Journal: The Journal of Physical Chemistry

Supporting Information

Theoretical studies of the ground and excited state structures of stilbene

Rajat K Chaudhuri*

Indian Institute of Astrophysics, Bangalore 560034,India

Karl F. Freed†

The James Franck Institute and Department of Chemistry, University of Chicago, Chicago, Il 60637, U.S.A.

Sudip Chattopadhyay‡

Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711103, India

Uttam Sinha Mahapatra§

Department of Physics, Maulana Azad College, 8 Rafi Ahmed Kidwai Road, Kolkata 700013, India

* e-mail: rkchaudh@iiap.res.in

† e-mail: freed@uchicago.edu

‡ e-mail: sudip_chattopadhyay@rediffmail.com

§ e-mail: uttam.mahapatra@linuxmail.org

TABLE I: S1:Normal mode frequencies (in cm^{-1}) for the ground state of planar *trans*-stilbene. Frequencies from (10/12) CASSCF[1,2] and B3LYP calculations[2] with an ANO basis are presented in parentheses.

I

Mode[a]	CASSCF	IVO-CASCI	B3LYP[3]	Expt.[4]	Mode.	CASSCF	IVO-CASCI	B3LYP[3]	Expt.[4]
A_u Sym.									
1	15i(10i)	18	28 (2)		8	1136 (1158)	1182	1073 (1113)	1071
2	61 (60)	68	59 (59)		9	1261 (1206)	1252	1155 (1217)	1155
3	303 (299)	306	292 (288)	268	10	1314 (1271)	1276	1176 (1266)	1182
4	439 (433)	444	408 (413)	410	11	1321 (1313)	1323	1223 (1266)	1220
5	566 (559)	574	546 (544)	520	12	1329 (1329)	1379	1260 (1306)	1264
6	745 (735)	750	681 (706)	692	13	1406 (1414)	1462	1329 (1373)	1300
7	819 (807)	831	761 (784)	764	14	1462 (1466)	1476	1344 (1388)	1332
8	894 (883)	852	819 (850)	847	15	1563 (1577)	1602	1442 (1503)	1450
9	973 (957)	911	885 (919)	909	16	1628 (1636)	1663	1486 (1551)	1494
10	1011 (1009)	993	941 (1014)	966	17	1715 (1730)	1738	1558 (1636)	1577
11	1034 (1022)	1057	953 (987)	971	18	1729 (1752)	1767	1585 (1664)	1597
12	1092 (1082)	1075	970 (962)	984					
B_g Sym.					A_g Sym.				
1	21 (48)	60	130 (70)		1	215	202	199 (206)	198
2	222 (223)	229	260 (223)	227	2	300	291	280 (288)	336
3	440 (434)	444	419 (414)	412	3	668	671	614 (633)	616
4	503 (495)	509	472 (478)	466	4	691	694	635 (655)	640
5	735 (724)	739	681 (701)	686	5	919	932	856 (886)	866
6	779 (774)	782	729‘ (754)	734	6	1054	1018	980 (1015)	998
7	844 (836)	909	821 (848)	838	7	1085	1141	1017 (1058)	1026
8	896 (885)	990	865 (880)	854	8	1131	1185	1075 (1116)	1093
9	976 (959)	1011	931 (930)	912	9	1195	1252	1156 (1194)	1156
10	1035 (1022)	1056	942 (963)	969	10	1261	1277	1175 (1219)	1184
11	1092 (1083)	1076	962 (993)	985	11	1283	1312	1179 (1223)	1193
B_u Sym.					12	1333	1419	1302 (1346)	1289
					13	1422	1449	1326 (1368)	1326
1	86 (86)	84	79 (82)		14	1451	1469	1330‘(1382)	1338
2	496 (494)	499	462 (474)	419	15	1555	1593	1433 (1494)	1445
3	580 (578)	583	535 (552)	541	16	1625	1652	1478 (1543)	1491
4	671 (668)	675	617 (637)	620	17	1700	1731	1553 (1631)	1573
5	868 (869)	879	808 (837)	824	18	1725	1761	1574 (1655)	1593
6	1057 (1064)	1084	981 (1015)	1001	19	1790	1801	1623 (1706)	1639
7	1084 (1105)	1137	1019 (1061)	1028					

[a]C-H stretches are not shown here

TABLE II: S2:Normal mode frequencies (in cm^{-1}) for the ground state of non-planar (C_2) *trans*-stilbene. C-H stretches are omitted.

