97	oop ring bend.	-0.618	1164	0.10	ring str.	0.011	3223	1.52	C-H str. a	-0.102
701	18.39	oop C-H bend. + oop ring bend.	-0.648	1199	19.34	C-N str.	0.210	3230	11.20	C-H str. a	-0.001
729	18.21	ip ring bend.	0.296	1222	1.44	ring str.	0.206	3239	10.24	C-H str. s	0.001
750	74.98	oop C-H bend + oop ring bend.	0.301	1263	5.25	ring str.	-0.026	3245	11.02	C-H str. s	0.219

Table 7: Displacements of the ground state normal modes relative to the $T_1(n\pi^*)$ and $S_2(\pi\pi^*)$ state normal modes in dimensional harmonic oscillator coordinates.

ν	Displ. (T_1)	Displ. (S_2)	ν	Displ. (T_1)	Displ. (S_2)	ν	Displ. (T_1)	Displ. (S_2)
3241	0.025	0.028	1284	0.467	-0.272	820	0.811	0.074
3231	0.233	0.012	1260	0.306	0.002	773	-0.839	0.601
3230	0.001	-0.028	1240	0.787	-0.327	757	0.146	0.000
3218	0.001	0.006	1160	0.21	0.078	706	-2.149	0.000
3206	-0.057	0.015	1155	-0.815	0.306	629	-1.014	0.524
3203	0.006	-0.013	1133	-0.373	0.152	602	-1.257	0.00
1661	-0.161	-0.056	1034	-1.001	0.688	526	-1.317	-0.020
1606	0.232	-0.004	1028	0.309	0.011	503	-0.594	1.112
1568	0.263	-0.272	963	-0.049	0	460	-1.111	0.000
1518	0.418	0.084	958	0.369	0	455	0.665	0.000
1476	0.373	0.769	953	0.242	0.256	363	0.452	0.072
1442	0.653	0.315	945	0.033	-0.001	363	2.388	0.000
1429	0.529	-0.082	860	-0.075	0.000	174	-1.105	0.000
1291	0.051	-0.341	846	-1.181	0.000	168	-1.896	0.000

References

[1] R. W. Mitchell, R. W. Glass, and J. A. Merritt. Infrered and reman spectra of some diazanaphthalenes. *J. Mol. Spectr.*, 36:310–327, 1970.