Accurate Vibrational Spectra of Large Molecules by Density Functional Computations beyond the Harmonic Approximation: The Case of Azabenzenes

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This paper compares harmonic and anharmonic frequencies of pyridine, pyridazine, pyrimidine, pyrazine, 1,2,3-triazine, 1,2,4-triazine, and s-tetrazine computed using the B3LYP density functional method and medium size basis sets. Anharmonic corrections cannot be neglected for quantitative studies but can be obtained quite effectively by a perturbative treatment including cubic force constants to the second order and semidiagonal quartic constants to the first order. Simple finite difference equations provide all the necessary terms by at most 6N-11 Hessian evaluations, where N is the number of atoms in the system. This approach has been recently coded in the Gaussian package and provides for all the azabenzenes mentioned above an absolute average error of fundamental bands below 10 cm^{-1} and a maximum error never exceeding 40 cm^{-1}. This level of agreement, obtained by a black box procedure without any scaling factor, allows to propose some revision of current spectral assignments based on less reliable harmonic computations.

1. Introduction

Theoretical computations of vibrational frequencies for polyatomic molecules have become in the past years unvaluable aids to spectroscopists thanks to the increasing availability of computer codes allowing the analytic evaluation of first and second energy derivatives[1] and to the increased power of affordable computers. Although scaling of harmonic frequencies computed even at the Hartree−Fock level gives reasonable results,[2] the development of effective algorithms for density functional analytical second derivatives[3] has allowed the computation of much improved harmonic frequencies at reasonable costs. This is pushing the application of such kind of investigations to the treatment of large molecules and transition metal complexes.[4] At the same time, it is becoming feasible to investigate if effective approaches going beyond the harmonic level can offer further significant improvements. For small molecules, converged ro-vibrational levels can be obtained by fully variational methods.[5−7] However, for large molecules some approximation becomes unavoidable concerning both the form of the potential and the ro-vibrational treatment. The most successful approaches are at present based on truncated two- or three-mode potentials and on self-consistent[8,9] and/or second order perturbative[10−20] vibrational treatments. A number of codes are available for this kind of treatments and, recently, they have become to be fully integrated in general electronic structure packages.[20−22] However, attention has been paid until now to relatively small systems. The recent introduction by the present author in the Gaussian code of an effective perturbative treatment of anharmonic effects[22] paves the route for the investigation of larger molecules.[23] This code will be used in the present paper to investigate the vibrational spectra of a number of azabenzenes.

From an experimental point of view, the infrared (IR) and Raman spectra of all the mono-, di-, and triazines have been recorded, whereas only s-tetrazine has been characterized.[24−33] The compounds containing five and six N atoms do not have a planar six-membered ring ground state and will not be considered in the following. This defines a series of seven azabenzenes, which are well characterized experimentally and whose harmonic force fields have been computed by several quantum mechanical approaches.[34−37] The importance of this series can be hardly overestimated since different diazines form the building blocks of biomolecules, ranging from DNA bases to pigments, and vitamins. Furthermore, derivatives of triazines are used in melamine-formaldehyde plastics, and s-tetrazine is being used for data storage at the molecular level.

2. Computational Details

All of the computations have been performed with a locally modified version of the G03 system of programs[38] using in most cases the B3LYP functional and the 6-31G(d) basis set.[39] Diffuse functions lead to much improved IR and Raman intensities[37,40] and are, more generally, particularly effective in DFT computations.[41,42] As a consequence, I will consider also a more extended basis set (referred to in the following as *ext*), which is obtained adding to the 6-31G set polarization functions optimized for correlated methods ($\zeta_p(H) = 0.75$, $\zeta_d(C) = 0.626$, $\zeta_{dp}(N) = 0.913$), together with field-induced polarization functions on carbon ($\zeta_{sp} = 0.02789$, $\zeta_d = 0.07907$) and nitrogen ($\zeta_{sp} = 0.03483$, $\zeta_d = 0.09874$) taken from ref 43.

Details about the implementation of anharmonic computations are given elsewhere.[22] In essence, starting from an optimized geometry, it is possible to build automatically third and semidiagonal fourth derivatives for any computational model for which analytical second derivatives are available, and next to evaluate vibrational frequencies using second-order perturbation theory (hereafter PT2). Note that, as explained elsewhere,[22] the best compromise between different error sources is obtained using a step size of 0.025 Å in the numerical differentiation of harmonic frequencies, tight geometry optimizations, and fine grids (at least 99 radial and 590 angular points) in both SCF and CPKS computations.

