Table 2: CASSCF/6-31G* 10e/10o computed skeletal bond lengths and angles of the ground state equilibrium structure of 4-*cis* γ,η-dimethyl-$C_9H_9NH_2^+$.

bond	(Å)	*angle*	(Degrees)
NC_α	1.296	$NC_\alpha C_\beta$	122.9
$C_\alpha C_\beta$	1.420	$C_\alpha C_\beta C_\gamma$	125.2
$C_\beta C_\gamma$	1.373	$C_\beta C_\gamma C_\delta$	115.8
$C_\gamma C_\delta$	1.458	$C_\gamma C_\delta C_\epsilon$	132.2
$C_\delta C_\epsilon$	1.364	$C_\delta C_\epsilon C_\zeta$	132.8
$C_\epsilon C_\zeta$	1.451	$C_\epsilon C_\zeta C_\eta$	125.7
$C_\zeta C_\eta$	1.363	$C_\zeta C_\eta C_\theta$	117.5
$C_\eta C_\theta$	1.472	$C_\eta C_\theta C_\iota$	126.1
$C_\theta C_\iota$	1.346	$C_\beta C_\gamma CH_3$	123.1
$C_\gamma CH_3$	1.508	$C_\zeta C_\eta CH_3$	125.1
$C_\eta CH_3$	1.511		

Table 3: CASSCF/6-31G* 10e/10o computed skeletal bond lengths and angles of the fully relaxed planar S_1 state structure of 4-*cis* γ-methyl-$C_9H_9NH_2^+$.

bond	(Å)	*angle*	(Degrees)
NC_α	1.339	$NC_\alpha C_\beta$	123.5
$C_\alpha C_\beta$	1.379	$C_\alpha C_\beta C_\gamma$	127.1
$C_\beta C_\gamma$	1.473	$C_\beta C_\gamma C_\delta$	116.2
$C_\gamma C_\delta$	1.364	$C_\gamma C_\delta C_\epsilon$	131.1
$C_\delta C_\epsilon$	1.484	$C_\delta C_\epsilon C_\zeta$	130.8
$C_\epsilon C_\zeta$	1.363	$C_\epsilon C_\zeta C_\eta$	120.9
$C_\zeta C_\eta$	1.436	$C_\zeta C_\eta C_\theta$	123.9
$C_\eta C_\theta$	1.402	$C_\eta C_\theta C_\iota$	122.2
$C_\theta C_\iota$	1.376	$C_\beta C_\gamma CH_3$	120.3
$C_\gamma CH_3$	1.513		

Table 4: Computed in plane vibrational frequencies and γ parameters of 4-*cis* γ,η-dimethyl-$C_9H_9NH_2^+$ and its $^{13}C_{14}$,$^{13}C_{15}-$, $C_{10}D-$ and $C_{14}D-$ isotopomers.

