J. Phys. Chem. A **2004,** *108,* 3085−3096

Vibrational Spectra of the Azabenzenes Revisited: Anharmonic Force Fields[†]

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Received: October 2, 2003; In Final Form: November 12, 2003

Anharmonic force fields and vibrational spectra of the azabenzene series (pyridine, pyridazine, pyrimidine, pyrazine, *s*-triazine, 1,2,3-triazine, 1,2,4-triazine, and *s*-tetrazine) and benzene are obtained using density functional theory (DFT) with the B97−1 exchange-correlation functional and a triple-ζ plus double polarization (TZ2P) basis set. Overall, the fundamental frequencies computed by second-order rovibrational perturbation theory are in excellent agreement with experiment. The resolution of the presently calculated anharmonic spectra is such that they represent an extremely useful tool for the assignment and interpretation of the experimental spectra, especially where resonances are involved.

I. Introduction

For atomization energies and geometries, density functional theory (DFT) constitutes a cost-effective alternative to wave function-based ab initio methods, being capable of accuracies on the order of a few kcal/mol and a few picometer, respectively, if basis sets of polarized triple-ζ quality are employed.[1,2]

As a result of this astonishing success, especially considering the modest computational cost of DFT methods, a variety of new applications are now being explored,[3−7] including, very recently, the calculation of molecular anharmonic potential energy surfaces.[8] Anharmonic potential energy surfaces (see refs 9 and 10 for pioneering SCF and CISD studies by the Schaefer group) allow for the prediction of molecular vibration−rotation spectra that can be compared directly to experiment, obviating the need to make estimations or approximations for the effect of anharmonicity. CCSD(T)/*spdf* anharmonic force fields can achieve accuracies on the order of 10 cm^{-1} or better for fundamentals (e.g., ref 11 and references therein), and even greater accuracy is achievable if still larger basis sets and corrections for inner-shell correlation are considered.[12,13]

DFT anharmonic force fields for small molecules have recently been the subject of two validation studies.[14,15] Our own validation study[15] suggested that, for fundamental frequencies, an RMS accuracy of about 18 cm^{-1} can be attained when using the B97-1 functional with sufficiently large basis sets. The question arises as to how capable DFT is to treat medium-sized organic molecules in this fashion. Particularly relevant here is the study the study of Miani et al.[16] on the fundamental frequencies of benzene, which employed the B3LYP[17,18] functional with the TZ2P (triple-ζ plus double polarization) basis set. This paper, as well as a more recent study of furan, pyrrole, and thiophene,[19] in fact yielded even more accurate results on these medium-sized organic systems than suggested by the small-molecule validation studies cited above.

The azabenzenes are obtained by systematically replacing CH moieties in benzene by nitrogen atoms. Numerous experimental spectra of these compounds are available in the literature, ranging from mono-azabenzene (pyridine) to 1,2,4,5-tetraazabenzene (s-tetrazine). Pentazine is quite elusive;[20] the equally elusive N_6 (hexazine or hexaazabenzene) molecule has been the subject of extensive theoretical studies:[21,22] at the CCSD(T)/cc-pVTZ level, the hexazine (hexaazabenzene) structure undergoes distortion from the idealized D_{6h} ring to a D_2 geometry, which is a local minimum situated some 23 kcal/mol above the C_{2h} diazide global minimum.[22] Straka recently made the interesting suggestion that cyclic N_6 may form very stable M(η^6-N_6) complexes with M = Ti, Zr, Hf, and Th.[23]

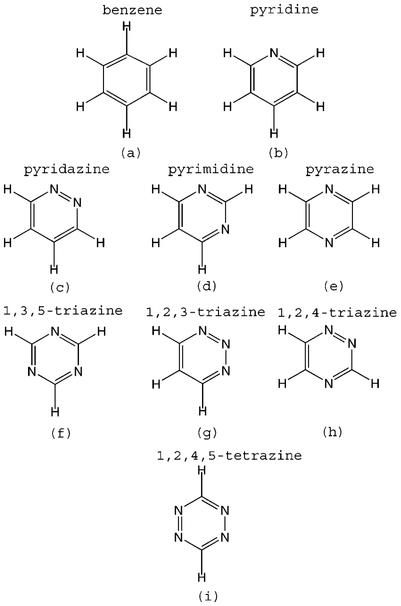

Figure 1. Molecules investigated in this study, including benzene and the azabenzene series up to 1,2,4,5-tetrazine.