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TABLE 1: Dipole Moments (μ in Debye) and Polarizabiliites (α in A.U.) of Azabenzenes Obtained by Different Methods

	μ			α		
molecule	6-31G(d)	ext	exper.	6-31G(d)	ext	exper.[d]
pyridine	2.19	2.31	2.22[a]	50.5	64.0	64.1
pyridazine	4.12	4.35	4.22[b]	46.6	58.7	59.3
pyrimidine	2.29	2.41	2.33[c]	46.1	58.2	
pyrazine	0.00	0.00	0.00	46.9	59.0	60.6
1,2,3-triazine	4.91	5.16		42.8	53.8	
1,2,4-triazine	2.57	2.70				
s-tetrazine	0.00	0.00	0.00	39.3	49.1	

[a] From ref 46. [b] From ref 44. [c] From ref 45. [d] From ref 47.

3. Results and Discussion

Table 1 compares computed and experimental values for dipole moments[44−46] and average polarizabilities[47] of azabenzenes. The results show that dipole moments within 0.1 D from experimental values can be obtained by both basis sets (underestimated by 6-31G(d) and overestimated by *ext*), whereas accurate polarizabilities can be obtained only by the *ext* basis set.

Since a number of test computations show that for DFT methods basis set extension above the 6-31G(d) level leads to modest variations of computed frequencies,[22,37] both 6-31G and *ext* basis sets will be used for harmonic computations, whereas anharmonic contributions will be evaluated only at the 6-31G(d) level. These computations can be routinely performed for molecules including up to 20 atoms. Note also that, since the finite difference evaluation of third and fourth derivatives is a textbook example of an "embarassingly parallel" computational problem,[48] much larger systems can be treated using clusters or grid architectures.

Table 2 compares the vibrational spectra of pyridine obtained by different methods. The agreement between PT2 results and experimental band origins is impressive for all the modes and there is no problem about any assignment. The absolute average error is reduced by nearly an order of magnitude (from 49.4 to 5.4 cm^{-1}) when anharmonicity and basis set extension are taken into account. At the harmonic level the 6b$_2$ band (1309 cm^{-1}) is quite far from the experimental value (1227 cm^{-1}), and this suggested a revision of the assignment.[37] However, PT2 computations indicate that the problem resides in an unusually large anharmonic correction (73 cm^{-1}), whose proper inclusion restores the agreement with experiment.

From a technical point of view, it is well known that for large molecules PT2 computations are plagued by Fermi resonances; however, the implementation used in the present study[22] automatically neglects nearly singular contributions (deperturbed computations), thus effectively removing interactions in the second order treatment, which are more properly treated in first order. This is accomplished by direct diagonalization of the corresponding part of the Hamiltonian matrix. Table 3 shows that the effect of these terms is often not negligible but can be properly dealt with by a black box procedure at least when only fundamental bands are investigated.

Table 4 compares the vibrational spectra of pyridazine obtained by different methods. Once again, the agreement between computed and experimental values is very good and the PT2 treatment allows an unambiguous assignment of all bands without any scaling and with comparable errors for all the modes, including CH stretchings.

Table 5 compares the vibrational spectra of pyrimidine obtained by different methods. The results are comparable with those of the previous molecules, except for the 1a$_2$ frequency, whose experimental value (927 cm^{-1}) is only an estimate, whereas a more plausible value could be about 970 cm^{-1}. Wiberg,[36] on the basis of his scaled HF/6-31+G(d) frequencies, suggested that the 955 cm^{-1} band be deassigned and the 980 cm^{-1} band be reassigned to 2b$_1$, while an unassigned band at 1024 cm^{-1} might correspond to 1b$_1$. This interpretation was advocated also by Martin and Van Alsenoy[37] on the basis of B3LYP/cc-pVTZ harmonic computations. However, PT2 results strongly support the original experimental assignment.