Mode	CASSCF	IVO-CASCI	SQM[a]	Expt.[b]	Mode.	CASSCF	IVO-CASCI	SQM	Expt.
A Sym.					B Sym.				
1	26	26	25		1	63	63	57	
2	63	62	55		2	120	121	114	
3	197	126	173	198	3	234	235	212	227
4	282	254	257	268	4	444	444	405	412
5	360	353	341	336	5	472	473	425	419
6	444	444	405	410	6	536	536	502	466
7	577	577	525	528	7	581	581	537	541
8	673	667	623	619	8	676	676	625	620
9	694	699	645	640	9	743	746	693	686
10	749	742	693	692	10	796	797	739	734
11	819	751	766	764	11	879	876	812	824
12	907	826	831	847	12	908	909	830	838
13	931	909	865	847	13	955	956	855	854
14	992	979	922	909	14	1011	1010	927	912
15	1034	1002	956	966	15	1034	1017	970	969
16	1060	1034	970	971	16	1058	1034	991	985
17	1073	1077	992	984	17	1076	1080	994	1001
18	1094	1109	994	998	18	1095	1087	1028	1028
19	1115	1115	1027	1026	19	1144	1137	1080	1071
20	1144	1165	1083	1093	20	1204	1200	1173	1155
21	1214	1254	1173	1156	21	1283	1280	1192	1182
22	1284	1286	1189	1193	22	1308	1311	1224	1220
23	1302	1314	1193	1184	23	1345	1346	1262	1264
24	1332	1343	1299	1289	24	1427	1425	1320	1300
25	1464	1463	1319	1326	25	1491	1492	1347	1332
26	1484	1487	1342	1338	26	1597	1599	1455	1450
27	1590	1592	1450	1445	27	1661	1661	1500	1494
28	1655	1651	1494	1491	28	1736	1721	1592	1577
29	1727	1715	1588	1573	29	1743	1746	1619	1597
30	1743	1744	1616	1593					
31	1876	1878	1651	1639					

[a]From Scaled Quantum Mechanical (SQM) force field calculations[4].

[b]Ref.[5,6]

TABLE III: S3:Vibrational frequencies (cm^{-1}) for the ground state of *cis*-stilbene. C-H stretches are not indicated.

Mode	CASSCF	IVO-CASCI	B3LYP[3]	Ref.[4]	Expt.[4]		Mode	CASSCF	IVO-CASCI	B3LYP[3]	Ref.[4]
					IR	Raman					
A Sym.							B Sym.				
1	37	53	28	36			1	32	33	23	23
2	72	74	73	65			2	162	163	153	149
3	162	158	156	149		166	3	283	282	240	259
4	269	219	257	248		261	4	444	442	398	403
5	442	430	392	407		403	5	477	478	443	440
6	449	448	402	420			6	539	539	498	500
7	559	550	512	521	519	519	7	672	668	615	623
8	589	589	554	557	561	561	8	721	718	673	676
9	673	667	616	625	619	619	9	756	748	686	695
10	752	748	683	695	698	699	10	766	756	721	724
11	804	786	740	751	752	752	11	825	817	773	774
12	826	816	757	776	771	769	12	915	900	824	834
13	916	833	827	835	844	846	13	930	922	847	861
14	983	901	896	919		912	14	1001	992	904	936
15	990	968	944	972	966	965	15	1039	1026	943	972
16	1039	977	952	984			16	1068	1032	959	992
17	1062	1026	961	992		992	17	1088	1066	982	995
18	1088	1038	982	998	1001	1001	18	1089	1076	1018	1022
19	1089	1065	1017	1026	1029	1029	19	1173	1133	1075	1082
20	1168	1124	1070	1078	1074		20	1243	1224	1155	1172
21	1234	1221	1136	1143	1156	1149	21	1288	1256	1174	1190
22	1245	1241	1156	1173	1180	1182	22	1298	1293	1193	1203
23	1288	1251	1176	1191		1193	23	1365	1346	1300	1295
24	1326	1313	1241	1244	1203	1234	24	1466	1438	1325	1336
25	1402	1377	1324	1312		1205	25	1559	1526	1405	1402
26	1469	1445	1329	1339	1336	1339	26	1598	1562	1440	1452
27	1581	1533	1432	1448	1444	1443	27	1627	1631	1482	1498
28	1624	1618	1478	1494	1490	1490	28	1712	1708	1556	1591
29	1709	1690	1553	1588	1576	1573	29	1764	1727	1583	1617
30	1752	1725	1578	1615	1600	1599					
31	1789	1777	1609	1656		1629					

