Supplementary Information

Figure S-1. IRMPD of the d_4-homodimers of 1-methylcytosine and of 1-methyl-d_3-cytosine

Figure S-2. IRMPD spectra of **1** compared with peaks predicted using Gaussian09 [a]

Table S-1. IRMPD band positions and assignments for **1** [a,b]

Figure S-3. IRMPD spectra of **2** compared with peaks predicted using Gaussian09 [a]

Table S-2. IRMPD band positions and assignments for **2** [a,b]

Figure S-4. IRMPD spectra of **3** compared with peaks predicted using Gaussian09 [a]

Table S-3. IRMPD band positions and assignments for **3** [a,b]

Figure S-5. IRMPD spectra of **6** compared with peaks predicted using Gaussian09 [a]

Table S-4. IRMPD band positions and assignments for **6** [a,b]

Figure S-6. IRMPD spectra of **4** compared with peaks predicted using Gaussian09 [a]

Table S-5. IRMPD band positions and assignments for **4** [a,b]

Figure S-7. IRMPD spectra of **5** compared with peaks predicted using Gaussian09 [a]

Table S-6. IRMPD band positions and assignments for **5** [a,b]

Figure S-8. Comparison of IRMPD spectra of heterodimers **4** and **5,** 2800-3600 cm^{-1}

Figure S-9. Solid state ^{1}H spectrum (600 MHz) of the iodide salt of **1**

Figure S-10. Solid state ^{13}C spectrum (100.6 MHz) of the iodide salt of **1** compared with theory [a]

Figure S-11. Solid state ^{15}N spectrum (40.5 MHz) of the iodide salt of **1** compared with theory [a].

Figure S-12. Single crystal IR of the iodide salt of **1** *vs* the IRMPD of gaseous **1**

Figure S-13. Powder IR of two crystal habits of the iodide salt of **1**

Figure S-14. Comparison of IR spectra of the iodide salt of **1** with its deuterium-exchanged isotopomer

[a] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[b] SBS= small basis set (B3LYP/6-31G**); LBS=large basis set (B3LYP/6-311++G**)

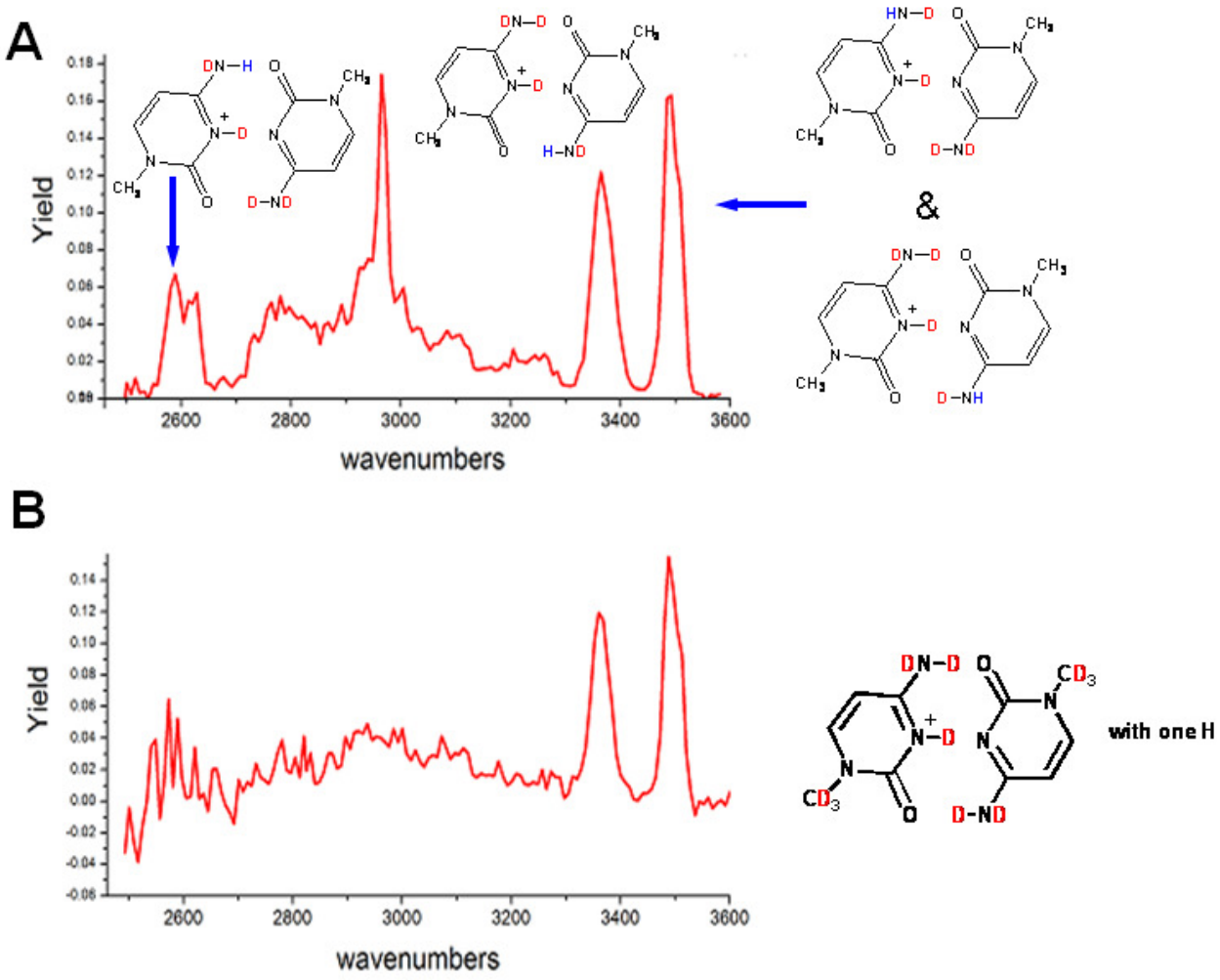

Figure S1: Comparison of the IRMPD spectrum of the d_4-homodimer of 1-methylcytosine (1-d_4, panel A) with that of the d_4-homodimer of 1-methyl-d_3-cytosine (panel B), demonstrating that the strong band near 3000 cm^{-1} comes from methyl CH stretching vibrations.