In practice, nine molecules are relevant to the present study: the parent benzene molecule, pyridine, pyridazine, pyrimidine, pyrazine, 1,2,3-triazine, 1,2,4-triazine, 1,2,5-triazine (*sym*-triazine), and 1,2,4,5-tetrazine (*s*-tetrazine). All molecules are displayed in Figure 1.

Azabenzene skeletons serve as building blocks in nature, e.g., pyridine in pyridixol (vitamin B_6), pyridazine and pyrimidine in pteridine, itself found in folic acid (vitamin vitamin B_{10}) and riboflavin (vitamin B_2). Moreover the four DNA bases are derivates of pyrimidine (C, T) and of purine (A, G), itself a pyrimidine-imidazole fused ring system. For these reasons,

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[†] Part of the special issue “Fritz Schaefer Festschrift”.

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10.1021/jp0369589 CCC: $27.50 © 2004 American Chemical Society
Published on Web 12/30/2003

azabenzene-like compounds figure in drug design, e.g., the reverse transcriptase inhibitors AZT (contains pyrimidine) or nevirapine (contains pyridine). Derivatives of pyridazine have been found to have potential therapeutic or plant growth inhibitory effects.

Quite different applications include melamine-based plastics (melamine is a derivative of *s*-triazine) and the potential use of s-tetrazine in molecular data storage applications (one of the relaxation mechanisms of the S_1 state leads to 2 HCN + N_2.[24−28]).

Innes, Ross, and Moomaw (IRM throughout this paper) published a compilation and critical review of experimental vibration spectroscopic data current to 1988.[29] One of us (with C. Van Alsenoy) carried out a harmonic-only B3LYP/cc-pVTZ study of the vibrational frequencies and geometries.[30] The limitations of this approach are obvious.

In the present contribution, we will consider DFT *anharmonic* force fields and anharmonic vibrational spectra−which are directly comparable to experiment, for the azabenzenes, and demonstrate their power as a spectroscopic assignment tool for medium-sized organic molecules.

II. Computational Details

In our validation study,[15] we considered a wide variety of exchange-correlation functionals, as well as convergence in terms of the basis set and the integration grids (both Kohn−Sham, KS, and coupled perturbed Kohn−Sham).

Especially for organic molecules, we found the best performance to be delivered by the B97-1 functional, which is Handy's reparametrization[31] of Becke's 1997 hybrid functional.[32] Satisfactory basis set convergence was generally found to be achieved with the TZ2P basis set.[33] This is therefore the functional/basis set combination employed for the present study.

We found[15] results for anharmonic force field calculations to be exceedingly dependent on the KS integration grid, much less so on the CPKS grid. For the present study, we ended up using a (200,974) grid, that is, the direct product of a 200-point Euler-MacLaurin radial grid with a 974-point Lebedev angular grid. For the CPKS steps, we employed a (75,194) grid, which considerably reduced the overall computational cost. Neither grid was pruned.

The quartic force fields were calculated by numerical central differences (in rectilinear normal coordinates) of analytical second derivatives,[39] using a stand-alone driver program adapted from the CADPAC electronic structure program system.[34] The actual DFT second derivative calculations were done using the Gaussian 98 revision A.11 program package.[35]

The step size in a numerical derivatives calculation always represents a compromise between discretization error and roundoff error. Based on experience, we determined the step size as a functions of both the absolute value of the harmonic frequency associated with the normal coordinate involved and the associated reduced mass $(1/\{\sum_{j,k}([l_{\mathrm{MW},jk}(i)]/\sqrt{m_j(i)})^2\})^{1/2}$:

$$q_{\mathrm{step}}(i) = 4\sqrt{\frac{1}{\sum_{j,k}\left(\frac{l_{\mathrm{MW},jk}(i)}{\sqrt{m_j(i)}}\right)^2}}\sqrt{\frac{1000\ \mathrm{cm}^{-1}}{\omega(i)}} \qquad (1)$$

To reduce roundoff error as much as possible, the KS and CPKS equations were basically converged to machine precision.

To calculate this factor, both the reduced mass of the mode m_j and the eigenvalues of the normalization matrix $l_{\mathrm{MW},jk}$ are needed. The last part of eq 1, depending on the harmonic frequencies ω, additionally ensures that each displaced geometry has approximately the same energy difference to the minimum geometry.