isotopically unsubstituted			$^{13}C_{14}$,$^{13}C_{15}-$			$C_{10}D-$			$C_{14}D-$		
ν^a	ν^b	γ	ν^a	ν^b	γ	ν^a	ν^b	γ	ν^a	ν^b	γ
1871	(1684)	0.04	1865	(1679)	0.03	1871	(1684)	0.04	1871	(1684)	0.04
1769	(1592)	0.11	1768	(1591)	0.10	1768	(1591)	0.07	1768	(1591)	0.11
1763	(1587)	0.01	1758	(1582)	0.09	1753	(1578)	—	1759	(1583)	0.06
1732	(1559)	0.26	1715	(1544)	0.08	1725	(1553)	0.21	1718	(1546)	0.16
1712	(1541)	0.03	1702	(1532)	0.09	1707	(1536)	0.13	1710	(1539)	0.07
1658	(1492)	0.03	1649	(1484)	0.04	1657	(1491)	0.05	1658	(1492)	0.04
1644	(1480)	—	1641	(1477)	0.01	1640	(1476)	—	1641	(1477)	0.01
1628	(1465)	0.01	1620	(1458)	0.03	1626	(1463)	0.02	1621	(1459)	0.05
1603	(1442)	0.07	1598	(1438)	0.05	1601	(1441)	0.06	1593	(1434)	0.04
1581	(1423)	—	1581	(1423)	—	1575	(1418)	0.01	1581	(1423)	—
1574	(1417)	0.01	1572	(1415)	0.02	1574	(1417)	0.01	1571	(1414)	0.01
1562	(1406)	—	1562	(1406)	—	1560	(1404)	—	1561	(1405)	—
1526	(1373)	0.07	1507	(1356)	0.13	1526	(1373)	0.07	1524	(1372)	0.08
1517	(1365)	0.03	1517	(1365)	—	1517	(1365)	0.03	1453	(1308)	0.13
1513	(1362)	0.01	1513	(1362)	—	1405?	(1265)	0.03	1513	(1362)	0.01
1431	(1288)	—	1431	(1288)	—	1434	(1291)	0.02	1428	(1285)	0.06
1413	(1272)	0.13	1411	(1270)	0.16	1417?	(1276)	0.09	1391	(1252)	—
1361	(1225)	0.09	1353	(1218)	0.05	1358	(1222)	0.14	1310	(1179)	0.09
1335	(1201)	0.09	1333	(1200)	0.10	1115?	(1004)	—	1334	(1201)	0.06
1293	(1163)	0.03	1283	(1155)	0.04	1292	(1163)	0.03	1216	(1094)	0.03
1186	(1067)	—	1185	(1067)	—	1200	(1080)	—	1185	(1067)	—
1177	(1059)	0.07	1176	(1058)	0.07	1172	(1055)	0.07	1174	(1057)	0.03
1149	(1034)	0.04	1138	(1024)	0.07	1156	(1040)	—	1014	(913)	0.05
1072	(965)	0.06	1067	(960)	0.06	1026?	(923)	0.09	1069	(962)	0.03
1048	(943)	0.01	1046	(941)	—	1051?	(946)	0.02	1051	(946)	0.04
894	(805)	—	894	(805)	—	867	(780)	0.01	894	(805)	—
865	(779)	—	858	(772)	—	862	(776)	—	846	(761)	—
751	(676)	—	749	(674)	0.01	747	(672)	0.01	748	(673)	0.01
606	(565)	0.06	605	(545)	0.05	603	(543)	0.06	605	(545)	0.05
537	(483)	0.24	535	(482)	0.25	536	(482)	0.24	536	(482)	0.26
482	(434)	0.14	480	(432)	0.12	478	(430)	0.15	478	(430)	0.11
445	(400)	0.03	442	(398)	0.03	442	(398)	0.02	442	(398)	0.04
347	(312)	—	345	(311)	—	346	(311)	—	346	(311)	—
328	(295)	0.05	327	(294)	0.04	327	(294)	0.05	327	(294)	0.05
243	(219)	0.08	242	(218)	0.08	242	(218)	0.07	243	(219)	0.08
189	(170)	0.60	188	(169)	0.60	189	(170)	0.60	188	(169)	0.60
89	(80)	0.02	89	(80)	0.02	89	(80)	0.03	89	(80)	0.02

[a] CASSCF/6-31G* 8e/8o//CASSCF/6-31G* 10e/10o vibrational frequencies

Table 5: Computed in plane vibrational frequencies and γ parameters of 4-*cis* γ,η-dimethyl-$C_9H_9NH_2^+$ and its $^{13}C_9-$, $^{13}C_{10},{}^{13}C_{11}-$, and $^{13}C_{13}-$ isotopomers.