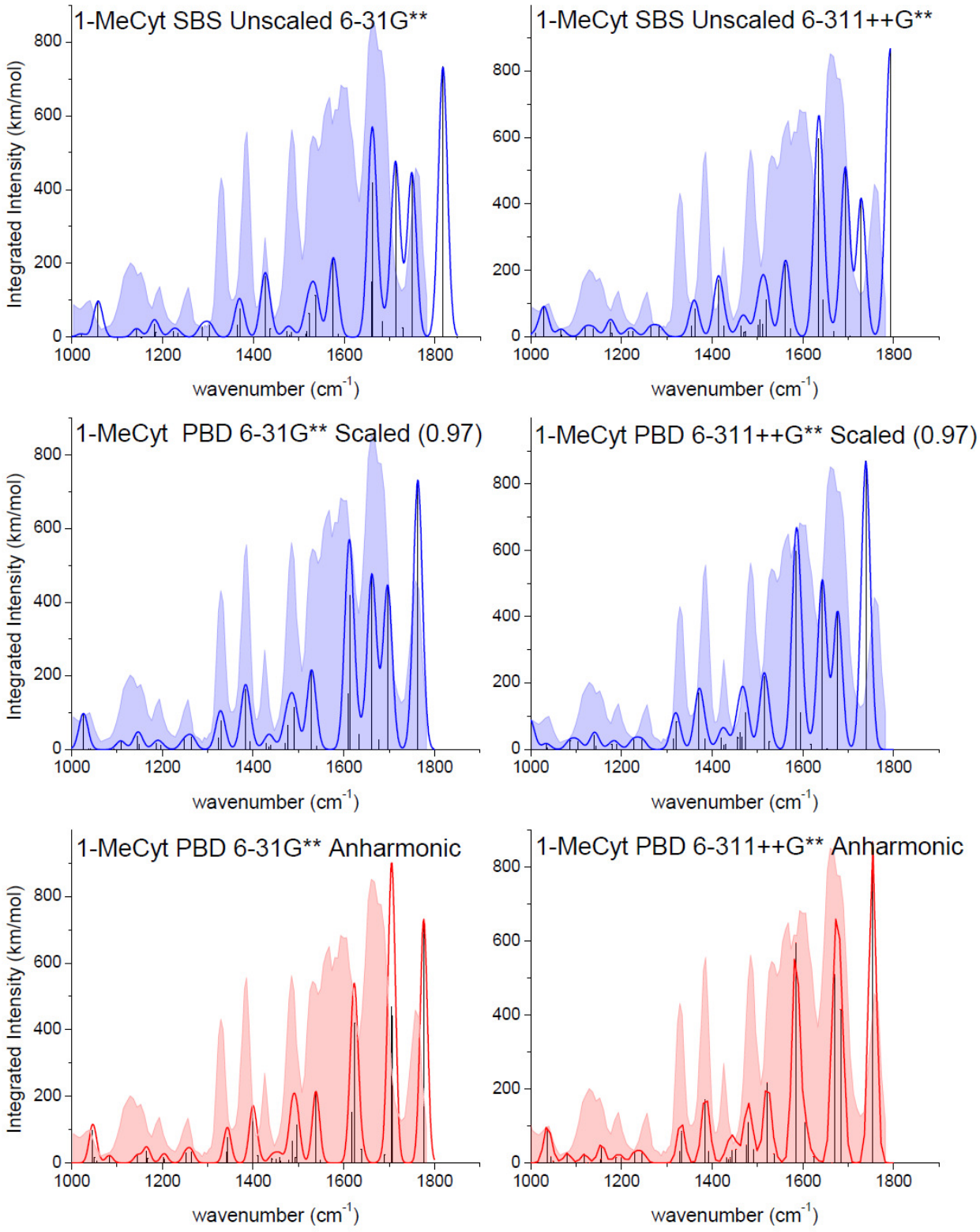

Figure S2: Comparison of scaled and unscaled harmonic and anharmonic calculated spectra of 1-methylcytosine proton-bound dimer (**1**) *vs* experimental IRMPD spectra of 1-methylcytosine proton-bound dimer (in silhouette). [19]

Exptl band	SBS Scaled Harmonic	SBS Anharmonic	LBS Scaled Harmonic	LBS Anharmonic	Assignment
1758	1763	1776	1739	1754	C=O stretch & in-plane NH bend
1682	1697	1707	1677	1683	NH in-plane bends
	1677	1690	1653	1665	C=O stretch
1661	1662	1704	1643	1671	NH in-plane bends
	1634	1639	1618	1624	C=C &C-NH_2 stretches
1606	1613 1610	1624 1618	1595 1585	1604 1584	NH in-plane bends & CO stretch
1567					
1531	1539	1548	1526	1536	C=N stretch & HCH bends
	1529	1538	1515	1521	C=C stretch & HCH bends
1485	1490 1477	1497 1486	1473 1466	1479 1491	HCH & NH in-plane bends C-NH_2 stretch
1426	1430	1459	1420	1444	methyl HCH bends
1386	1394 1383	1410 1399	1384 1371	1393 1385	CH_3 umbrella, in-plane ring CH bends
1329	1330 1324	1344 1341	1321 1314	1332 1329	ring CH in-plane bends
1257	1265 1248	1264 1251	1245 1227	1246 1229	N-CO stretches
1194	1197	1205	1189	1199	ring CH in-plane bends
	1187	1203	1179	1188	
1152	1149 1146	1168 1164	1143 1140	1155 1156	HC=CH in-plane bends
	1119	1134	1114	1129	CH_3 umbrella, HNH
1128	1118 1108	1132 1145	1113 1104	1123 1119	in-plane rocking
	1042	1055	1037	1050	
1040	1038	1050	1034	1044	N-H-N out-of-plane bend
	1026	1046	999	1036	CH_3 rocking

Table S1: Comparison of calculated bands and experimental IRMPD bands for 1-methylcytosine proton-bound homodimer (**1**). [19]

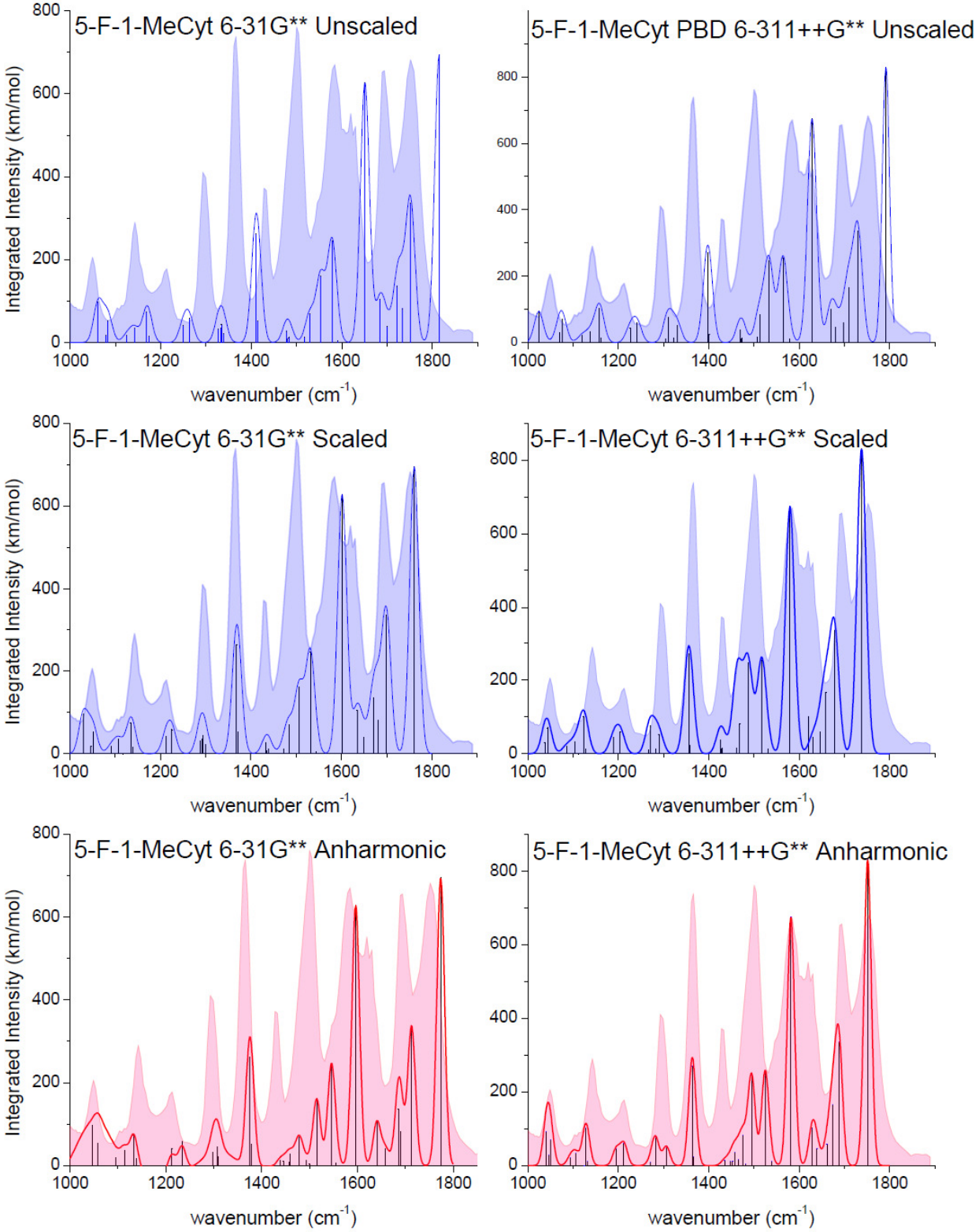

Figure S3: Comparison of scaled and unscaled harmonic and anharmonic calculated spectra of 5-fluoro-1-methylcytosine proton-bound homodimer (**2**) *vs* experimental IRMPD spectra of 1-methylcytosine proton-bound dimer (in silhouette). [19]