TABLE 1: Harmonic Frequencies of Benzene (cm^{-1})

	calculated			derived from experiment		
	B97-1	B3LYP[16]	CCSD(T)[46]	HMA[a] [47]	HW[b] [44]	MCPTH[d] [16]
			In-Plane			
a_{1g}	3189	3192	3210	3198	3191	3218
	1008	1012	1003	1001	1008	1003
a_{2g}	1380	1392	1380	1378	1367	1392
b_{2g}	1012	1017	1009	1000	990	1012
	718	723	709	712	718	717
e_{2g}	3165	3168	3183	3182	3174	3210
	1628	1635	1637	1623	1607	1645
	1195	1201	1194	1185	1178	1197
	617	624	611	610	613	617
e_{1g}	863	864	865	856	847	861
a_{2u}	686	686	687	680	686	683
b_{1u}	3155	3159	3173	3173	3174	
	1022	1031	1020	1016	1024	1030
			Out-of-Plane			
b_{2u}	1330	1333	1326	1313	1318	1338
	1170	1178	1163	1158	1167	1163
e_{2u}	987	992	985	978	967	987
	408	412	406	402	1058	1056
e_{1u}	3180	3183	3200	3186	3181	3212
	1509	1519	1509	1503	1494	1522
	1055	1060	1056	1048	1058	1057

[a] ω_{av} Handy, Murray and Amos, based on the experiments of Goodman et al.[45] [b] Handy and Willets, experimental ν_{i} (Goodman et al.[45]) − HF ($\nu_{\mathrm{i}} - \omega_{\mathrm{i}}$). [b] Miani, Cane, Palmieri, Trombetti, and Handy, experimental ν_{i} − B3LYP/TZ2P ($\nu_{\mathrm{i}} - \omega_{\mathrm{i}}$).

In this manner, we obtain a complete cubic force field, as well as all of the diagonal and semidiagonal quartic force constants. These are sufficient for second-order rovibrational perturbation theory analyses,[36−40] which were carried out using the SPECTRO[41] and POLYAD[42] programs developed in the Cambridge group and at Weizmann, respectively.

III. Results and Discussion

A. Benzene. The parent molecule of our series, benzene (Figure 1a), has been the subject of a few previous anharmonic force field studies, two at the SCF/DZP level,[43,44] and a very recent one at the B3LYP/TZ2P level.[16] An extensive experimental literature exists on the subject (see refs 16 and 45 for reviews): high-resolution data are available for many of the fundamentals, and all of the assignments can be regarded as conclusive. (An analysis of the B3LYP/cc-pVTZ normal modes of benzene and the azabenzenes in terms of Pulay's redundant internal coordinates can be found in Table 17 of ref 30.)

Experimentally obtaining harmonic frequencies for a molecule this large, even with such high symmetry, is a nearly impossible task. In Table 1, we compare computed harmonic frequencies with selected prior calculations (in particular CCSD(T)/*spdf* data[46]), as well as several sets of experimentally derived data. The first such set are the "ω_{av}" estimates of Handy, Murray, and Amos (HMA),[47] themselves obtained as averages of an empirical estimate by Goodman, Ozkabak, and Thakur (GOT)[45] and their own combination of experimental fundamentals with the SCF/DZP computed anharmonicities of Maslen et al.[43] The second set are derived from the experimental fundamentals and a new SCF/DZP anharmonic analysis by Handy and Willetts (HW).[44] The third set is derived from the experimental fundamentals and the B3LYP/TZ2P anharmonicities[16] and is expected to be the most reliable.

TABLE 2: Computed and Observed Fundamental Frequencies (cm^{-1}) of Benzene[a]

	calculated			experiment		
	mode	B97-1/TZ2P	B3LYP/TZ2P	CCSD(T)/B97-1	GOT[45]	MCP[16]
			In-Plane			
a_{1g}	1	3048	3051	3069	3074	3073
	2	992	995	987	993	993
a_{2g}	3	1348	135[b]	1348	1350	1350
b_{2g}	7	987	997	984	990	993
	8	707	708	698	707	702
e_{2g}	15	3032[b]	3028	3050	3057	3057
	16	1611[b]	1613[b]	1620	1601	1610
	17	1178	1181	1177	1178	1178
	18	613	615[b]	607	608	608
e_{1g}	11	841	846	843	847	847
a_{2u}	4	672	677	673	674	674
b_{1u}	5	3004[b]	2988[b]	3022	3057	3057
	6	1006	1015	1004	1010	1014
			Out-of-Plane			
b_{2u}	9	1309	1305	1305	1309	1309
	10	1156	1163	1149	1150	1148
e_{2u}	19	964	972	962	967	968
	20	400	403	398	398	398
e_{1u}	12	3031[b]	3023[b]	3051	3064	3048
	13	1486	1484	1486	1484	1484
	14	1045	1038	1046	1038	1038
B3LYP			RMS deviation experiment-theory		15.2 (4.2)	17.0 (4.8)
B97-1			RMS deviation experiment-theory		12.2 (2.8)	13.7 (4.5)
CCSD(T)/B97-1			RMS deviation experiment-theory		7.8 (4.5)	7.4 (4.1)