TABLE 2: Vibrational Spectrum of Pyridine Obtained by Different Methods

	6-31G(d)[a]	6-31G(d)[b]	ext[a]	ext[b]	exper.[c]
a1	3216	3069	3213	3066	3070
	3192	3054	3190	3052	3057
	3172	3020	3169	3017	3025
	1644	1603	1631	1590	1581
	1531	1500	1509	1478	1483
	1254	1235	1238	1219	1217
	1101	1081	1091	1071	1069
	1051	1035	1046	1030	1030
	1012	997	1010	995	991
	614	608	612	606	603
b2	3207	3076	3205	3074	3079
	3169	3034	3167	3032	3034
	1639	1596	1625	1582	1574
	1487	1459	1469	1441	1437
	1398	1365	1378	1345	1355
	1309	1236	1304	1231	1227
	1181	1169	1164	1152	1146
	1086	1060	1077	1051	1069
	670	664	665	659	654
b1	1010	992	1009	991	1007
	957	940	954	937	941
	763	752	758	747	747
	719	708	713	702	703
	422	414	418	410	406
a2	994	978	998	982	980
	898	882	889	873	884
	386	379	382	375	380
av.abs.error	49.4	8.9	42.0	5.4	
max error	147	23	144	18	

[a] Harmonic. [b] PT2 corrections at the 6-31G(d) level. [c] From ref 27.

TABLE 3: Deperturbed and First Order Corrected Band Origins (cm^{-1}) for the Azine Fundamentals Involved in Fermi Resonances

molecule	modes	depert	first order
pyridine	3a1/4a1+5a1	3035	3020
	2b2/1b1+1a2	3037	3034
	5b2/4a1+3b2	1369	1365
pyrimidine	7a1/4b1+5b1	1068	1059
	6b2/2a2+3b1	1206	1203
1,2,3-triazine	1b2/3a1+2b2	3062	3054
	7b2/3b1+2a2	659	664
	6a1/3b1+4b1	1079	1083
1,2,4-triazine	3a′/4a′+5a′	3028	3021
	11a′/4a″+6a″	1082	1074
	15a′/6a″+6a″	624	618
s-tetrazine	2b2u/1au+2b2g	1127	1117

Table 6 compares the vibrational spectra of pyrazine obtained by different methods. The only discrepancy outside the ordinary concerns the 3b$_{2u}$ mode, which corresponds to dissociation into 2HCN + C$_2$H$_2$.

1,2,3-Triazine belongs to the C_{2v} point group and the 21 fundamental modes of vibration may be reduced to the symmetry species 8a$_1$ + 2a$_2$ + 4b$_1$ + 7b$_2$, all of which are Raman active and all but the two a$_2$ modes are IR active. Table 7 compares the vibrational spectra obtained by different methods.

TABLE 4: Vibrational Spectrum of Pyridazine Obtained by Different Methods

	6-31G(d)[a]	6-31G(d)[b]	ext.[a]	ext.[b]	exper.[c]
in plane					
a1	3220	3049	3215	3044	3064[d]
	3196	3050	3191	3045	3052[d]
	1625	1584	1615	1574	1570
	1493	1460	1478	1445	1446
	1204	1167	1200	1163	1159
	1181	1168	1167	1154	1131
	1100	1075	1094	1069	1061
	1016	996	1014	994	963
	682	675	678	671	664
b2	3207	3072	3203	3068	3085[d]
	3190	3052	3186	3048	3056[d]
	1620	1575	1610	1565	1563
	1452	1424	1434	1406	1415
	1323	1297	1309	1283	1283
	1091	1068	1083	1060	1061
	1055	1040	1053	1038	1012
	632	625	630	623	629
out of plane					
a2	1016	1002	1015	1001	989
	946	926	939	919	938
	768	759	770	761	753
	376	369	373	366	363[e]
b1	978	960	978	960	963
	765	753	757	745	760
	378	369	375	366	369
av.abs.error	48.5	11.9	42.7	9.9	
max error	156	37	151	31	

[a] Harmonic. [b] PT2 with anharmonic terms at the 6-31G(d) level. [c] From ref 24 except when explicitly noted. [d] From ref 29. [e] From ref 28.