Exptl band	SBS Scaled Harmonic	SBS Anharmonic	LBS Scaled Harmonic	LBS Anharmonic	Assignment
1752	1761	1774	1738	1751	C=O stretch & in-plane NH bend
1694	1699 1682 1671	1713 1689 1686	1678 1659 1647	1688 1674 1661	C-NH_2 stretch and HNH i.p. bends C=C stretch, NHN ip bend
1630	1649	1659	1631	1639	C=C stretch, NHN i.p. bend, HNH i.p. bend
1620	1634	1641	1620	1629	C=C stretch, NHN i.p. bend, HNH i.p. bend
1615	1602	1597	1580	1582	C=O stretch, HNH i.p. bends, NHN i.p. bend
1585					
1550	1544 1531	1555 1546	1531 1517	1539 1525	NHN ip bend, HNH i.p. bend, non C=C ring stretches
1500	1507 1484	1515 1478	1487 1468	1495 1476	HCH, HNH, NHN bends, N-C ring stretches
1428	1439 1439	1439 1446	1429 1429	1435 1447	HCH bends
1366	1372 1368	1379 1375	1359 1356	1366 1363	non C=C ring stretches, CH_3 umbrella
1293	1299 1294 1293 1288	1309 1308 1307 1298	1290 1283 1271 1266	1306 1307 1282 1271	C=CH in-plane bends HNH in-plane bend, N-CO-N ring stretches, C-F stretch
1213	1225 1212	1234 1213	1204 1190	1212 1195	N-CO-N ring stretch, HNH i.p. bend, C-F stretch, C=CH in-plane bends
1143	1139 1134	1139 1132	1127 1123	1131 1128	HNH, NHN, C=CH bends N-CH_3 stretch
1123	1118 1117	1132 1127	1113 1112	1125 1126	HCH torsions
1108	1107 1091	1114 1096	1104 1086	1106 1094	NHN, HNH,C=CH in-plane bends CH_3 rock
1049	1051 1047 1030	1058 1058 1047	1043 1038 994	1050 1046 1041	CH_3 rock, HNH i.p. bend, N-CH ring stretches NHN, HNH o.o.p. bends

Table S2: Comparison of calculated bands and experimental IRMPD bands for 5-fluoro-1-methylcytosine proton-bound homodimer (**2**). [19]

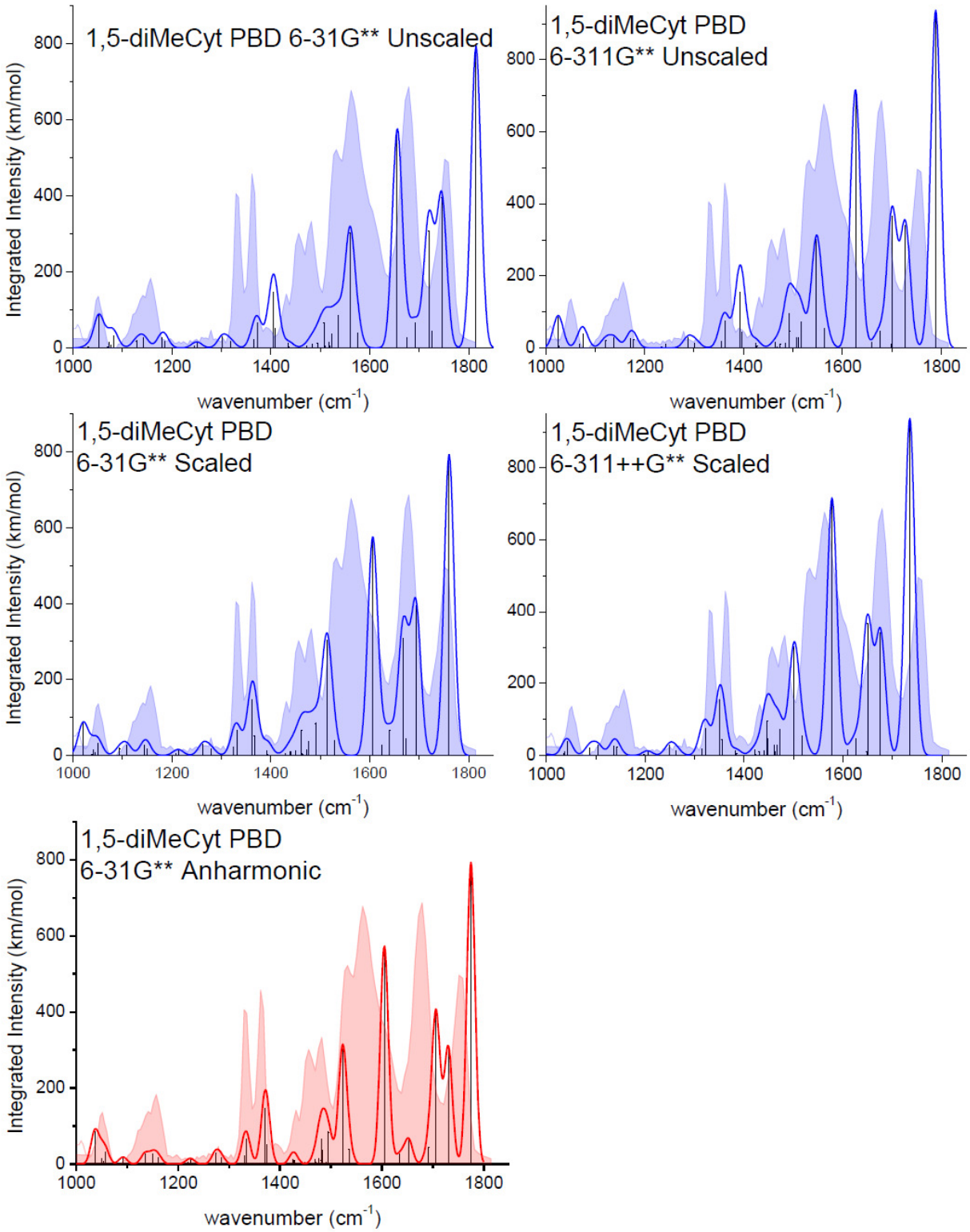

Figure S4: Comparison of scaled and unscaled harmonic and anharmonic calculated spectra of 1,5-dimethylcytosine proton-bound homodimer (**3**) *vs* experimental IRMPD spectra of 1-methylcytosine proton-bound dimer (in silhouette). [19]

Exptl band	SBS Scaled Harmonic	SBS Anharmonic	LBS Scaled Harmonic	Assignment
1752	1760	1775	1735	C=O stretch & in-plane NH bend
1679	1693	1706	1675	C-NH_2, C=O, C=C stretches
	1674	1692	1649	NH_2 scissoring & N-H
	1668	1730	1647	in-plane bends
1606	1606	1605		C=C stretch & NH scissoring
1563			1578	C=C stretch & NH scissoring
1533	1528	1535	1517	ring C-C & C-N stretch,
	1513	1523	1501	N-H and C-H rocking
1482	1491	1495	1472	C-NH_2, ring C-N stretches, &
	1477	1483	1466	NH_2 scissoring
	1473	1471	1462	HCH, HNH, NHN bends,
	1472	1476	1461	
1457	1464	1490	1448	C-NH_2 stretch
	1462	1482	1447	HCH, HNH, NHN bends,
	1450	1481	1440	methyl torsions
	1450	1468	1439	
1432	1440	1426	1430	HCH scissoring
	1439	1429	1430	
	1431	1447	1423	CH_3 umbrella motions
	1429	1449	1421	
1390	1394	1425	1385	CH_3 umbrella motions
	1392	1425	1383	
1362	1367	1374	1355	Ring C-N stretches &
	1362	1371	1351	CH_3 umbrella motions
1330	1332	1334	1322	C=C-H bends
	1325	1331	1314	C-N ring stretches
1279	1279	1284	1262	Ring N-CO & N-CN stretches
	1263	1273	1249	
1157	1150	1161	1143	C=C-H bends & N-CH_3 stretch
1142	1144	1151	1136	C=C-H bends & N-CH_3 stretch
1109	1119	1117	1113	N-CH_3 rocking
	1118	1116	1112	
	1109	1135	1104	H-N-H rocking
1051	1051	1057	1043	H-N-H rocking,
	1045	1053	1036	C-CH_3 bends
	1041	1049	1036	C-CH_3 rocking
	1038	1052	1034	
1020	1021	1037	997	C-CH_3 rocking & NH_2 stretches

Table S3: Comparison of calculated bands and experimental IRMPD bands for 1,5-dimethylcytosine proton-bound homodimer (**3**). [19]