[a] For the deviations experiment-theory, values in parentheses are exclusive of C−H stretching frequencies. [b] Band affected by Fermi resonance.

Both sets of DFT numbers compare about equally well with the CCSD(T) data. The C−H stretching frequencies are underestimated by about 20 cm^{-1}, whereas all other frequencies are being reproduced very accurately. (As an aside, we note that the C−H underestimation problem also occurs[48] at the Møller−Plesset perturbation theory (MP2) level.) Although the C−H stretches are reproduced marginally worse by the B97-1 functional (3 cm^{-1}) compared to the reference CCSD(T)/*spdf* values, the overall performance is improved: the mean absolute error decreases from 9.3 (B3LYP) to 6.5 (B97-1) cm^{-1}, and the RMS deviation from 10.6 (B3LYP) to 9.6 (B97-1). The smaller decrease for the RMS error (compared to the mean absolute error) can be attributed to the greater proportional weight given to larger errors. When excluding the C−H stretching frequencies, the RMS errors decrease to 8.4 (B3LYP) and 4.3 cm^{-1} (B97-1). Considering the computational cost of density functional theory, the B3LYP results are already spectacular compared to the reference ab initio data. The B97-1 functional, however, reduces the RMS error of the non C−H stretching frequencies by an additional 50%.

Both functionals yield excellent agreement with experiment for the fundamental frequencies (Table 2). The experimental data were taken from the earlier compilation of GOT[45] and from more recent gas-phase measurements.[16] The two sets of experimental data agree very well with each other, except for ν_{16} and ν_{12} which are involved in strong Fermi resonances. To obtain the B97-1/TZ2P fundamentals, we had to take the following Fermi resonances into consideration: $\nu_3 + \nu_{16}$ and ν_{15} (with the deperturbed frequency ν_{15} at 3018 cm^{-1} and the combination at 2947 cm^{-1}), $\nu_{13} + \nu_{16}$ and ν_{12} (unperturbed ν_{20} at 3040 and the combination band at 3082 cm^{-1}), $\nu_{16} + \nu_{13}$ and ν_5 (with the unperturbed frequencies at 3064 and 3020 cm^{-1}), and $\nu_2 + \nu_{18}$ and ν_{16} (with ν_{16} (unperturbed) at 1600, $\nu_2 + \nu_{18}$ at 1603 cm^{-1}).

Interestingly, because of the small differences in the harmonic frequencies between the B3LYP/TZ2P and the B97-1/TZ2P calculations and the different force field, now new Fermi resonances are predicted. Furthermore, the fundamentals affected by these resonances are the ones which differ the most when using the B3LYP or B97−1 functional. Because of the Fermi resonances, the difference between different functionals and methods becomes more important than on the harmonic level of approximation. The results of both functionals compared to experiment are, however, very similar, with mean absolute errors (compared to the latest experimental results of Miani et al.[16]) of 9.4 (B3LYP) and 8.3 (B97-1) cm^{-1} and RMS errors of 17.0 and 13.7 cm^{-1}, respectively. Again, all frequencies are very well described with the exception of the C−H stretches, which are underestimated by 16−30 cm^{-1} (discounting ν_5 which is severely perturbed by resonances). Without the C−H stretches, the mean absolute errors are reduced to 3.7 (B3LYP) and 3.9 (B97-1) cm^{-1} and the RMS errors to 4.8 (B3LYP) and 4.5 cm^{-1} (B97-1). Hence, while clearly better for harmonic frequencies, the B97-1 functional is only slightly better for predicting the fundamental frequencies of benzene. Nevertheless, the accuracy obtained by density functional theory, which yields RMS errors of less than 5 cm^{-1} for frequencies other than C−H stretches, is very good.