TABLE 5: Vibrational Spectrum of Pyrimidine Obtained by Different Methods

	6-31G(d)[a]	6-31G(d)[b]	ext.[a]	ext.[b]	exper.[c]
in plane					
a1	3222	3070	3218	3066	3074
	3193	3061	3188	3056	3052
	3175	3035	3172	3032	3038
	1628	1585	1616	1573	1564
	1449	1420	1435	1406	1398
	1169	1149	1160	1140	1139
	1085	1059	1080	1054	1065
	1012	997	1012	997	992
	697	688	692	683	678
b2	3178	3039	3175	3036	3039[d]
	1626	1580	1617	1571	1568
	1511	1481	1491	1461	1466
	1409	1380	1388	1359	1370
	1271	1240	1263	1232	1225
	1236	1203	1227	1194	1159
	1102	1083	1092	1073	1071
	633	626	632	625	623
out of plane					
b1	1020	1003	1022	1005	980
	978	960	978	960	955[d]
	825	811	818	804	811
	738	725	735	722	721
	354	347	315	344	344
a2	1001	982	997	978	/
	410	403	407	400	399
av.abs.error	45.8	8.8	40.2	6.1	
max error	148	23	144	25	

[a] Harmonic. [b] PT2 with anharmonic terms at the 6-31G(d) level. [c] From ref 29 except when explicitly noted. [d] From ref 26.

TABLE 6: Vibrational Spectrum of Pyrazine Obtained by Different Methods

	6-31G(d)[a]	6-31G(d)[b]	ext.[a]	ext.[b]	exper.[c]
in plane					
ag	3196	3046	3191	3041	3055
	1633	1587	1623	1577	1580
	1264	1246	1250	1232	1233
	1046	1029	1040	1023	1016
	608	600	609	601	602
b3g	3174	3029	3171	3026	3040
	1594	1551	1585	1542	1525
	1388	1358	1368	1338	1346
	722	714	716	708	704
b1u	3175	3002	3172	2999	3012
	1531	1498	1511	1478	1483
	1172	1144	1164	1136	1130
	1033	1016	1033	1016	1018
b2u	3190	3060	3186	3056	3069
	1457	1430	1440	1413	1411
	1244	1202	1240	1198	1149[d]
	1100	1074	1090	1064	1063
out of plane					
au	993	978	996	981	960
	351	343	349	341	350
b1g	947	930	938	921	927
b2g	985	968	984	967	983
	775	762	773	760	756
b3u	806	794	799	787	785
	435	428	432	425	418
av.abs.error	48.2	10.9	41.6	7.7	
max error	163	26	160	21	

[a] Harmonic. [b] PT2 with anharmonic terms at the 6-31G(d) level. [c] From ref 29. [d] Not included in error evaluation (see text).

TABLE 7: Vibrational Spectrum of 1,2,3-Triazine Obtained by Different Methods

	6-31G(d)[a]	6-31G(d)[b]	ext.[a]	ext.[b]	exper.[c]
in plane					
a1	3224	3138	3219	3133	3107
	3196	2997	3190	2992	3045[d]
	1605	1563	1595	1553	1597[d]
	1396	1359	1388	1351	1336
	1144	1127	1138	1121	1124(5b2)
	1096	1083	1092	1079	1069
	1012	991	1012	991	979
	680	671	679	670	660
b2	3201	3054	3196	3050	3046
	1602	1557	1596	1551	1545
	1451	1422	1434	1405	1410
	1234	1211	1222	1199	1195
	1110	1086	1102	1078	1080(5a1)
	990	944	997	951	935
	666	664	665	663	653
out of plane					
b1	1015	996	1015	996	
	822	809	824	811	819
	780	767	781	768	769
	307	301	309	303	318
a2	994	973	989	968	
	363	355	365	357	365
av.abs.error	40.8	12.2	36.9	9.1	
max error	155	31	150	26	

[a] Harmonic. [b] PT2 with anharmonic terms at the 6-31G(d) level. [c] From ref 30. The original assignment of some bands is given in parentheses. [d] Not considered in error evaluation (see text).