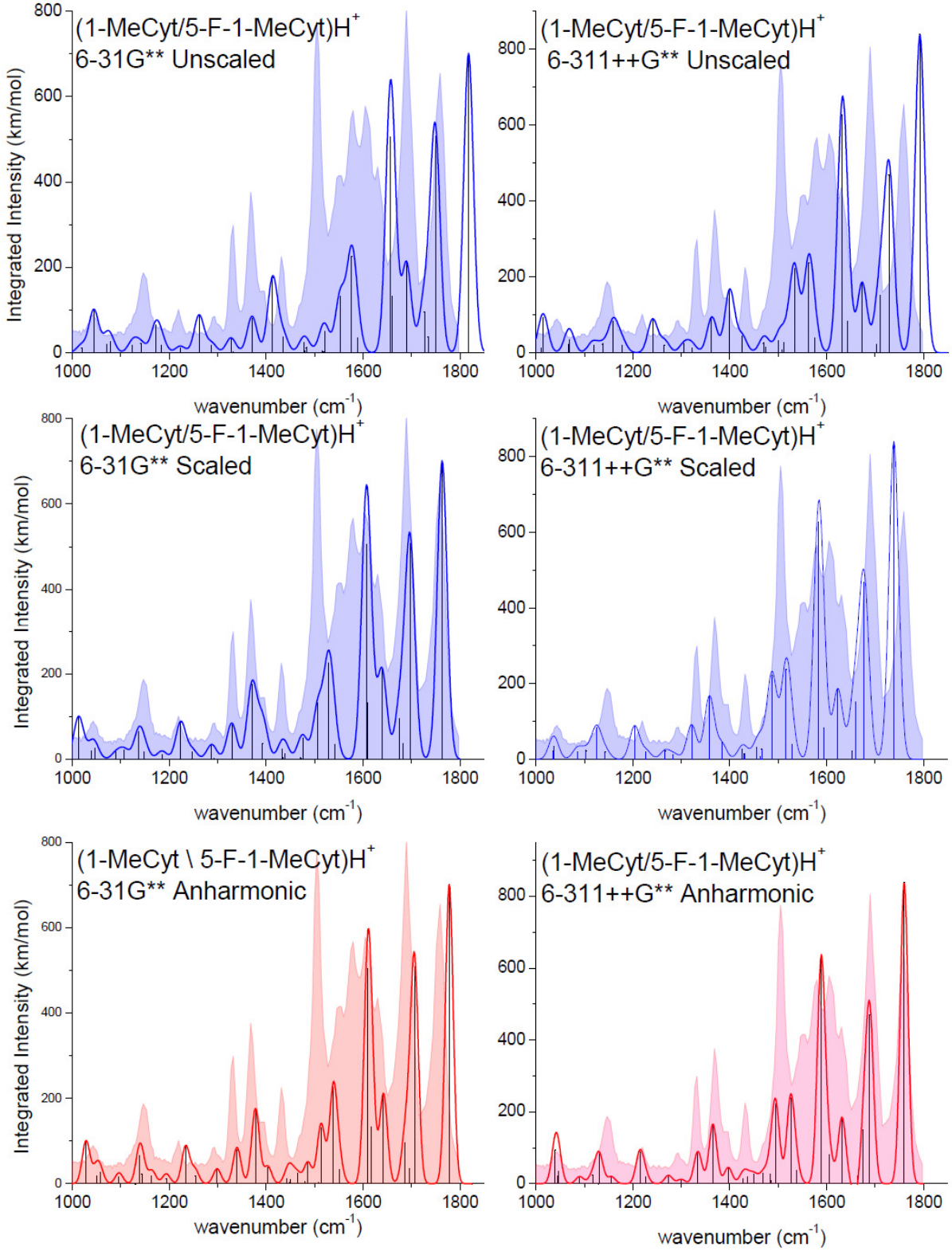

Figure S5: Comparison of scaled and unscaled harmonic and anharmonic calculated spectra of 1-methylcytosine/5-fluoro-1-methylcytosine proton-bound heterodimer (**6**) *vs* experimental IRMPD spectra of 1-methylcytosine/5-fluoro-1-methylcytosine proton-bound dimer (in silhouette). [19]

Exptl band	SBS Scaled Harmonic	SBS Anharmonic	LBS Scaled Harmonic	LBS Anharmonic	Assignment
1759	1763	1778	1739	1760	C=O stretch & in-plane NH bends
1690	1697	1707	1676	1689	C-NH_2 stretch & NH bends
1662	1682 1675	1695 1687	1660 1652	1675 1663	HNH in-plane bends, C=C & C=O stretches
1630	1639	1642	1623	1632	HNH & NH i.p. bends, CO & C=C stretches
1605	1610 1607	1618 1610	1593	1605	HNH & NH in plane bends, C=C, C=O, & C-NH_2 stretches
1580			1583	1589	HNH & NH in-plane bends, CO stretch
1551	1541	1552			NH i.p. bends, NC-CH & NH_2C-CF stretches
1523	1529	1514	1516	1526	NH i.p. bends, NC-CH & NH_2C-CF stretches
1505	1507	1508	1488	1494	NH_2C=N stretch & NH_2 scissoring
1479	1476 1473 1470	1486 1480 1464	1466 1463 1456	1483 1485 1469	NH & CH_3 in-plane bends, C-NH_2 stretches
1431	1439 1439 1435 1433	1450 1448 1443 1404	1430 1429 1426 1425	1427 1428 1437 1450	methyl CH_3 bends & umbrella motions
1392	1393	1378	1383	1397	HC=CH bends, CH_3 umbrella, CN-CH stretch
1368	1371	1340	1358	1365	FC=CH bends, CH_3 umbrella CN-CH stretch
1332	1330	1307	1321	1334	HC=CH bends, CH_3 rocking, CN-CH stretch
1294	1293	1299	1283	1300	FC=CH bends, CH_3 rocking CN-CO stretch
1277	1288	1254	1267	1273	FC=CH bends, NH_2C-N-CO stretches
1219	1248 1224	1234 1194	1227 1203	1226 1214	H_3CN-CO-N-CNH_2 stretches & NH_2 rocking N-CO-N & FC-CNH_2 stretches, NH_2 bends

Table S4: Comparison of calculated bands and experimental IRMPD bands for the 1-methylcytosine/5-fluoro-1-methylcytosine proton-bound heterodimer (**6**). [19]

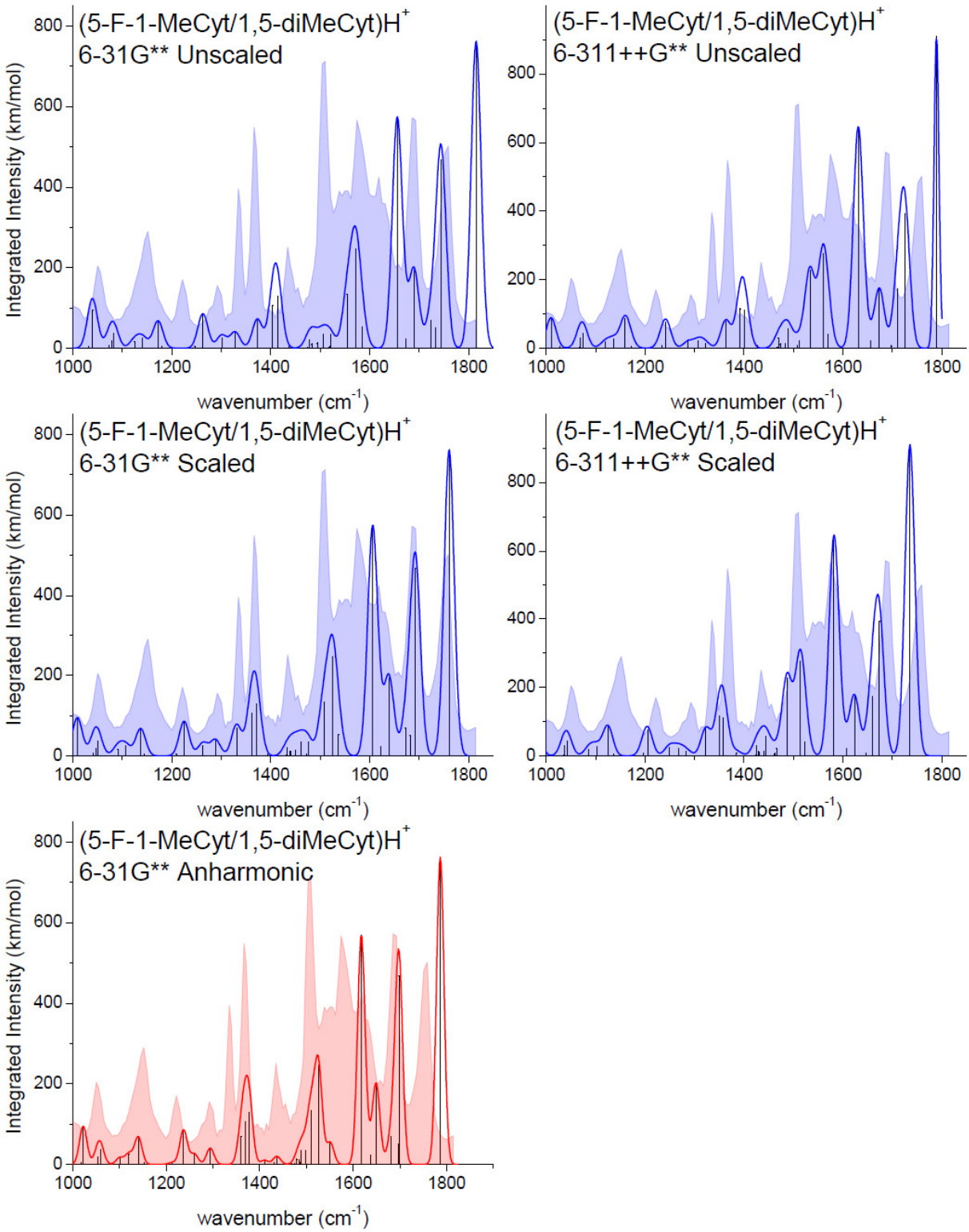

Figure S6: Comparison of scaled and unscaled harmonic and anharmonic calculated spectra of 5-fluoro-1-methylcytosine/1,5-dimethylcytosine proton-bound heterodimer (**4**) *vs* experimental IRMPD spectra of the 5-fluoro-1-methylcytosine/1,5-dimethylcytosine proton-bound dimer (in silhouette). [19]

