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Vibrational spectroscopy of salicylideneaniline molecule in solid phase and confined state

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Electronic Supplementary Information

- Cartesian coordinates of all optimized structures, EEM/HI atomic charges calculated with the EEM parameters of set T1, ref [1].
- Table with the assignment of vibrational modes of the most stable cis-enol SA isomer.
- Simulated Raman, infrared, and INS spectra of the salicylideneaniline isomers; the *x*-axis on the spectra refers to the unscaled values of vibrational frequencies (in cm^{-1}).

Contents

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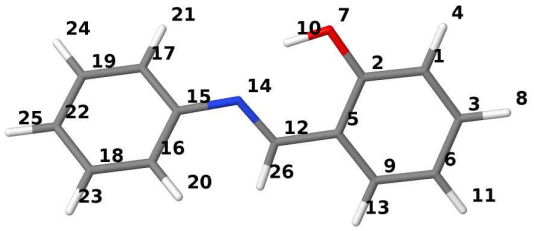
1 Cis-enol salicylideneaniline isomer



Atom	x/Å	y/Å	z/Å	q/$\lvert e^{-}\rvert$
C1	3.669613	1.013101	0.246394	−0.227
C2	2.278245	0.863711	0.193832	0.455
C3	4.498349	−0.070718	−0.003152	−0.094
H4	4.072630	1.989896	0.484874	0.162
C5	1.722915	−0.406661	−0.115927	−0.122
C6	3.966708	−1.329990	−0.312390	−0.089
O7	1.507132	1.933426	0.438048	−0.631
H8	5.573629	0.062841	0.041878	0.108
C9	2.592317	−1.485177	−0.366027	−0.125
H10	0.560550	1.646454	0.351263	0.416
H11	4.622652	−2.169605	−0.506367	0.101
C12	0.288963	−0.608872	−0.179336	0.114
H13	2.162374	−2.453179	−0.604201	0.104
N14	−0.553965	0.343188	0.027081	−0.515
C15	−1.942098	0.103501	0.016344	0.402
C16	−2.517289	−1.060326	0.548190	−0.242
C17	−2.777687	1.100021	−0.506436	−0.218
C18	−3.898838	−1.232411	0.523782	−0.065
C19	−4.155652	0.916231	−0.537468	−0.077
H20	−1.886714	−1.811113	1.010469	0.124
H21	−2.328299	2.006084	−0.895823	0.142
C22	−4.722997	−0.250882	−0.024476	−0.105
H23	−4.333027	−2.131389	0.947120	0.101
H24	−4.789838	1.689447	−0.956342	0.104
H25	−5.798094	−0.387192	−0.038592	0.099
H26	−0.050457	−1.621122	−0.428206	0.077

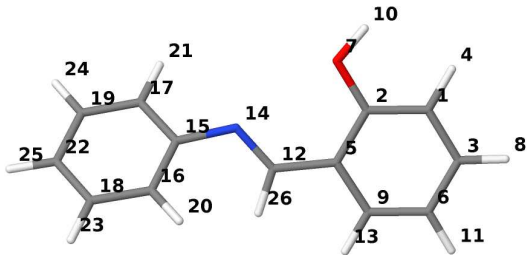
Table 1: Assignement of vibrational modes of the cis-enol SA molecule. Potential energy distribution analysis (PED) reports internal coordinates and the corresponding percentage (in parentheses) of three largest contributions for each mode. Methods used for the mode assignment: IR, INS, R for the infrared, inelastic neutron scattering, and Raman techniques, respectively. D_m^k is the amplitude localization criterion, eqn (3) of article, where P, B, and I stand for the phenol ring, benzene ring, and of the imine group, respectively. Internal coordinates definition: R – bond-stretching, δ – angle-bending, ω – out-of-plane, τ – torsion; numbering of atoms corresponds to the figure above and to Figure 2 of article.