isotopically unsubstituted			$^{13}C_9-$			$^{13}C_{10},{}^{13}C_{11}-$			$^{13}C_{13}-$		
ν^a	ν^b	γ	ν^a	ν^b	γ	ν^a	ν^b	γ	ν^a	ν^b	γ
1871	(1684)	0.04	1871	(1684)	0.04	1871	(1684)	0.04	1871	(1684)	0.04
1769	(1592)	0.11	1765?	(1589)	0.03	1767	(1590)	0.07	1768	(1591)	0.12
1763	(1587)	0.01	1758?	(1583)	0.03	1746	(1572)	0.02	1763	(1587)	0.02
1732	(1559)	0.26	1732	(1558)	0.25	1721	(1549)	0.20	1724	(1552)	0.27
1712	(1541)	0.03	1705	(1534)	0.07	1704	(1534)	0.08	1705	(1535)	—
1658	(1492)	0.03	1656	(1490)	0.03	1650	(1485)	0.06	1655	(1490)	0.03
1644	(1480)	—	1644	(1480)	—	1643	(1479)	—	1642	(1478)	—
1628	(1465)	0.01	1623	(1461)	—	1623	(1460)	0.01	1623	(1461)	0.01
1603	(1442)	0.07	1598	(1439)	0.08	1599	(1440)	0.07	1603	(1443)	0.07
1581	(1423)	—	1580	(1422)	—	1580	(1422)	0.01	1581	(1423)	—
1574	(1417)	0.01	1574	(1416)	0.01	1573	(1416)	0.01	1571	(1414)	0.01
1562	(1406)	—	1557	(1401)	—	1556	(1400)	—	1562	(1406)	—
1526	(1373)	0.07	1526	(1373)	0.07	1526	(1373)	0.08	1524	(1372)	0.10
1517	(1365)	0.03	1517	(1366)	0.03	1517	(1365)	0.03	1501	(1351)	—
1513	(1362)	0.01	1498	(1349)	0.02	1508	(1357)	0.01	1513	(1362)	0.01
1431	(1288)	—	1430	(1287)	—	1430	(1287)	—	1431	(1288)	—
1413	(1272)	0.13	1412	(1271)	0.13	1408	(1267)	0.13	1410	(1269)	0.13
1361	(1225)	0.09	1360	(1224)	0.11	1360	(1224)	0.09	1353	(1218)	0.07
1335	(1201)	0.09	1318	(1186)	0.08	1333	(1200)	0.08	1333	(1200)	0.12
1293	(1163)	0.03	1292	(1163)	0.02	1289	(1160)	0.04	1284	(1156)	0.02
1186	(1067)	—	1184	(1066)	—	1178	(1060)	0.02	1185	(1067)	—
1177	(1059)	0.07	1177	(1059)	0.07	1166	(1049)	0.06	1177	(1059)	0.07
1149	(1034)	0.04	1149	(1034)	0.04	1145	(1031)	0.02	1147	(1032)	0.04
1072	(965)	0.06	1070	(963)	0.06	1069	(962)	0.07	1068	(961)	0.07
1048	(943)	0.01	1043	(939)	0.02	1041	(937)	0.02	1046	(941)	—
894	(805)	—	891	(802)	—	887	(798)	—	894	(805)	—
865	(779)	—	865	(779)	—	862	(776)	—	862	(776)	—
751	(676)	—	751	(676)	—	747	(672)	—	750	(675)	—
606	(565)	0.06	604	(543)	0.06	603	(543)	0.06	604	(544)	0.05
537	(483)	0.24	536	(483)	0.24	532	(479)	0.25	536	(482)	0.25
482	(434)	0.14	482	(434)	0.14	479	(431)	0.15	482	(434)	0.14
445	(400)	0.03	445	(400)	0.03	443	(399)	0.02	445	(401)	0.03
347	(312)	—	347	(312)	—	346	(311)	—	347	(312)	—
328	(295)	0.05	328	(295)	0.05	327	(294)	0.04	328	(295)	0.05
243	(219)	0.08	242	(218)	0.08	242	(218)	0.08	243	(219)	0.08
189	(170)	0.60	189	(170)	0.60	188	(169)	0.60	188	(169)	0.60
89	(80)	0.02	89	(80)	0.02	89	(80)	0.03	89	(80)	0.02

[a] CASSCF/6-31G* 8e/8o//CASSCF/6-31G* 10e/10o vibrational frequencies

[b] scaled uniformly by 0.9

Table 6: Computed in plane vibrational frequencies and γ parameters of 4-*cis* γ,η-dimethyl-$C_9H_9NH_2^+$ and and its $C_{11}D-$, $C_{12}D-$, $C_{15}D-$ and $C_{11}D, C_{12}D-$ isotopomers.