The assignment of ref 30 was based on scaled HF/6-31G(d,p) and MP2/6-31G(d,p) harmonic frequencies. PT2 computations confirm the original assignment except for the inversion of $5a_1$ and $5b_2$ bands; they are also in agreement with the experimental assignment of the $4b_2$ band, which was challenged by the computations of ref 30. The only serious discrepancy concerns the $3a_1$ band, whose PT2 value (1553 cm^{-1}) is about 40 cm^{-1} lower than the experimental estimate of 1597 cm^{-1}. However, in view of the results obtained for other azabenzenes, the

TABLE 8: Geometrical Parameters of 1,2,4,-Triazine Obtained by Different Methods

	MP2/TZVP[a]	B3LYP/6-31G(d)	B3LYP/*ext*
N1N2	1.341	1.337	1.333
N2C3	1.336	1.336	1.337
C3N4	1.342	1.342	1.343
N4C5	1.332	1.329	1.330
C5C6	1.394	1.399	1.402
N1C6	1.336	1.334	1.334
C3H	1.079	1.087	1.088
C5H	1.081	1.089	1.088
C6H	1.080	1.087	1.090
N1N2C3	118.1	118.0	118.2
N2C3N4	127.5	127.3	126.9
C3N4C5	113.9	114.2	114.4
N4C5C6	120.7	120.7	120.6
C5C6N1	122.3	121.7	121.6
C6N1N2	117.5	118.2	118.3

[a] From ref. 31.

experimental value could be doubtful. In addition, the harmonic MP2 computations of ref 30 (contrary to their HF counterparts) underestimate the experimental value by about 40 cm^{-1}.

1,2,4-Triazine is one of the less studied azabenzenes because the ring system is readily hydrolyzed, particularly in the presence of moisture and acids.[49,50] In particular, there is no structural information available for this molecule since crystal twinning does not allow to obtain a single-crystal X-ray diffraction structure and the presence of three ^{14}N centers and asymmetric rotor structure make microwave spectral determination complex. At the same time, the very close length of all ring bonds except C_5C_6 (about 1.33 Å according to several quantum mechanical computations) makes an electron diffraction study somewhat problematic. As a consequence, only theoretical structures are available, the most significant of which are given in Table 8. It is remarkable that MP2 and B3LYP results are quite close and that basis set extension has a negligible effect.

The vibrational spectrum is now quite well characterized thanks to the studies by Palmer and co-workers,[31,32] which complete an old IR investigation.[25] Table 9 compares harmonic and anharmonic frequencies computed at the B3LYP level with the experimental band origins. Once again, the agreement between PT2 results and experiment is very good if some changement in the original assignment (based on less reliable harmonic computations) is allowed. The modifications are explicitly noted in the table and none of them is in contrast with the direct experimental evidence. This example points out the potentialities of a computational model whose average absolute errors are about five times lower than those of the current harmonic approaches.

TABLE 9: Vibrational Spectrum of 1,2,4,-Triazine Obtained by Different Methods

	6-31G(d)[a]	6-31G(d)[b]	ext.[a]	ext.[b]	exper.[c]
		in plane			
a′	3213	3049	3205	3041	3060[d]
	3210	3075	3203	3068	3090[d]
	3181	3021	3174	3014	3035[d]
	1613	1567	1604	1558	1558
	1577	1534	1570	1527	1523
	1483	1450	1469	1436	1433
	1415	1389	1399	1373	1374
	1326	1298	1313	1285	1285
	1187	1176	1180	1169	1161(10a′)
	1159	1121	1154	1116	1132(3a″+5a″)
	1107	1074	1103	1069	1097
	1067	1047	1067	1047	1044
	1020	998	1021	999	993(15a′+5a″)
	732	723	728	719	713
	632	616	633	617	613
		out of plane			
a″	1008	990	1009	991	
	988	968	986	966	964(13a′)
	861	845	857	841	841(1a″)
	788	774	790	776	769(3a″)
	381	375	384	378	371
	321	312	322	313	323
av.abs.error.	44.3	10.1	39.2	8.3	
max error	153	23	145	28	

[a] Harmonic. [b] PT2 with anharmonic terms at the 6-31G(d) level. [c] From ref 31 except when explicitly noted. The original assignment of some bands is given in parentheses. [d] From ref 25.

TABLE 10: Vibrational Spectrum of s-Tetrazine Obtained by Different Methods

	harm[a]	PT2[a]	harm[b]	PT2[b]	harm[c]	PT2[c]	exper.[d]
			in plane				
ag	3233	3094	3222	3083	3134	2985	3010[e]
	1482	1432	1486	1436	1364	1311	1415
	1050	1028	1050	1028	985	961	1009
	757	747	755	745	729	717	736
b1u	3231	3092	3221	3082	3133	2984	3086
	1236	1210	1233	1207	1170	1142	1204
	1096	1079	1098	1081	1056	1033	1093
b2u	1487	1455	1474	1442	1428	1395	1435
	1157	1117	1153	1113	1102	1085	1103
	988	946	997	955	911	863	882[e]
b3g	1571	1521	1565	1516	1476	1426	1525
	1335	1306	1323	1294	1287	1251	1291
	648	644	648	644	626	618	640
			out of plane				
au	341	334	351	344	293	284	335
b2g	994	974	994	974	956	934	994
	822	809	826	813	790	775	801
b3u	926	907	926	907	886	858	904
	257	249	259	251	160	164	255
av.abs.error	35.3	10.5	33.5	9.3	29.9	55.5	
max errror	145	20	135	21	95	104	