No.	ω_{exp} (cm^{-1})		ω_{sc} (cm^{-1})	Method	PED (%)	D_m^k (%)		
	Solid SA	SA@silicalite			P	B	I	
1			46		τ_{N14C15} (92), τ_{C5C12} (31), $\delta_{C16C15N14}$ (18)	26.1	72.3	1.6
2	67		62	R	τ_{C2C5} (82), τ_{C12N14} (43), τ_{C5C9} (34)	46.2	39.0	14.8
3	83		81	R	$\delta_{C12N14C15}$ (91), τ_{C15C16} (23), $\delta_{C5C12N14}$ (19)	39.7	49.1	11.2
4	161	152	149	R	τ_{C2C5} (93), τ_{C5C9} (26), τ_{O2H7} (22)	48.8	43.7	7.5
5	203		199	INS, R	τ_{C2C5} (92), $\delta_{C16C15N14}$ (20), τ_{C1C2} (18)	43.6	50.5	5.9
6	218	231	219	INS, R	τ_{C2C5} (89), τ_{C1C2} (37), τ_{C5C12} (19)	56.6	6.0	37.4
7	262	265	264	INS, R	τ_{C15C16} (63), τ_{C15C17} (42), τ_{C5C12} (30)	27.8	61.6	10.6
8	313		316	INS, R	τ_{C5C12} (73), τ_{C5C9} (46), $\delta_{C16C15N14}$ (25)	24.7	10.7	64.6
9	360	342	342	INS	τ_{C5C9} (78), τ_{C1C3} (34), ω_{C1H4} (26)	45.9	29.1	25.0
10	416		416	INS, R	τ_{C16C18} (75), τ_{C17C19} (65), τ_{C19C22} (6)	0.4	99.2	0.4
11	434		440	R	τ_{C1C3} (71), δ_{C5C2O7} (33), $\delta_{C16C15N14}$ (30)	72.8	11.6	15.6
12	448	445	452	INS, R	τ_{C1C3} (72), δ_{C1C2O7} (43), τ_{C6C9} (28)	73.6	13.6	12.8
13	494		493	INS, R	$\delta_{C16C15N14}$ (66), τ_{C1C3} (37), τ_{C6C9} (37)	54.5	25.5	20.0
14	523		526	INS, R	ω_{C22H25} (51), τ_{C3C6} (50), τ_{C19C22} (37)	29.6	65.5	4.9
15	548		547	R	$\delta_{C16C15N14}$ (48), $\delta_{C2C5C12}$ (44), τ_{C3C6} (39)	45.2	40.2	14.6
16	554		555	INS, R	τ_{C3C6} (93), τ_{C6C9} (16), τ_{C1C3} (16)	74.4	20.1	5.5
17	571	574	574	R	δ_{C3C1C2} (55), δ_{C5C9C6} (45), $\delta_{C17C15C16}$ (33)	71.2	19.1	9.7
18	617	618	622	INS, R	$\delta_{C22C19C17}$ (53), $\delta_{C16C18C22}$ (52), $\delta_{C15C16C18}$ (46)	0.7	97.6	1.7
19	657	658	660	IR, INS, R	δ_{C6C3C1} (40), $\delta_{C5C12N14}$ (38), $\delta_{C17C15C16}$ (36)	55.4	36.8	7.8
20	692		692	IR, INS	ω_{C18H23} (52), ω_{C19H24} (46), τ_{C16C18} (43)	0.4	99.5	0.1
21	735		731	IR	τ_{C1C2} (56), τ_{C1C3} (50), ω_{C3H8} (44)	77.1	18.2	4.7
22	752	752	750	IR	ω_{C6H11} (80), ω_{C9H13} (39), τ_{C5C9} (32)	98.7	1.1	0.2
23	756		757	R	ω_{C22H25} (80), τ_{C16C18} (38), τ_{C17C19} (38)	19.1	77.2	3.7
24	781	782	781	IR, R	ω_{C22H25} (61), R_{C2C5} (49), τ_{C16C18} (36)	33.9	51.4	14.7
25			827		ω_{C16H20} (55), ω_{C17H21} (51), ω_{C19H24} (37)	0.3	99.7	0.0
26	822		834	IR	τ_{O2H7} (94), ω_{C1H4} (26), ω_{C9H13} (16)	98.8	0.4	0.8
27	845	844	843	IR, R	R_{N14C15} (71), R_{C15C16} (38), $\delta_{C18C22C19}$ (24)	29.4	56.1	14.4
28			855		ω_{C1H4} (81), τ_{C3C6} (41), ω_{C9H13} (34)	98.8	0.6	0.7
29	896		892	IR, R	ω_{C22H25} (62), τ_{C16C18} (44), ω_{C17H21} (39)	15.2	76.1	8.7
30	918		913	IR, R	ω_{C22H25} (56), ω_{C16H20} (48), ω_{C17H21} (45)	10.7	79.1	10.2
31	946		934	R	ω_{C9H13} (76), τ_{C6C9} (45), ω_{C6H11} (29)	94.6	0.6	4.8
32			960		τ_{C16C18} (70), τ_{C17C19} (46), ω_{C18H23} (41)	0.2	99.5	0.3
33			966		τ_{C3C6} (65), ω_{C3H8} (50), τ_{C1C3} (42)	99.5	0.1	0.4
34			978		ω_{C22H25} (69), τ_{C17C19} (45), ω_{C19H24} (38)	0.1	98.8	1.1
35	980	980	981	IR, INS, R	ω_{C12H26} (95), τ_{C12N14} (20), ω_{C9H13} (19)	7.6	8.5	83.9
36	1000	1000	994	R	ω_{C12H26} (51), $\delta_{C17C15C16}$ (37), $\delta_{C16C18C22}$ (29)	1.7	65.6	32.7
37	1024	1026	1023	IR, R	R_{C19C22} (72), R_{C18C22} (61), $\delta_{C15C17H21}$ (14)	2.4	97.5	0.1