Expt l band	SBS Scaled Harmonic	SBS Anharmonic	LBS Scaled Harmonic	Assignment
1759	1761	1787	1735	C=O stretch & in-plane NH bend
1686	1693 1682 1672	1698 1697 1681	1674 1660	C-NH_2 Stretch and HNH i.p. bends C=C stretch, NHN ip bend
1659	1639	1650	1647	C=C stretch, NHN i.p. bend, HNH i.p. bend
1619	1623 1606	1638 1618	1624 1607	C=C stretch, NHN i.p. bend, HNH i.p. bend C-NH_3 stretch
1575			1582	
1544	1537	1551		NH i.p. bends, non C=C ring stretches
1510	1525 1508	1526 1510	1523 1513	C-C-N ring stretches NH in-plane bends
1456	1461 1450	1474 1469	1466 1463	C-NH_2 stretch, NH in-plane bends & CH_3 bends
1435	1440 1439 1433 1431	1437 1430 1410	1440 1430 1429 1425	N-CH_3 bending & umbrella motions
1367	1371 1362	1378 1360	1358 1351	N-CH stretch & CH_3 umbrella CH in-plane bend
1335	1332		1323	C-H in-plane bend, C-N-C stretches
1292	1293 1288	1294 1290	1283 1267	C-H in-plane bend, C-N-C stretches
1222	1225 1209	1237 1213	1248 1205	N-C=O stretch & NH_2 rocking C-CH_3 stretch
1152	1145 1137	1153 1141	1136 1124	N-CH_3 stretch, C-H bends & NH_2 rocking
1050	1050 1046	1059 1054	1043 1037	NH_2 and CH_3 rocking

Table S5: Comparison of calculated bands and experimental IRMPD bands for 5-F-1-methylcytosine/1,5-dimethylcytosine proton-bound heterodimer (**4**). [19]

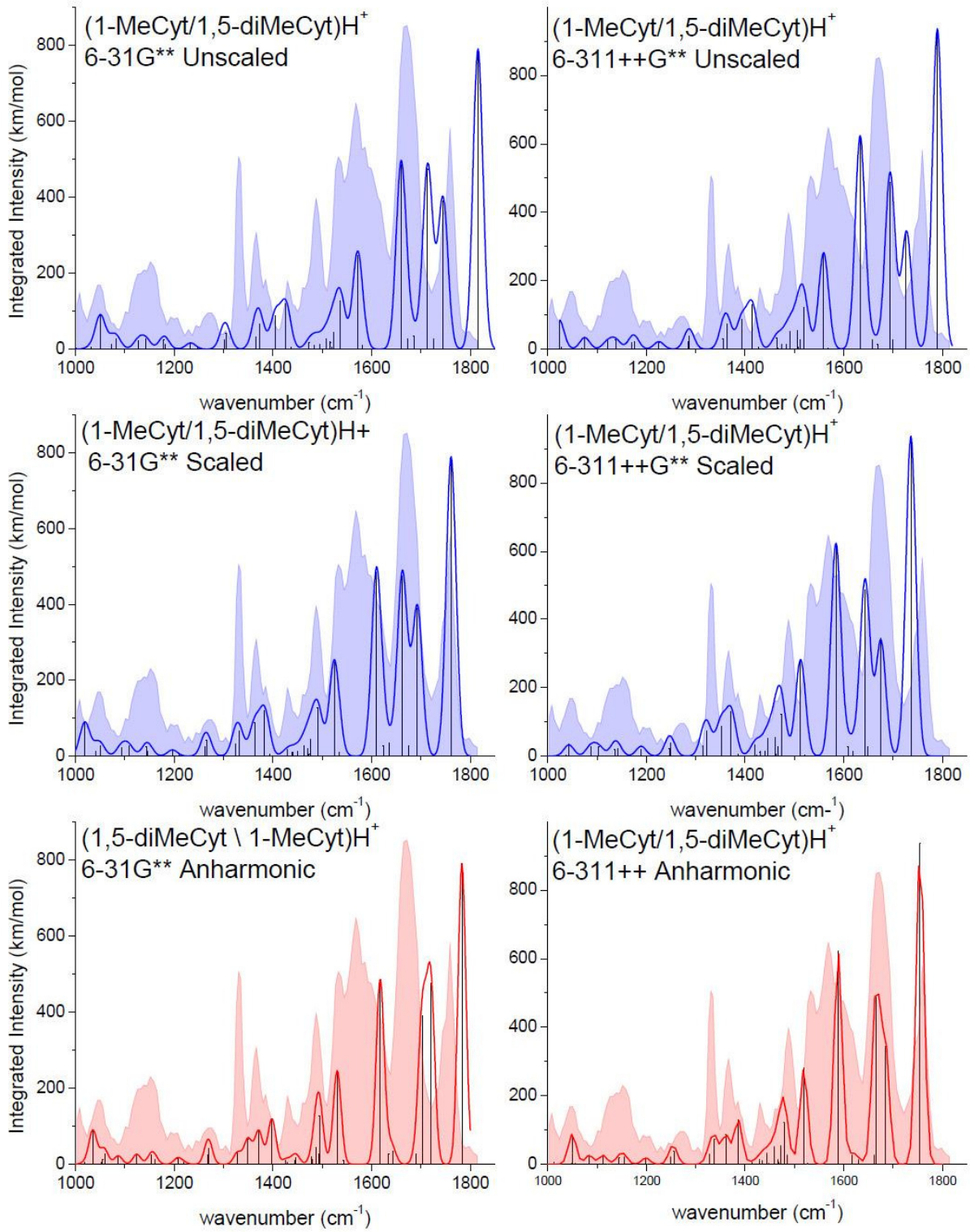

Figure S7: Comparison of scaled and unscaled harmonic and anharmonic calculated spectra of 1,5-dimethylcytosine/5-fluoro-1-methylcytosine proton-bound heterodimer (5) *vs* experimental IRMPD spectra of the 1,5-dimethyl-cytosine/5-fluoro-1-methylcytosine proton-bound dimer (in silhouette). [19]

Exptl band	SBS Scaled Harmonic	SBS Anharmonic	LBS Scaled Harmonic	LBS Anharmonic	Assignment
1752	1761	1783	1736	1755	C=O stretch coupled with N-H in plane bends
1679	1693 1675 1662	1703 1691 1720	1674 1649 1643	1684 1661 1666	NH_2 in plane bend with C-NH_2 , C=C, & C=O stretches
1638	1635	1643	1618	1629	C=C stretch with NHN, NH_2,
1625	1624	1635		1616	HC=CH, & HC-CCH_3 in plane bends
1600	1610	1617	1608		C=O & C=C stretches, N-H in plane bends
1587			1584	1589	C=O & C=C stretches, N-H in plane bends
1569					
1539	1534 1525	1543 1530	1520 1512	1526 1519	C-C stretches & NH_2 rocking NHN in-plane bend
1488	1491 1477	1494 1487	1473 1466	1479 1485	HCH bends, i.p. NH bends, N=C-NH_2 stretches
1471	1473 1471	1487 1479	1462 1461	1469 1472	Methyl CH_3 bends, N-H ip bends, HC=CHbends
1430	1440 1439	1444 1426	1430 1430	1429 1434	N-Methyl H-C-H bends
1386	1383	1398	1371	1386	N-methyl CH_3 umbrella HC=CH bends
1367	1363	1371	1352	1361	CH_3 umbrella, HC=CH bends, OCN-CH stretch
1335	1332 1324	1350 1329	1322 1314	1338 1327	H_3CC=CH & HC=CH bends (O)C-N-C ring stretches
1252	1266 1263	1270 1268	1248 1246	1256 1250	ring N-CO stretches, methyl rocking ring CH bends,
1200	1210	1219	1198	1202	ring C-H i.p. bends, N-C(O) & C-CH_3 stretches
1159	1196 1147	1207 1161	1189 1141	1199 1155	HC=CH in-plane bends, N-CH3 stretch C-CH_3 stretch, H_3CC=CH bends
1145	1144	1154	1136	1144	HC=CH in-plane bends & methyl rocking
1133	1118 1118	1134 1118	1113 1113	1127 1122	CH_3 methyl torisons
1108	1108	1124	1103	1112	CH_3 and NH2 i.p. rock
1090	1094	1087	1088	1084	CH_3 and NH2 i.p. rock
1056	1050 1041	1059 1053	1043 1037	1050 1049	N-CH_3 i.p. bends CH ring bends, & NH_2 rocking