[a] B3LYP/6-31G(d). [b] B3LYP/*ext*. [c] BLYP/6-31G(d). [d] From ref 29. [e] Not included in error evaluation (see text).

Table 10 compares harmonic and anharmonic frequencies computed at the B3LYP level with the experimental band origins of s-tetrazine. The B3LYP results show the same pattern already discussed for the other azabenzenes, and there are no particular problems in assignments, except for the 3b$_{2u}$ band, whose computed origin is more than 70 cm^{-1} higher than the experimental estimate. The consistency of all the results discussed until now is strongly in favor of a misassignment of this band. For purposes of comparison, harmonic and anharmonic frequencies were computed also at the BLYP level. The results are quite interesting since the agreement with experimental values is now better for harmonic than for anharmonic computations. This confirms that inclusion of some Hartree–Fock exchange in density functionals is mandatory for quantitative evaluation of the vibrational spectra of organic molecules. The better agreement of BLYP computations claimed by some authors is due to an error compensation between neglecting of anharmonicity and intrinsic underestimation of vibrational frequencies by this functional. As a consequence, disappointing results are obtained when improving the vibrational model either by the method employed in the present study or by Car-Parrinello dynamics.[51]

After completion of this paper, I became aware of a parallel study on the same subject by Boese and Martin.[52] A comparison of the results of both studies confirms the reliability of the assignments discussed above and the closeness of fundamental

TABLE 11: Zero Point Energies (ZPE in kJ/mol), Enthalpy Variations (kJ/mol), and Entropies (S in J mol^{-1} K^{-1}) at 298 K Obtained at the Harmonic and Anharmonic Levels for Azabenzenes

molecule	ZPE^a	ZPE^b	H$-$H$_0$^{a}	H$-$H$_0$^{b}	S^a	S^b
pyridine	233.8	233.0	13.7	13.9	281.4	282.2
pyridazine	200.5	198.2	13.6	13.7	281.1	281.8
pyrimidine	202.9	200.5	13.5	13.6	280.3	281.0
pyrazine	202.3	199.9	13.4	13.6	274.4	275.1
1,2,3-triazine	166.8	165.2	13.6	13.8	281.5	282.2
1,2,4-triazine	169.1	167.3	13.4	13.6	286.1	286.9
s-tetrazine	135.3	133.8	13.5	13.8	275.8	276.6

^{a} Harmonic. ^{b} PT2.

frequencies obtained by different hybrid functionals (B3LYP and B97-1) and basis sets (6-31+G(d,p) and TZ2P).

From another point of view, it has been recently shown[53] that PT2 anharmonic frequencies obtained at the B3LYP/6-31G(d) level allow the computation of very reliable thermodynamic functions. Table 11 collects the corresponding values for all the azabenzenes studied in the present work. It is quite apparent that anharmonic corrections are not very large, but cannot be neglected in quantitative studies. Although experimental values are not available for these molecules, the reported values are the most reliable published until now.

4. Conclusion

The present paper reports the main results of a comprehensive study of azabenzene vibrational spectra computed using second-order perturbation theory, including constant, linear, and quadratic terms in the vibrational treatment. The results show that this model is very useful for semirigid molecules and that a remarkable accuracy is obtained at the B3LYP level with medium size basis sets. For all the azabenzenes, the absolute average error of fundamental bands is always below 10 cm^{-1} and the maximum error never exceeds 40 cm^{-1}. As a matter of fact, this level of agreement is largely sufficient for most purposes and is obtained by a black box procedure without any scaling factor. The efficiency, scaling, and ease of use of the computational approach paves the route for more reliable interpretations of IR and Raman spectra of large systems. To this end, the whole procedure has been included in the G03 package.

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