Table 1 – continued

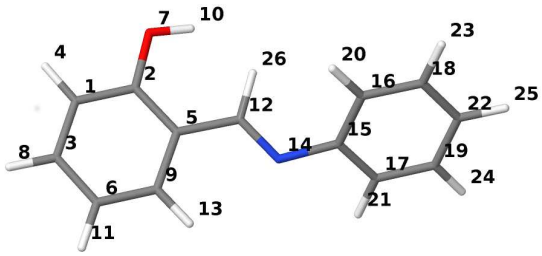
No.	ω_{exp} (cm^{-1})		ω_{sc} (cm^{-1})	Method	PED (%)	D_m^k (%)		
	Solid SA	SA@silicalite			P	B	I	
38	1031	1043	1029	IR, R	R_{C3C6} (91), R_{C1C3} (28), R_{C9C6} (18)	96.2	3.6	0.2
39			1079		R_{C16C18} (53), R_{C17C19} (49), R_{C18C22} (28)	0.1	98.4	1.5
40			1114		R_{C9C6} (66), δ_{C6C3H8} (33), R_{C1C3} (30)	98.8	0.4	0.8
41	1149	1157	1152	IR, R	$\delta_{C3C6H11}$ (44), $\delta_{C9C6H11}$ (42), δ_{C6C3H8} (41)	98.0	1.4	0.6
42			1155		$\delta_{C18C22H25}$ (53), $\delta_{C19C22H25}$ (53), $\delta_{C22C19H24}$ (38)	1.6	98.3	0.0
43	1169	1169	1166	IR, R	$\delta_{C18C16H20}$ (49), $\delta_{C22C18H23}$ (38), $\delta_{C19C17H21}$ (36)	1.8	97.8	0.4
44	1187	1185	1185	IR, R	R_{N14C15} (73), R_{C5C12} (48), R_{C1C2} (26)	41.8	47.1	11.1
45	1224		1222	R	R_{N14C15} (62), R_{C1C2} (53), δ_{C2C1H4} (32)	81.7	12.7	5.6
46	1239	1240	1237	R	R_{C5C9} (53), R_{N14C15} (37), R_{C2O7} (36)	61.6	7.7	30.7
47	1273	1283	1287	IR	R_{C2O7} (94), δ_{C1C3H8} (15), R_{C5C12} (15)	78.7	8.2	13.2
48			1290		R_{C15C16} (61), R_{C15C17} (55), R_{C18C22} (29)	5.5	84.2	10.3
49			1320		$\delta_{C15C16H20}$ (44), $\delta_{C18C16H20}$ (40), $\delta_{C15C17H21}$ (35)	2.4	97.2	0.4
50	1319	1328	1325	R	R_{C2C5} (63), R_{C1C3} (43), R_{C9C6} (42)	64.2	32.4	3.3
51	1361	1367	1364	IR, R	$\delta_{N14C12H26}$ (79), $\delta_{C5C12H26}$ (51), R_{C12N14} (22)	16.2	6.0	77.8
52	1401	1411	1418	IR, R	$\delta_{C2O7H10}$ (90), R_{C1C3} (23), R_{C5C9} (16)	97.6	0.2	2.2
53	1450	1452	1446	IR, R	R_{C16C18} (44), $\delta_{C18C22H25}$ (43), $\delta_{C19C22H25}$ (43)	3.5	95.4	1.1
54	1456	1463	1456	IR, R	R_{C2O7} (50), R_{C2C5} (49), R_{C9C6} (41)	89.8	7.0	3.2
55	1484	1487	1481	IR, R	R_{C15C17} (31), $\delta_{C18C16H20}$ (30), $\delta_{C16C18H23}$ (30)	17.6	82.0	0.4
56	1498		1497	IR, R	$\delta_{C2O7H10}$ (72), R_{C3C6} (42), $\delta_{C9C6H11}$ (31)	86.6	12.3	1.1
57	1571	1577	1570	IR, R	R_{C12N14} (57), $\delta_{C2O7H10}$ (53), R_{C1C3} (39)	85.2	7.1	7.7
58	1580		1577	R	R_{C19C22} (67), R_{C15C16} (49), R_{C18C22} (38)	0.2	98.9	0.8
59	1590	1594	1593	IR, R	R_{C16C18} (54), R_{C17C19} (52), R_{C15C17} (33)	27.3	69.1	3.6
60			1623		R_{C1C2} (55), R_{C9C6} (54), $\delta_{C2O7H10}$ (48)	95.9	1.1	3.1
61	1615	1622	1626	IR, R	R_{C12N14} (96), R_{C5C12} (16), $\delta_{C5C12H26}$ (14)	16.5	19.0	64.5