Table S6: Comparison of calculated bands and experimental IRMPD bands for the 1,5-dimethylcytosine / 1-methylcytosine proton-bound heterodimer (**5**). [19]

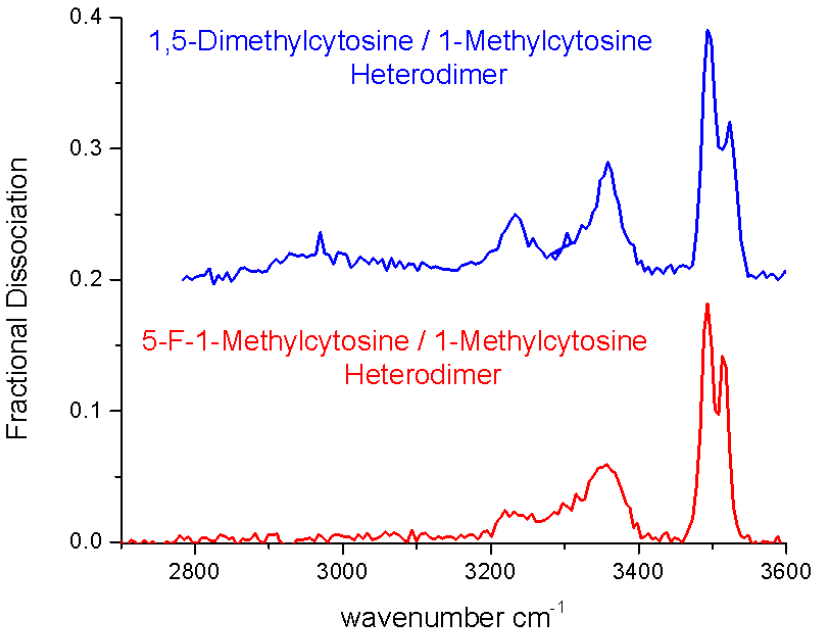

Figure S8: Comparison of the IRMPD spectra of heterodimer **4** (lower red trace) and heterodimer **5** (upper blue trace). The upper trace shows absorptions from CH stretches (small, sharp band near 2885 cm^{-1}) not observed in the lower trace, which are therefore assigned to the methyl group at the 5-position of the 1,5-dimethylcytosine partner in the dimer.

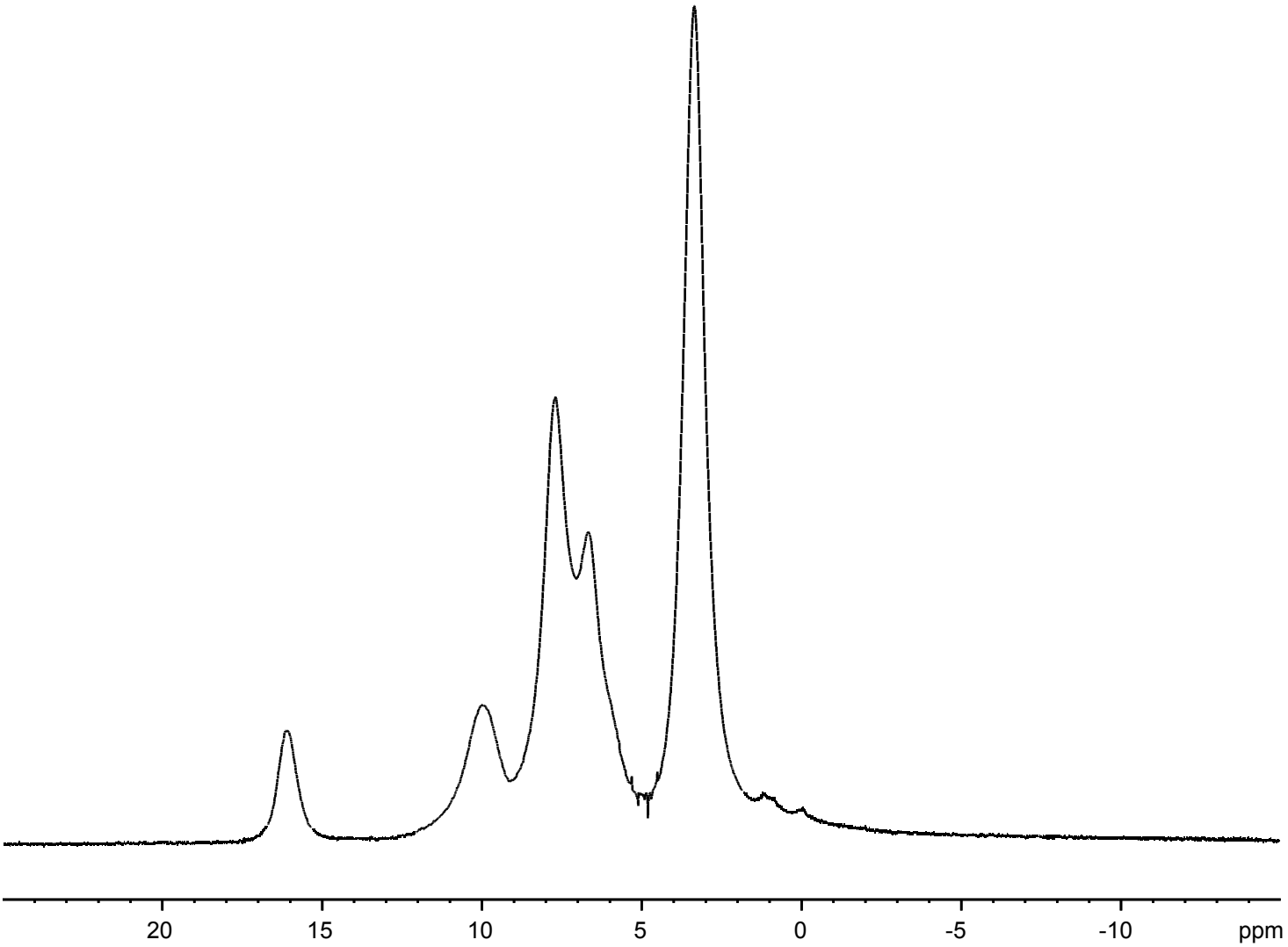

Figure S9: Experimental solid state MAS NMR ^{1}H spectrum (600 MHz) of the iodide salt of **1**