In the third column, we added the B97-1/TZ2P anharmonic corrections to the CCSD(T)/ANO4321 harmonic frequencies of ref 46, to see how such a ‘hybrid’ ab initio-DFT approach would perform. The principal improvement seen is for the C−H stretches, which are thus all bought into the range of the experimental values, except for ν_5, which is in resonance with $\nu_{16} + \nu_{13}$ as discussed above. When discounting C−H stretching frequencies, the improvement compared to a pure B97-1/TZ2P calculation is quite modest, to 3.1 cm^{-1} for the mean absolute error and to 4.1 cm^{-1} for the RMS error. The corresponding error statistics including C−H stretching frequencies change rather more significantly, to a mean absolute error of 4.0 cm^{-1} and an RMS error of 7.4 cm^{-1}.

Summarizing, B97−1/TZ2P is likely to be a useful tool for analysis of vibrational spectra (and verification of their assign-

TABLE 3: Computed and Observed Fundamental Frequencies (cm^{-1}) of Pyridine (Infrared Intensities in km/mol for IR Active Modes Given in Parentheses)[a]

		calculated			experiment					
		B3LYP/pVTZ	B97-1/TZ2P		IR		Raman			INS
		ref 30	this work		ref 77	ref 78	Klots (ref 49)	Klots (ref 49)	ref 79	ref 50
	mode	harmonic	harmonic	fundamental	liquid	vapor	vapor	liquid	solution	refined
					In-Plane					
a_1	1	3195(7.4)	3191(4.4)	3054^b	3070	3094(0.0)	3094	3090		3089
	2	3171(5.2)	3168(4.0)	3043^b	3057	3073(1.5 ± 1.0)	3067	3056		3075
	3	3147(6.8)	3147(3.5)	3012^b	3025	3030(8.5 ± 1.0)	3030	3021		3057
	4	1626(23.8)	1620(23.3)	1575^b	1581	1584(17.9 ± 1.8)	1590	1588		1582
	5	1518(3.2)	1512(3.4)	1483	1483	1483(4.0 ± 0.4)	1483	1482		1482
	6	1244(3.2)	1240(3.5)	1221	1217	1218(4.3 ± 0.4)	1218	1217		1209
	7	1096(3.0)	1091(3.6)	1071	1069	1072(4.5 ± 0.5)	1072	1068		1058
	8	1052(7.7)	1044(6.8)	1028	1030	1032(7.7 ± 0.8)	1032	1031		1030
	9	1012(5.7)	1006(4.9)	990	991	991(5.4 ± 0.5)	991	991		991
	10	617(4.7)	610(4.1)	604	603	601(4.4 ± 0.4)	601	603		603
b_2	14	3186(26.7)	3183(17.3)	3090^b	3079	3094(15.9 ± 1.6)	3087	3079		3034
	15	3144(29.9)	3145(20.7)	2971^b	3034	3042(5.1 ± 1.5)	3042	3035		3018
	16	1621(8.9)	1614(8.3)	1575	1574	1581(7.3 ± 1.8)	1581	1573		1580
	17	1477(27.2)	1468(28.0)	1442	1437	1442(31.1 ± 3.1)	1442	1438		1437
	18	1391(0.1)	1384(0.1)	1356	1355	1362(0.5 ± 0.2)	1355	1355		1355
	19	1283(0.07)	1280(0.0)	1237^b	1227	1227(0.0)	1225	1228		1230
	20	1173(2.4)	1166(2.5)	1155	1146	1143(3.6 ± 0.4)	1143	1147		1137
	21	1080(0.1)	1073(0.01)	1045	1069	1079(0.0)	1052	1053		1045
	22	670(0.2)	664(0.3)	658	654	652(1.1 ± 0.2)	654	653		654
					Out-of-Plane					
b_1	23	1023(0.02)	1012(0.02)	993	1007	1007(0.0)	991	995	988	1005
	24	964(0.01)	957(0.04)	940	941	937(0.0)	937	941	931	948
	25	769(5.9)	761(9.9)	749	747	744(12.9 ± 1.3)	744	749	744	748
	26	721(63.1)	715(69.4)	704	703	700(67.5 ± 6.7)	700	708	700	710
	27	422(3.5)	414(3.5)	406	406	403(7.2)	403	407	405	406
a_2	11	1011	1003	980	980	966	982	982	979	984
	12	899	895	877	884	871	875	884	873	895
	13	385	379	371	380	373	371	379	374	380
B97-1		RMS deviation experiment-theory			6.5	8.4	5.3	5.2		

[a] All RMS deviations exclude C−H stretches. [b] Band affected by Fermi resonance.

ments) of aromatic organic molecules in general and of the azabenzene series in particular.