2 Cis-enol salicylideneaniline isomer, form 2



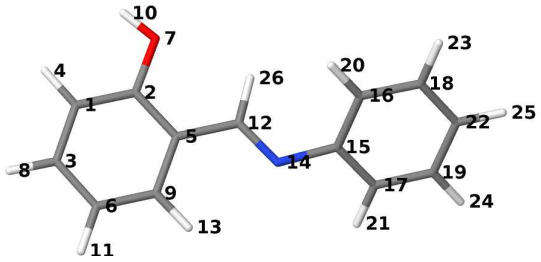
Atom	x/Å	y/Å	z/Å	q/$\lvert e^{-}\rvert$
C1	3.785550	0.865935	0.216621	−0.299
C2	2.387283	0.860504	0.208822	0.440
C3	4.508277	−0.285733	−0.073847	−0.051
H4	4.307309	1.788458	0.455966	0.120
C5	1.690177	−0.330961	−0.100328	−0.024
C6	3.840697	−1.470720	−0.379557	−0.095
O7	1.683404	1.983647	0.496900	−0.583
H8	5.591805	−0.253736	−0.060442	0.101
C9	2.452681	−1.476564	−0.387319	−0.163
H10	2.297552	2.699064	0.697033	0.294
H11	4.394324	−2.373353	−0.606855	0.100
C12	0.232293	−0.474687	−0.141958	0.030
H13	1.922930	−2.393801	−0.623402	0.108
N14	−0.617633	0.461263	0.031738	−0.238
C15	−1.989675	0.160934	0.019415	0.271
C16	−2.534618	−0.955856	0.673460	−0.210
C17	−2.854356	1.057386	−0.626910	−0.182
C18	−3.908916	−1.182755	0.650033	−0.066
C19	−4.222453	0.813793	−0.662490	−0.081
H20	−1.883493	−1.622590	1.227432	0.119
H21	−2.428640	1.932910	−1.102676	0.141
C22	−4.757745	−0.306868	−0.024306	−0.100
H23	−4.317989	−2.042647	1.169431	0.097
H24	−4.876917	1.507032	−1.179467	0.101
H25	−5.826708	−0.485813	−0.039677	0.096
H26	−0.099134	−1.499991	−0.364527	0.074

3 Trans-enol salicylideneaniline isomer



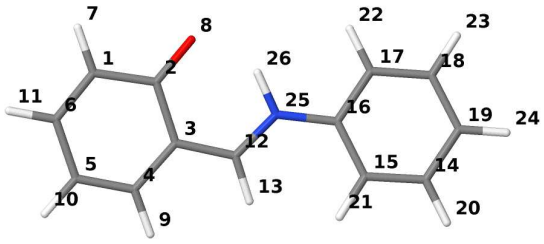
Atom	x/Å	y/Å	z/Å	q/$\lvert e^{-}\rvert$
C1	−3.995889	0.647072	−0.143929	−0.200
C2	−2.633429	0.940201	−0.246139	0.402
C3	−4.409054	−0.635758	0.181894	−0.094
H4	−4.708495	1.440705	−0.332339	0.162
C5	−1.668419	−0.060683	−0.006825	−0.107
C6	−3.468305	−1.647775	0.408653	−0.122
O7	−2.328255	2.229482	−0.584243	−0.616
H8	−5.469008	−0.851298	0.256531	0.109
C9	−2.119371	−1.355543	0.314527	−0.079
H10	−1.384821	2.330903	−0.742525	0.297
H11	−3.792983	−2.649930	0.661404	0.107
C12	−0.234543	0.226794	−0.065285	0.072
H13	−1.369019	−2.115765	0.493220	0.150
N14	0.663172	−0.679901	0.003495	−0.372
C15	2.022952	−0.327572	0.029662	0.339
C16	2.519155	0.750340	0.780487	−0.229
C17	2.924300	−1.129293	−0.686577	−0.201
C18	3.882606	1.035644	0.782470	−0.064
C19	4.281170	−0.827562	−0.693702	−0.079
H20	1.842142	1.336464	1.391838	0.126
H21	2.536831	−1.976802	−1.239530	0.138
C22	4.767609	0.256226	0.039780	−0.103
H23	4.255082	1.862836	1.376755	0.101
H24	4.964701	−1.446442	−1.264284	0.102
H25	5.828110	0.479877	0.045294	0.099
H26	0.068602	1.280376	−0.166995	0.062