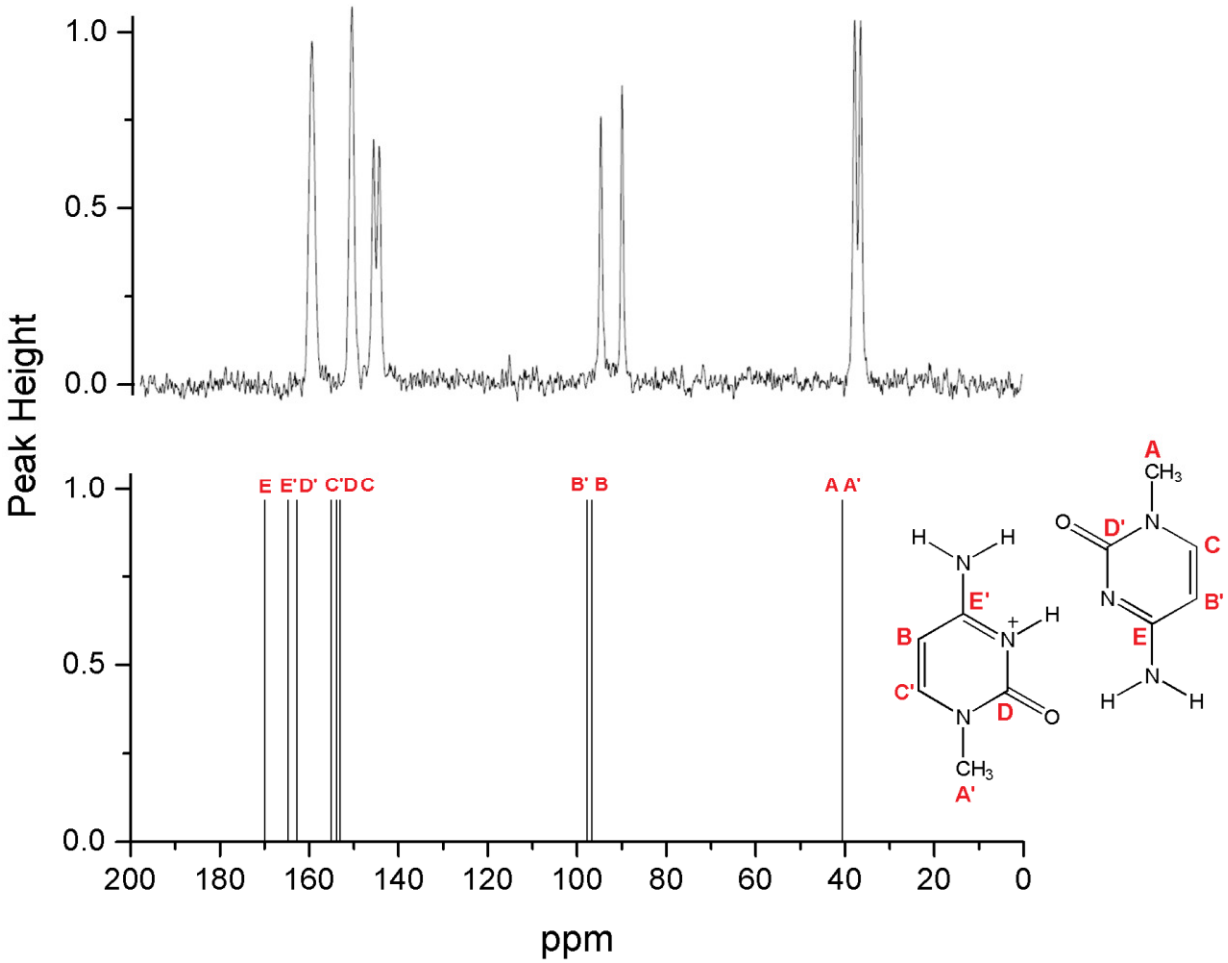

Figure S10: Comparison of experimental solid state ^{13}C spectrum (top) of the iodide salt of **1** (B form) and the predicted ^{13}C spectrum for isolated **1** (bottom) computed using Gaussian09 at B3LYP/6-311++G**.

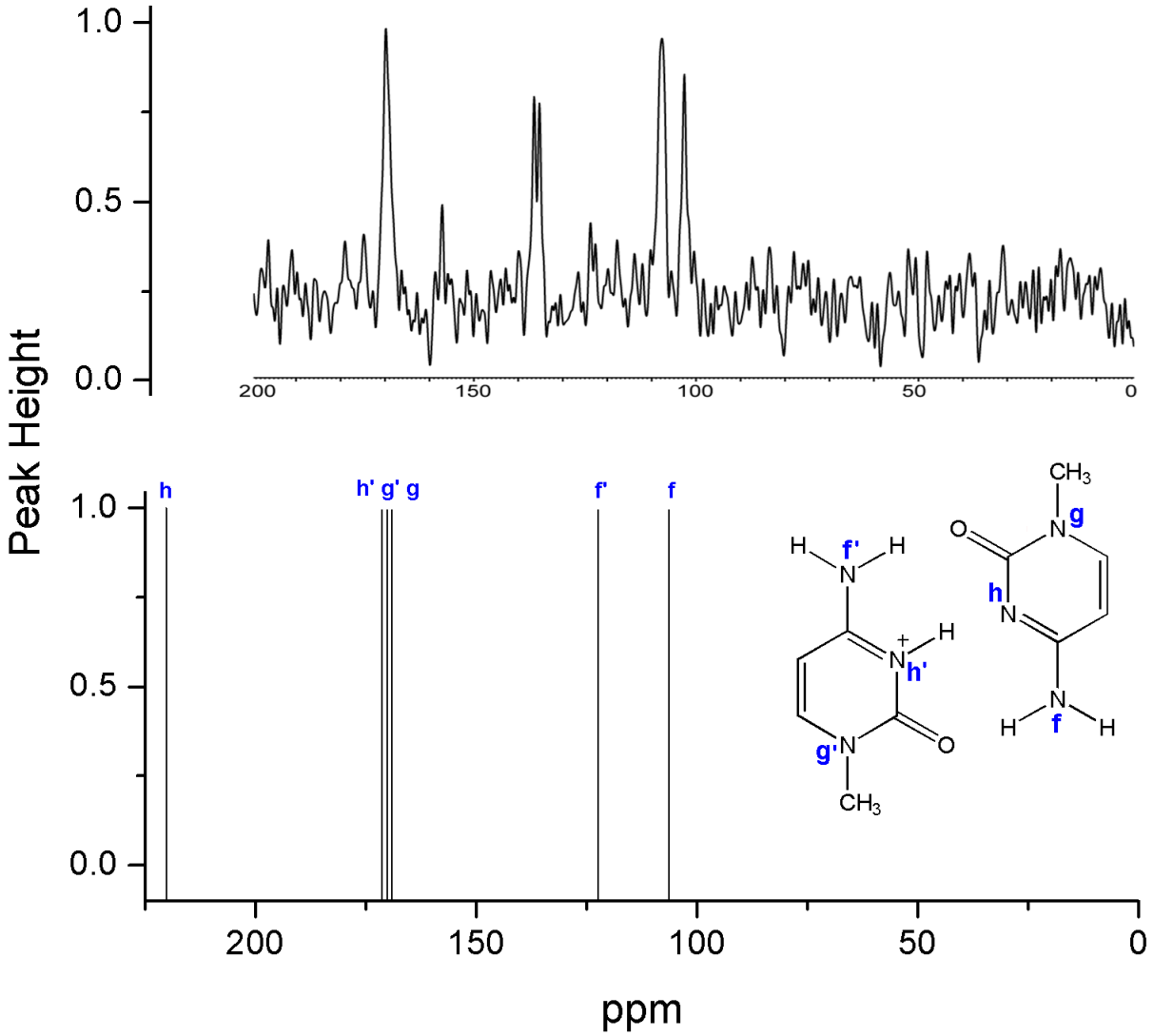

Figure S11: Comparison of experimental solid state ^{15}N spectrum (top) of the iodide salt of **1** and the predicted ^{15}N spectrum for isolated **1** (bottom) computed using Gaussian09 at B3LYP/6-311++G**.