isotopically unsubstituted			$C_{11}D-$			$C_{12}D-$			$C_{15}D-$			$C_{11}D, C_{12}D-$		
ν^a	ν^b	γ	ν^a	ν^b	γ	ν^a	ν^b	γ	ν^a	ν^b	γ	ν^a	ν^b	γ
1871	(1684)	0.04	1871	(1684)	0.04	1871	(1684)	0.04	1865	(1679)	0.03	1871	(1684)	0.04
1769	(1592)	0.11	1768	(1591)	0.08	1769	(1592)	0.11	1768	(1591)	0.11	1768	(1591)	0.09
1763	(1587)	0.01	1751	(1576)	—	1761	(1585)	—	1759	(1583)	0.07	1750	(1575)	—
1732	(1559)	0.26	1722	(1550)	0.28	1729	(1556)	0.28	1721	(1549)	0.07	1718	(1546)	0.32
1712	(1541)	0.03	1711	(1540)	0.06	1695	(1526)	0.01	1698	(1528)	0.13	1693	(1524)	—
1658	(1492)	0.03	1652	(1487)	0.09	1657	(1491)	0.04	1646	(1481)	0.12	1651	(1486)	0.08
1644	(1480)	—	1643	(1479)	0.02	1642	(1478)	—	1644	(1480)	—	1640	(1476)	0.03
1628	(1465)	0.01	1627	(1464)	—	1627	(1464)	0.01	1622	(1460)	—	1623	(1461)	—
1603	(1442)	0.07	1592	(1433)	0.01	1482	(1334)	0.10	1600	(1440)	0.15	1400	(1260)	0.06
1581	(1423)	—	1576	(1418)	—	1583	(1425)	—	1581	(1423)	—	1582	(1424)	0.01
1574	(1417)	0.01	1571	(1414)	0.01	1574	(1417)	—	1574	(1417)	0.01	1574	(1417)	—
1562	(1406)	—	1552	(1397)	—	1571	(1414)	0.03	1562	(1406)	—	1569	(1412)	0.01
1526	(1373)	0.07	1525	(1373)	0.09	1535	(1382)	0.01	1439	(1295)	—	1525	(1373)	0.05
1517	(1365)	0.03	1496	(1346)	—	1521	(1369)	0.15	1519	(1367)	—	1504	(1354)	0.01
1513	(1362)	0.01	1514	(1363)	0.02	1514	(1363)	—	1512	(1361)	0.01	1519	(1367)	0.08
1431	(1288)	—	1428	(1285)	0.02	1429	(1286)	0.02	1431	(1288)	—	1430	(1287)	0.04
1413	(1272)	0.13	1111	(1000)	0.07	1239	(1115)	—	1411	(1270)	0.17	1110	(999)	0.07
1361	(1225)	0.09	1362	(1226)	0.13	1369	(1232)	0.01	1052	(947)	0.07	1330	(1197)	0.11
1335	(1201)	0.09	1339	(1205)	0.09	1338	(1204)	0.16	1340	(1206)	0.02	1339	(1205)	0.05
1293	(1163)	0.03	1307	(1176)	0.02	1298	(1168)	0.04	1318	(1186)	0.03	1243	(1119)	0.01
1186	(1067)	—	1186	(1067)	—	1079	(971)	0.02	1187	(1068)	—	1078	(970)	—
1177	(1059)	0.07	1175	(1058)	0.10	1179	(1061)	0.04	1177	(1059)	0.07	1179	(1061)	0.04
1149	(1034)	0.04	1149	(1034)	0.03	1154	(1039)	0.06	1154	(1039)	0.09	1154	(1039)	0.06
1072	(965)	0.06	1051	(946)	0.02	1065	(959)	0.05	1071	(964)	0.04	1051	(946)	0.03
1048	(943)	0.01	1038	(934)	—	1014	(913)	—	1048	(943)	0.02	991	(892)	—
894	(805)	—	893	(804)	—	890	(801)	—	894	(805)	—	886	(797)	—
865	(779)	—	851	(766)	—	856	(770)	—	860	(774)	—	847	(762)	—
751	(676)	—	748	(673)	—	742	(668)	—	750	(675)	—	739	(665)	—
606	(565)	0.06	599	(539)	0.04	604	(544)	0.05	604	(544)	0.04	598	(538)	0.04
537	(483)	0.24	531	(478)	0.29	531	(478)	0.27	532	(479)	0.25	525	(473)	0.31
482	(434)	0.14	478	(430)	0.12	481	(433)	0.12	480	(432)	0.12	477	(429)	0.10
445	(400)	0.03	443	(399)	0.02	444	(400)	0.03	442	(398)	0.03	442	(398)	0.02
347	(312)	—	346	(311)	—	347	(312)	—	347	(312)	—	346	(311)	—
328	(295)	0.05	328	(295)	0.04	328	(295)	0.04	326	(293)	0.04	327	(294)	0.04
243	(219)	0.08	243	(219)	0.08	243	(219)	0.08	243	(219)	0.08	243	(219)	0.07
189	(170)	0.60	188	(169)	0.60	188	(169)	0.60	188	(169)	0.61	187	(168)	0.60
89	(80)	0.02	89	(80)	0.03	89	(80)	0.02	89	(80)	0.02	89	(80)	0.03