4 Trans-enol salicylideneaniline isomer, form 2



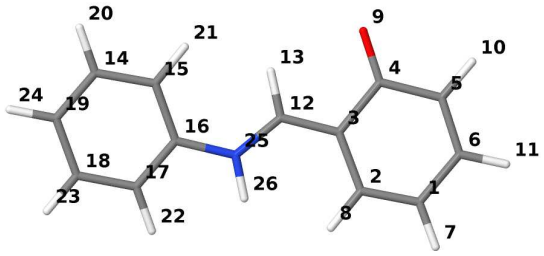
Atom	x/Å	y/Å	z/Å	q/$\lvert e^{-}\rvert$
C1	−3.984511	0.646003	−0.144212	−0.278
C2	−2.620227	0.933768	−0.216582	0.411
C3	−4.409410	−0.647258	0.139602	−0.048
H4	−4.710054	1.437122	−0.310442	0.118
C5	−1.663623	−0.076924	−0.004064	−0.045
C6	−3.475191	−1.663452	0.353797	−0.129
O7	−2.167321	2.195761	−0.493177	−0.649
H8	−5.471117	−0.859911	0.193220	0.101
C9	−2.120630	−1.372711	0.282264	−0.109
H10	−2.914827	2.788329	−0.623591	0.311
H11	−3.806029	−2.670937	0.575572	0.105
C12	−0.230959	0.230086	−0.080297	0.085
H13	−1.374846	−2.141123	0.444916	0.154
N14	0.664076	−0.669302	0.079672	−0.400
C15	2.024607	−0.316951	0.058744	0.346
C16	2.525918	0.847901	0.661994	−0.235
C17	2.923819	−1.207635	−0.546469	−0.199
C18	3.890140	1.125474	0.627643	−0.061
C19	4.282340	−0.915505	−0.592293	−0.080
H20	1.849592	1.515585	1.183438	0.127
H21	2.532964	−2.118462	−0.984614	0.137
C22	4.773125	0.252272	−0.005829	−0.104
H23	4.265376	2.023224	1.106848	0.100
H24	4.963276	−1.606286	−1.077256	0.101
H25	5.834521	0.470977	−0.029002	0.098
H26	0.028778	1.270101	−0.297151	0.142

5 Cis-keto salicylideneaniline isomer



Atom	x/Å	y/Å	z/Å	q/$\lvert e^{-}\rvert$
C1	−3.635082	1.136794	0.074304	−0.261
C2	−2.207122	0.934432	0.058199	0.500
C3	−1.755826	−0.460578	−0.030882	−0.134
C4	−2.709388	−1.522185	−0.100591	−0.124
C5	−4.050809	−1.267215	−0.081828	−0.092
C6	−4.503680	0.083206	0.007898	−0.075
H7	−3.985089	2.160102	0.141280	0.159
O8	−1.390266	1.894068	0.114209	−0.512
H9	−2.344876	−2.543495	−0.168021	0.102
H10	−4.769924	−2.075261	−0.133400	0.101
H11	−5.572313	0.274197	0.022681	0.107
C12	−0.391148	−0.751779	−0.052848	0.172
H13	−0.068008	−1.785502	−0.127867	0.075
C14	3.957610	−1.296123	0.125067	−0.070
C15	2.568360	−1.215372	0.137309	−0.233
C16	1.942456	0.030165	0.004051	0.446
C17	2.725494	1.184791	−0.125442	−0.243
C18	4.112363	1.092092	−0.131122	−0.065
C19	4.737462	−0.148388	−0.009637	−0.108
H20	4.432182	−2.265111	0.230012	0.102
H21	1.986818	−2.119831	0.264315	0.118
H22	2.238578	2.148500	−0.225553	0.138
H23	4.705435	1.993575	−0.233020	0.105
H24	5.818479	−0.219911	−0.014898	0.100
N25	0.545465	0.191165	0.004403	−0.707
H26	0.118454	1.143001	0.053103	0.399