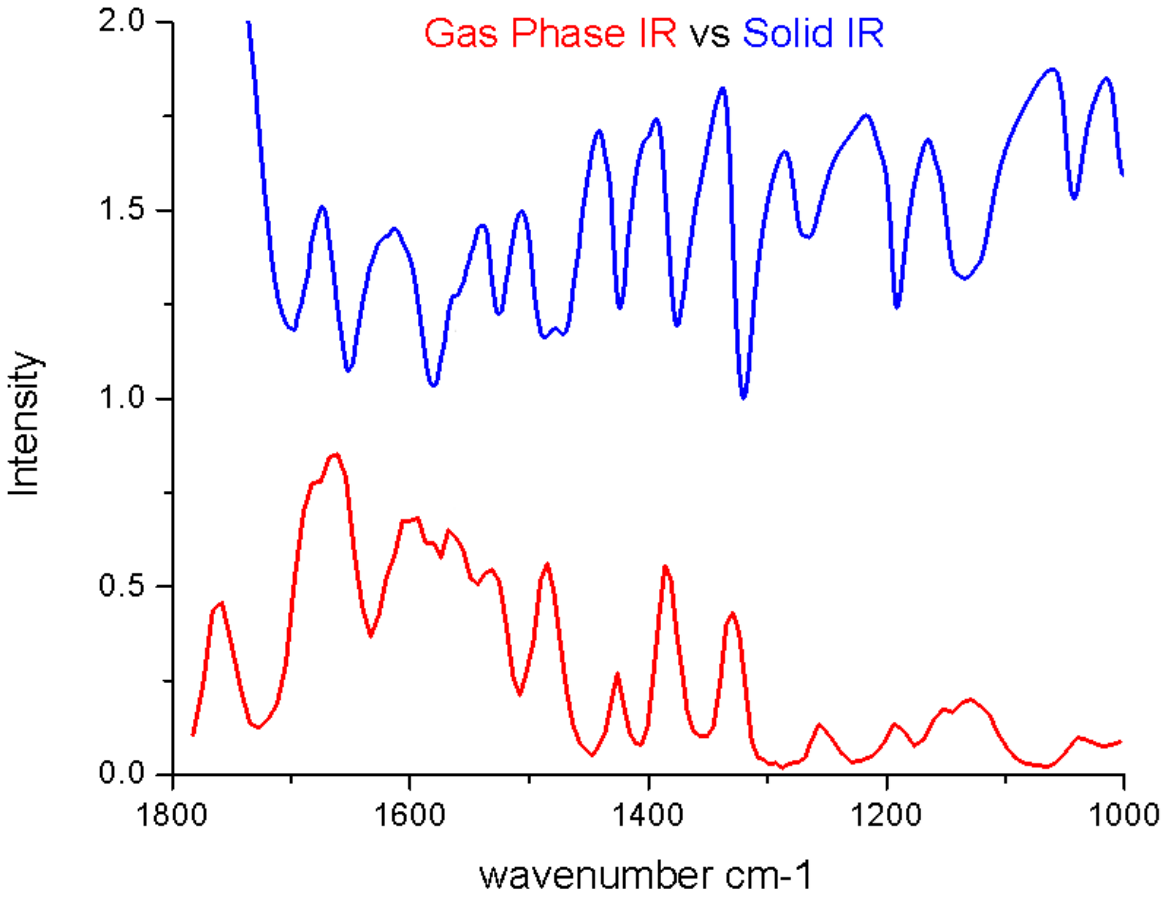

Figure S12: Comparison of experimental IRMPD spectrum (red) of gaseous **1** and the experimental powder IR spectrum (blue; mixture of polymorphs) of the iodide salt of **1** in the 1000-1800 cm^{-1} domain

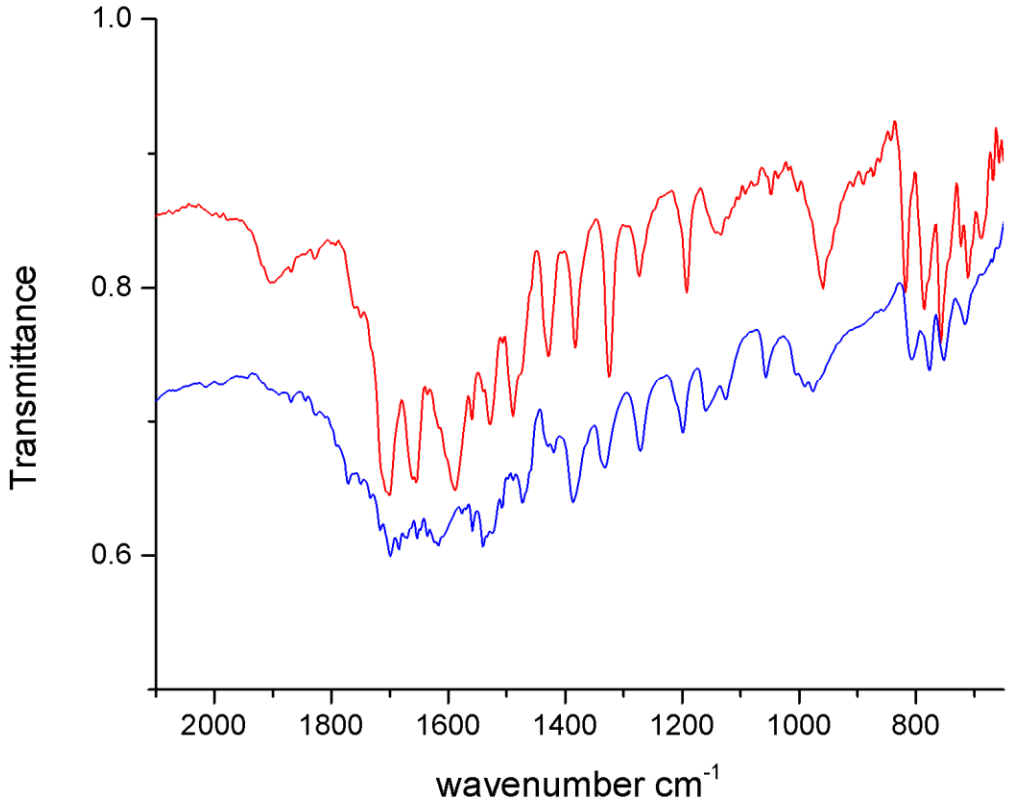

Figure S13: Comparison of single crystal IR spectra of the iodide salt of **1** principally in the B crystal habit (red) and principally in the A crystal habit (blue, corresponding to previously published crystal structure of the iodide salt of the proton-bound dimer of 1-methylcytosine [6]).

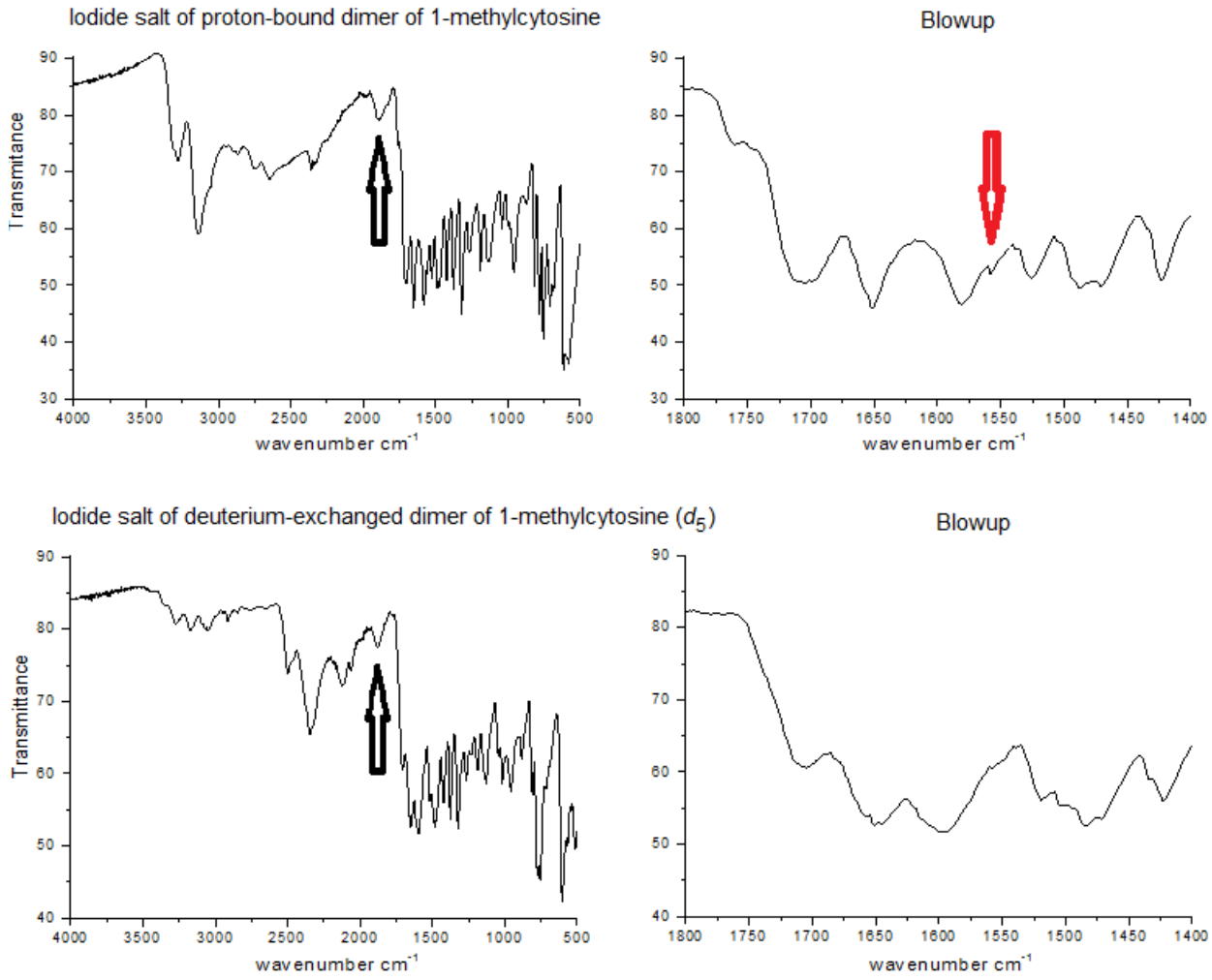

Figure S-14: FT-IR spectra of the crystalline iodide salts of the proton-bound dimer of 1-methylcytosine and of its d_5 deuterium-exhanged isotopomer. Black arrows indicate the 1890 cm^{-1} band present in both spectra. Red arrow in the top blowup indicates the band that coincides with the 1570 cm^{-1} band observed by IRMPD for gaseous ion **1**.