[a] CASSCF/6-31G* 8e/8o//CASSCF/6-31G* 10e/10o vibrational frequencies

[b] scaled uniformly by 0.9

Table 7: Comparison between computed (for 4-*cis* γ,η-dimethyl-$C_9H_9NH_2^+$) and observed bands in the finger-print region of the RR spectra of PSB11 and its isotopomers.

PSB11		$^{13}C_{14}$,$^{13}C_{15}-$		$C_{10}D-$		$C_{14}D-$		$^{13}C_9-$		$^{13}C_{10}$,$^{13}C_{11}-$		$^{13}C_{13}-$	
$\nu_{calc}{}^a$	$\nu_{obs}{}^b$	$\nu_{calc}{}^a$	$\nu_{obs}{}^b$	$\nu_{calc}{}^a$	$\nu_{obs}{}^b$	$\nu_{calc}{}^a$	$\nu_{obs}{}^b$	$\nu_{calc}{}^a$	$\nu_{obs}{}^b$	$\nu_{calc}{}^a$	$\nu_{obs}{}^b$	$\nu_{calc}{}^a$	$\nu_{obs}{}^b$
1272	1276	1270	1275	1291	1295	1308	1319	1271	1275	1267	1272	1269	1274
1225	1237	1218	1233	1276	1273	1285	1272	1224	1235	1224	1237	1218	1234
1201	1218	1200	1216	1222	1232	1200	1221	1186	1203	1200	1216	1200	1210
1163	1190	1154	1173	1163	1189	1179	1182	1160	1187	1160	1185	1155	1192
PSB11		$C_{11}D-$		$C_{12}D-$		$C_{15}D-$		$C_{11}D, C_{12}D-$					
$\nu_{calc}{}^a$	$\nu_{obs}{}^c$	$\nu_{calc}{}^a$	$\nu_{obs}{}^c$	$\nu_{calc}{}^a$	$\nu_{obs}{}^c$	$\nu_{calc}{}^a$	$\nu_{obs}{}^c$	$\nu_{calc}{}^a$	$\nu_{obs}{}^c$				
1272	1267	1285	1317	1334	1321	1270	1265	1287	1314				
1225	1237	1226	1237	1287				1260	1274				
1201	1215	1205	1223	1204	1218	1206		1205	1209				
1163	1190	1177	1210	1169	1202	1186	1214	1197	1209				

[a] CASSCF/6-31G* 8e/8o//CASSCF/6-31G* 10e/10o vibrational frequencies, scaled by 0.9

[b] bands observed in the RR spectrum of PSB11 in methanol solution, from ref. [9].

[c] bands observed in the RR spectrum of rhodopsin, from ref. [12].

Table 8: Computed in plane vibrational frequencies of 4-*cis* γ,η-dimethyl-$C_9H_9NH_2^+$ (PSB11 model **2**) and γ parameters employed to simulate the RR spectrum

ν^a	γ
1761	0.10
1675	0.06
1664	0.02
1628	0.05
1625	0.40
1577	0.10
1510	—
1501	0.01
1477	0.07
1451	—
1428	—
1427	0.03
1421	—
1396	0.02
1389	0.02
1340	—
1315	0.10
1274	0.06
1236	0.08
1205	0.01
1107	0.01
1075	0.03
1045	0.03
975	0.08
952	0.02
840	0.01
819	0.01
702	0.01
558	0.15
501	0.34
439	0.10
396	0.07
308	0.02
288	0.01
222	0.15
128	0.94
31i	—

[a] B3LYP/6-31G*//CASSCF/6-31G* 10e/10o vibrational frequencies