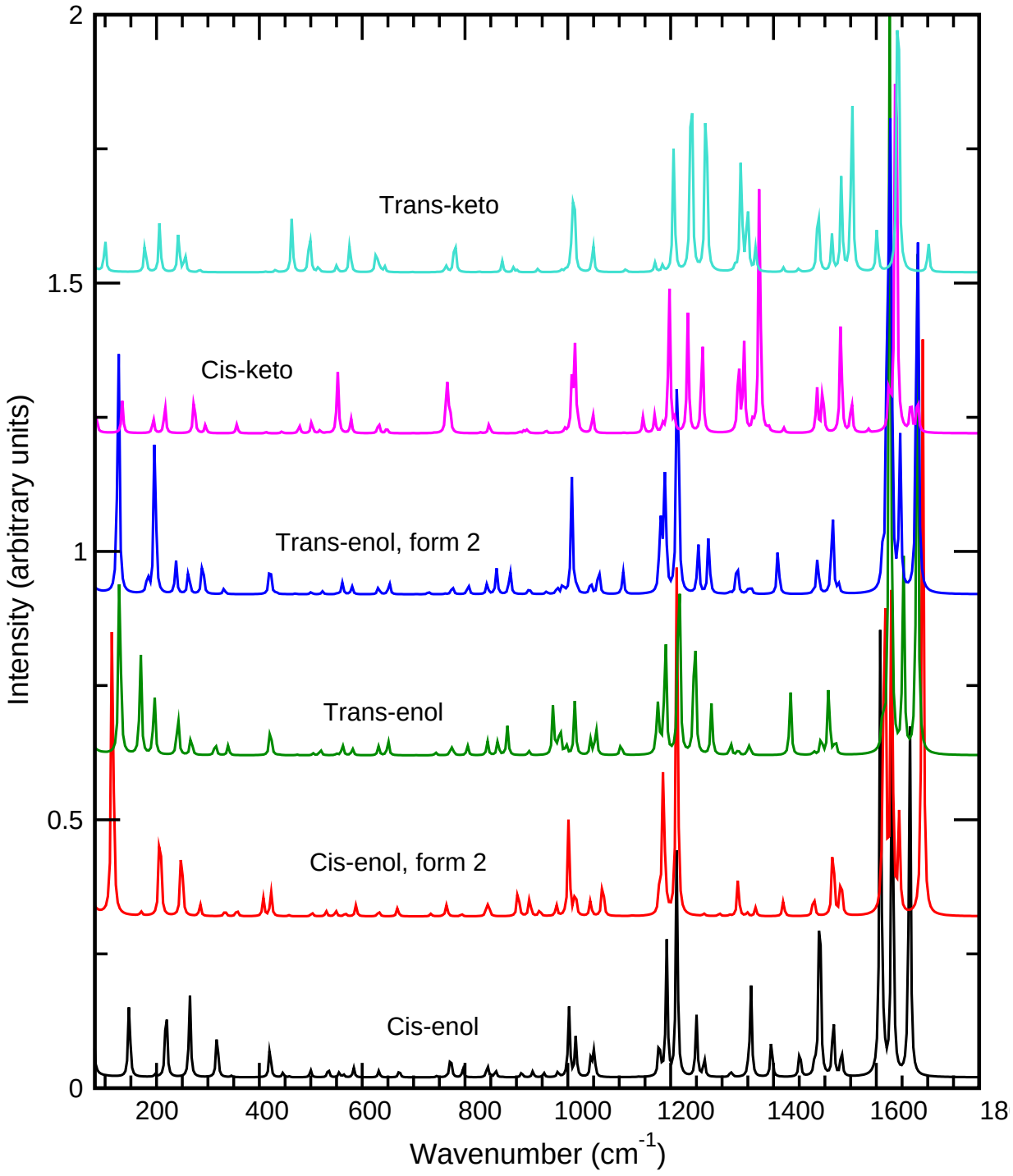
6 Trans-keto salicylideneaniline isomer



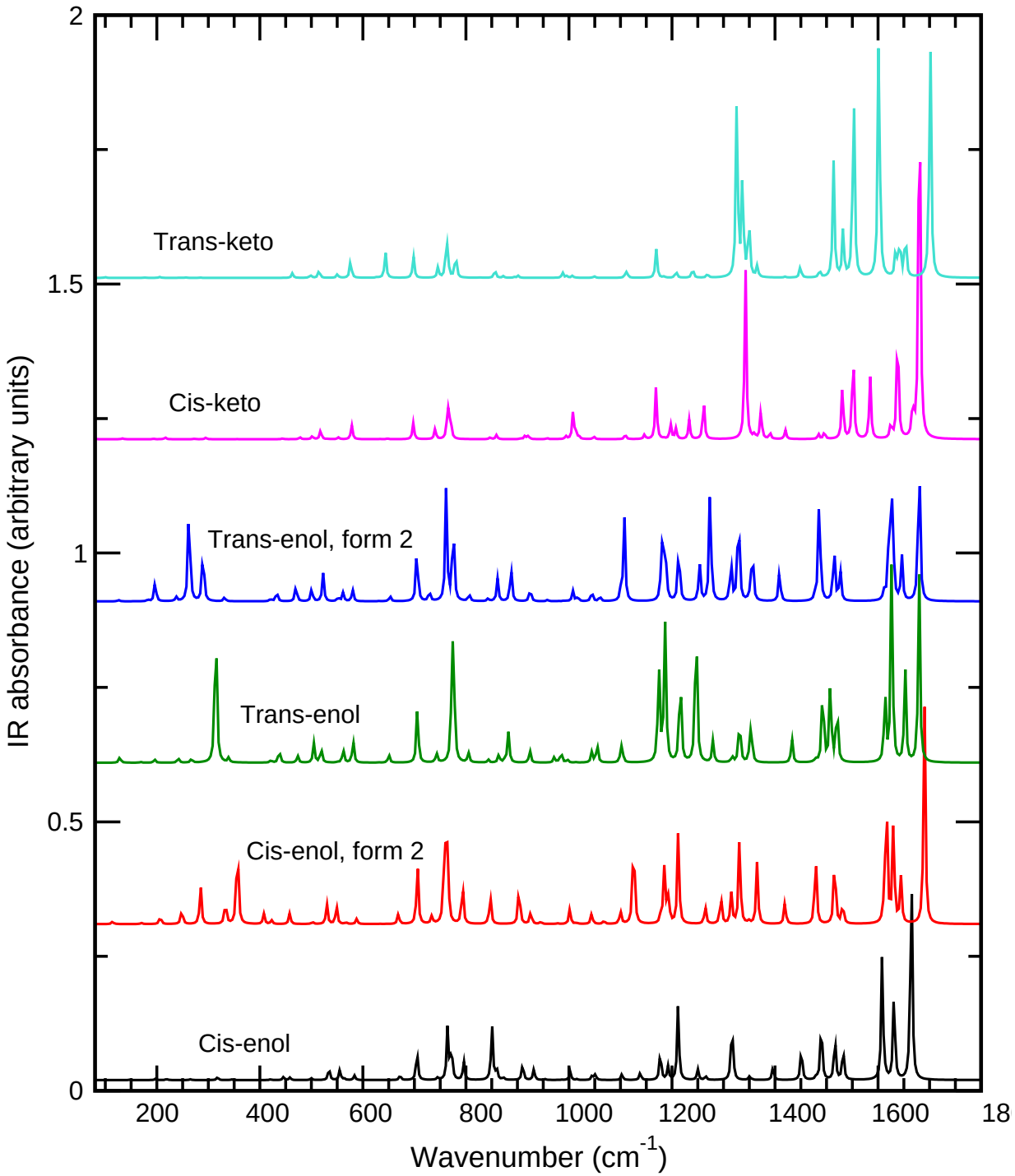
Atom	x/Å	y/Å	z/Å	q/$\lvert e^{-}\rvert$
C1	3.544119	−1.658599	0.100405	−0.118
C2	2.208262	−1.406619	0.082850	−0.074
C3	1.703973	−0.064386	−0.000895	−0.138
C4	2.651585	1.083549	−0.067607	0.448
C5	4.068502	0.724941	−0.042143	−0.241
C6	4.478497	−0.567201	0.035422	−0.070
H7	3.914145	−2.674598	0.165703	0.104
H8	1.517108	−2.243954	0.139083	0.102
O9	2.272154	2.257820	−0.140092	−0.449
H10	4.773946	1.546265	−0.089640	0.157
H11	5.540220	−0.793885	0.051119	0.107
C12	0.366162	0.265131	−0.024889	0.194
H13	0.135282	1.322284	−0.081429	0.129
C14	−3.888828	1.292675	0.146685	−0.065
C15	−2.518859	1.047010	0.153812	−0.241
C16	−2.050204	−0.263817	0.008443	0.454
C17	−2.968496	−1.312357	−0.130133	−0.245
C18	−4.334499	−1.054155	−0.129475	−0.062
C19	−4.804400	0.251081	0.006009	−0.111
H20	−4.240042	2.311898	0.259508	0.107
H21	−1.832237	1.873410	0.281156	0.128
H22	−2.609448	−2.330579	−0.244157	0.119
H23	−5.031513	−1.877021	−0.238322	0.103
H24	−5.868523	0.453592	0.004973	0.102
N25	−0.677050	−0.585477	0.004474	−0.711
H26	−0.471703	−1.575150	0.010523	0.271

7 Raman spectra of SA isomers

The Raman spectra were computed for the exciting radiation wavelength of 632 nm and for temperature T=300 K.