[a]Quantum mechanical force field (QMFF) calculations with 3-21G basis.

TABLE IV: S4:Vibrational frequencies (cm^{-1}) for the ground state of ^1A from 4a,4b-dihydrophenanthrene IVO-CASCI calculations. [C-H stretches are omitted.]

Mode.	CASSCF	IVO-CASCI[a]		HF		Mode	CASSCF	IVO-CASCI		HF	
	B1	B1	B2	B2	B3[7]		B1	B1	B2	B2	B3[7]
A Sym.						B Sym.					
1	58	57	48	59	32	1	88	87	86	90	70
2	198	197	169	210	170	2	199	198	199	203	169
3	235	235	240	234	201	3	398	398	395	406	326
4	396	394	393	410	324	4	402	400	402	418	332
5	409	402	415	412	350	5	477	477	475	491	409
6	487	485	480	497	430	6	517	516	515	528	447
7	540	549	543	575	460	7	617	617	615	624	519
8	581	580	583	598	488	8	673	674	669	716	563
9	671	672	662	682	571	9	703	704	698	739	587
10	700	701	714	777	598	10	744	744	741	784	638
11	779	782	767	849	659	11	788	788	781	866	664
12	855	858	853	877	730	12	878	879	873	892	734
13	956	956	944	1010	774	13	955	955	944	966	762
14	970	968	958	1022	802	14	965	965	953	1019	810
15	995	997	985	1032	813	15	976	977	963	1038	813
16	1026	1026	1022	1081	833	16	1015	1014	1009	1093	853
17	1040	1040	1026	1095	928	17	1038	1038	‘1030	1098	927
18	1088	1088	1080	1102	948	18	1167	1168	1157	1170	996
19	1174	1175	1163	1151	1003	19	1259	1259	1240	1253	1041
20	1200	1201	1196	1201	1043	20	1289	1289	1266	1275	1045
21	1253	1252	1236	1250	1049	21	1308	1307	1283	1291	1064
22	1316	1316	1296	1303	1089	22	1359	1359	1339	1340	1123
23	1328	1328	1307	1314	1128	23	1427	1427	1401	1402	1158
24	1420	1420	1395	1399	1156	24	1501	1501	1486	1491	1244
25	1484	1484	1458	1457	1183	25	1525	1525	1498	1504	1264
26	1524	1524	1499	1498	1255	26	1574	1574	1547	1556	1317
27	1536	1536	1521	1530	1279	27	1693	1693	1687	1789	1399
28	1587	1587	1561	1567	1312	28	1770	1770	1758	1834	1492
29	1641	1639	1637	1773	1327	29	1848	1847	1837	1880	1519
30	1701	1700	1696	1797	1432						
31	1780	1779	1769	1865	1515						

[a]B1: 6-31G*. B2: cc-pVDZ. B3:4-21G. The experimental frequencies (Raman) for the symmetric modes (A symmetry) are 769, 1035, 1080, 1147, 1201, 1298, 1474, 1534, and 1555 cm^{-1}

TABLE V: S5: Vibrational frequencies (cm^{-1}) for the first excited ^1B_u and ^3A_g states of *trans*-stilbene. [C-H stretches are omitted.]