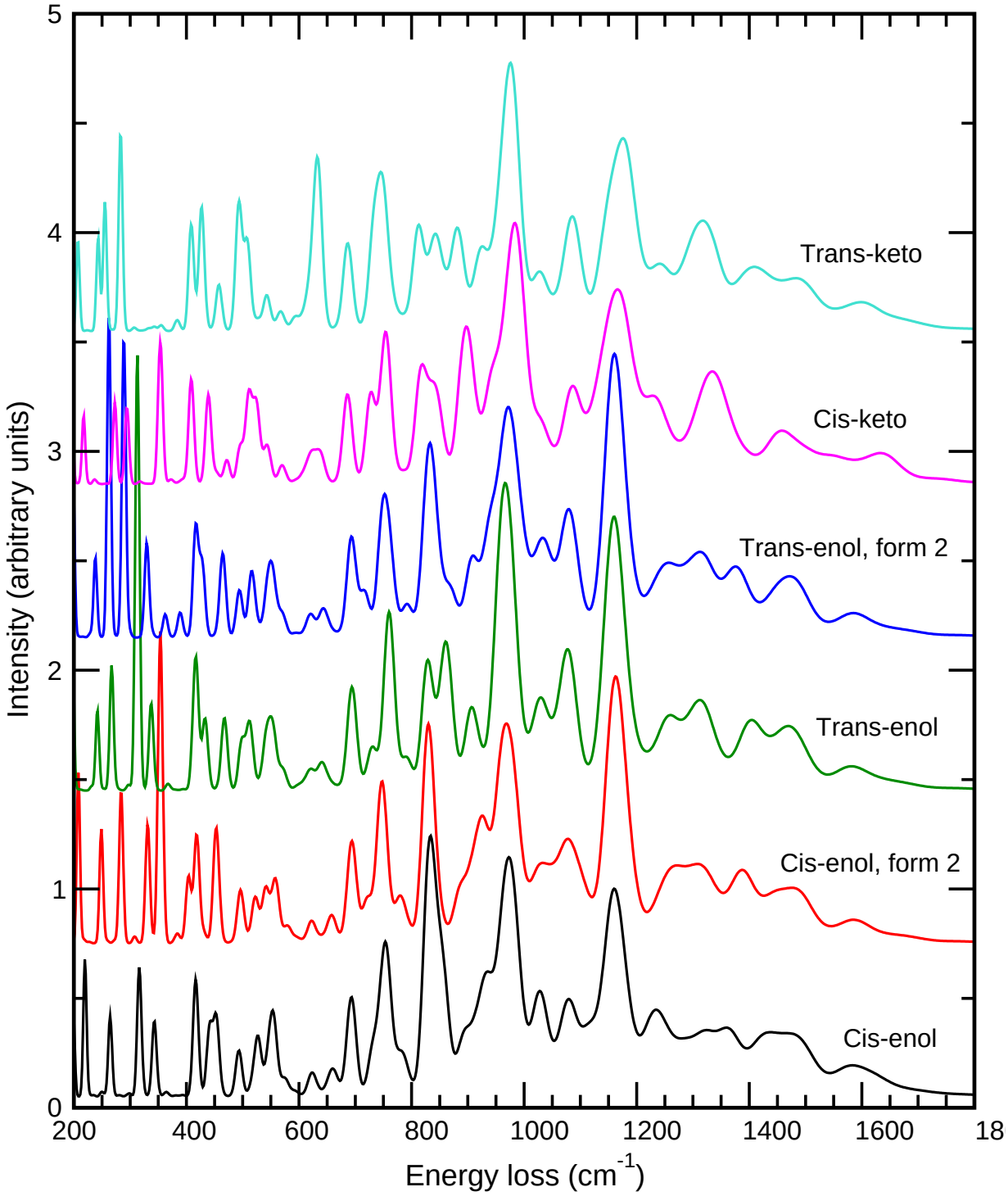


8 Infrared spectra of SA isomers



9 Inelastic neutron scattering spectra of SA isomers

The spectra were obtained by convolution of the scattering intensities with the resolution function of LAGRANGE spectrometer, ILL Grenoble, France.



References

[1] T. Verstraelen, P. Bultinck, V. Van Speybroeck, P. W. Ayers, D. Van Neck and M. Waroquier, *J. Chem. Theory Comput.*, 2011, **7**, 1750-1764.