				^1B_u				^3A_g			
Mode	IVO-CASCI	CASSCF[1]	Expt.[a]	Mode	IVO-CASCI	CASSCF[1]	Expt.[a]	Mode	IVO-CASCI	Mode	IVO-CASCI
A_u Sym.									A_u Sym.		
1	30	50	35	8	1089	1115		1	18	8	1126
2	55	54	47.5	9	1100	1132		2	54	9	1186
3	206	248	276	10	1332	1252		3	180	10	1274
4	357	370	358	11	1348	1328		4	382	11	1310
5	507	517	418	12	1492	1400		5	425	12	1381
6	636	651		13	1506	1462		6	614	13	1476
7	744	707		14	1565	1515		7	674	14	1481
8	748	773		15	1587	1540		8	778	15	1526
9	834	833		16	1607	1574		9	785	16	1582
10	918	889		17	1773	1690		10	859	17	1640
11	978	925		18	1944	2490		11	941	18	2047
12	1020	1043						12	1086		
B_g Sym.					A_g Sym.				B_g Sym.		A_g Sym.
1	115	129		1	223	209	198	1	56	1	197
2	328	301	248	2	309	284	280	2	237	2	287
3	408	385	331	3	642	625	591	3	426	3	632
4	496	485	410	4	672	650	622	4	446	4	654
5	622	643		5	900	906	849	5	622	5	870
6	734	704		6	1057	1020	995	6	695	6	970
7	750	758		7	1072	1055	973	7	783	7	1053
8	835	813		8	1099	1114	1070	8	868	8	1135
9	917			9	1250	1231		9	946	9	1211
10	978			10	1295	1239		10	994	10	1273
11	1038			11	1305	1267	1170	11	1101	11	1305
B_u Sym.				12	1394	1290	1332		B_u Sym.	12	1402
1	87	87		13	1513	1426	1430	1	83	13	1422
2	501	502		14	1528	1515	1464	2	492	14	1494
3	568	536		15	1567	1536	1249	3	557	15	1522
4	595	620		16	1612	1575		4	633	16	1592
5	890	892		17	1674	1611	1554	5	737	17	1620
6	957	986		18	1677	1631	1530	6	955	18	1750
7	1075	1038		19	1762	1675	1548	7	1077	19	1817

[a]Ref.[5,8–11]

TABLE VI: S6:Vibrational frequencies (cm^{-1}) for the first excited states of *cis*-stilbene and 4a,4b-dihydrophenanthrene from IVO-CASCI calculations. Frequencies from on consistent force field calculations[12] are shown in the parentheses.

	cis-stilbene ^{1}B			4a,4b-di-hydro-phenanthrene ^{3}B			
Mode	IVO- CASCI	Mode	IVO-CASCI	Mode	IVO-CASCI	Mode	IVO-CASCI
A Sym.		B Sym.		A Sym.		B Sym.	
1	39 (52)	1	32 (76)	1	94	1	65
2	83 (88)	2	162 (175)	2	160	2	227
3	172 (228)	3	252 (305)	3	237	3	358
4	285 (300)	4	376 (403)	4	374	4	408
5	385 (390)	5	448 (461)	5	415	5	481
6	399 (427)	6	541 (548)	6	503	6	507
7	536 (504)	7	645 (619)	7	540	7	615
8	576 (587)	8	656 (661)	8	584	8	625
9	653 (635)	9	713 (724)	9	668	9	678
10	677 (670)	10	788 (743)	10	685	10	745
11	743 (738)	11	802 (819)	11	754	11	757
12	791 (817)	12	859 (835)	12	824	12	848
13	810 (825)	13	896 (904)	13	914	13	871
14	882 (911)	14	924 (930)	14	962	14	931
15	929 (930)	15	954 (1007)	15	993	15	968
16	961 (1006)	16	965 (1022)	16	1044	16	1024
17	1049 (1016)	17	1081 (1029)	17	1072	17	1055
18	1082 (1038)	18	1128 (1046)	18	1111	18	1117
19	1113 (1042)	19	1208 (1098)	19	1141	19	1141
20	1158 (1088)	20	1300 (1155)	20	1165	20	1264
21	1242 (1148)	21	1303 (1174)	21	1240	21	1300
22	1299 (1158)	22	1467 (1277)	22	1291	22	1332
23	1305 (1176)	23	1558 (1382)	23	1332	23	1359
24	1417 (1281)	24	1590 (1441)	24	1382	24	1441
25	1504 (1376)	25	1612 (1483)	25	1425	25	1534
26	1567 (1431)	26	1640 (1540)	26	1474	26	1548
27	1613 (1501)	27	1691 (1547)	27	1513	27	1575
28	1632 (1522)	28	1725 (1573)	28	1552	28	1645
29	1691 (1550)	29	1919 (1665)	29	1640	29	1694
30	1722 (1590)			30	1686		
31	1821 (1660)			31	1832		

[1] Gagliardi, L.; Orlandi, G.; Molina, V.; Malmqvist, P-A.; Roos, B. O. Theoretical Study of the Lowest 1BU States of *trans*-Stilbene. *J. Phys. Chem. A* **2002**, *106*, 7355-7361 and references therein.

[2] Orlandi, G.; Gagliardi, L.; Melandri, S.; Caminati, W. Torsional Potential Energy Surfaces and Vibrational Levels in *trans* Stilbene. *J. Mol. Struct.*, **2002**, *612*, 383-391.

[3] Choi, C. H.; Kertesz, M. Conformational Information from Vibrational Spectra of Styrene, *trans*-Stilbene, and *cis*-Stilbene. *J. Phys. Chem. A* **1997**, *101*, 3823-3831.

[4] Arenas, J. F.; Tocón, I. L.; Otero, J. C.; Marcos, J. I. A Priori Scaled Quantum Mechanical Vibrational Spectra of trans- and cis-Stilbene. *J. Phys. Chem.* **1995**, *99*, 11392-11398.

[5] Meic, Z.; Güsten, H. Vibrational Studies of Trans-Stilbenes-I. Infrared and Raman spectra of Trans-Stilbene and Deuterated Srans-Stilbenes. *Spectrochimica Acta A*, **1978**, *34A*, 101-111 and references therein.

[6] Palmö, K. Normal Coordinate Analysis of Trans-Stilbene and Tolane. *Spectromchim Acta A*, **1988**, *44*, 341-353.

[7] Zhou, X.; Liu, R. Geometry, Force Field, and Fundamental Frequencies of 4a,4b-Dihydrophenanthrene, a Scaled Quantum-Mechanical Force Field Study. *Chem. Phys. Letts.* **1992**, *191*, 477-482.

[8] Suzuki, T.; Mikami, N.; Ito, M. Two-Color Stimulated Emission Spectroscopy of Trans-Stilbene: Large Amplitude Torsional Motion in the Ground State and Its Role in Intramolecular Vibrational Redistribution. *J. Phys. Chem.* **1986**, *90*, 6431-6440.

[9] Bree, A.; Edelson, M. An Investigation of the Low-Frequency Torsional Modes of Trans-Stilbene using Raman spectroscopy *Chem. Phys.* **1980**, *51*, 77-88.

[10] Urano, T.; Hamaguchi, H.; Tasumi, M.; Yamanouchi, K.; Tsuchiya, S.; Gustafson, T. L. Vibrational Assignments and Intensity Considerations of the Fluorescence Excitation Spectra of Jet-cooled S1 *trans*-stilbene and its three isotopic analogues. *J. Chem. Phys.* **1991**, *91*, 3884-3894.

[11] Baranovic, G.; Meic, Z.; Gusten, H.; Mink, H.; Keresztury, G. Intramolecular Vibrational Coupling in the Ground Electronic State (S0) of Trans-Stilbene. *J. Phys. Chem.* **1990**, *94*, 2833-2843.

[12] Warshel, A. Calculation of Vibronic Structure of the $\Pi \rightarrow \Pi^*$ Transition of Trans- and Cis-Stilbene. *J. Chem. Phys.* **1975**, *62*, 214-221.