B. Pyridine. Because pyridine is the simplest azabenzene (Figure 1b) and the closest to the parent molecule, we may anticipate similar accuracy as for benzene. As expected for this chemically important species, many experimental spectra are available, in both liquid and gas phases. Most of the experimental results and the latest experimental assignments are summarized by Klots.[49] The computed and observed vibrational frequencies are presented in Table 3. As expected, the C−H stretching frequencies are not well described. Here, they are also heavily perturbed, and, considering performance for the corresponding bands in benzene, our method may not be sufficiently accurate to assist in the experimental assignment. Thus, although we will attempt to elaborate on the C−H stretching frequencies for most azabenzenes, the results are more tentative. Additionally, a small change in the original unperturbed fundamental frequencies will cause large changes in the perturbed frequencies. Nevertheless, the two asymmetric stretches ν_{14} and ν_{15} do not follow the general trend of being underestimated by 20−40 cm^{-1}. Although the perturbed ν_{14} is close to the experimental value, ν_{15} differs by 70 cm^{-1}. Especially, the latter appears too large to be accounted for merely by deficiencies in our DFT calculation. Here, the severe Fermi resonance seems to be responsible for this assignment, as its deperturbed value is at 3021 cm^{-1}. This mode is resonating with (deperturbed frequencies given) ν_{14} at 3053 cm^{-1}, $\nu_4 + \nu_{17}$ at 3015 cm^{-1}, and $\nu_{16} + \nu_5$ at 3054 cm^{-1}, with the perturbed $\nu_4 + \nu_{17}$ now appearing at 3023 cm^{-1}. It appears that the latter value is more in line with experiment, and that perhaps this assignment might be more reasonable. Nevertheless, some caution is appropriate as the C−H harmonic stretching frequencies are not as well described by DFT as the remaining modes. Large basis set CCSD(T) harmonic frequencies would be helpful here, but would require inordinate amounts of CPU time.

Another picture emerges for the non C−H frequency modes. Here, we primarily compare to the medium resolution Raman vapor data of Klots (Klots2):[49] their assignments seem to be in line with most other experiments, although they differ from the most recent data obtained by Partal et al.[50] Comparing them to these latter inelastic neutron scattering (INS) data, however, amounts to comparing apples and oranges, as the INS data are based on further refinement of a DFT computed *harmonic* force field by maximizing agreement between simulated and observed INS spectral. The pseudo-harmonic frequencies from the refined force field correspond neither to true harmonic nor to true fundamental frequencies, in effect, they are neither fish nor fowl.

We can confirm the assignment of Klots[49] of ν_{21} to the lower value of 1053 cm^{-1}. Difficult assignments seem to result from the Fermi resonances for both ν_4 and ν_{19}, because these are the only fundamentals which give errors of 10 cm^{-1} or larger. The deperturbed mode of ν_4 at 1578 cm^{-1} resonates with $\nu_9 + \nu_{10}$ at 1593 cm^{-1} resulting in perturbed modes at 1575 and 1596 cm^{-1}. This assignment agrees with the earlier experimental studies,[77,78] and the present calculated ordering of the bands refutes the arguments of Klots[49] for swapping the assignments. ν_{19}, on the other hand, seems to be very difficult to assign from experimental data because of its depolarized character. The problem is further exacerbated as ν_{19} is located at the shoulder of ν_6. Although ν_{19} is involved in a Fermi resonance, this is

TABLE 4: Computed and Observed Fundamental Frequencies (cm^{-1}) of Pyridazine

		calculated		experiment						
		B97-1/TZ2P		IR			Raman			INS
	mode	harmonic	fundamental	ref 55	ref 54	ref 52	ref 53	ref 55	ref 54	ref 51
				In-Plane						
a_1	1	3193	3061[a]	3068		3082	3086	3064	3070	3086
	2	3166	3034[a]	3056		3052	3071	3052	3053	3071
	3	1604	1558	1570	1555	1568	1570	1572	1570	1547
	4	1477	1446	1415	1440	1418	1444	1417	1441	1465
	5	1180	1145		1340	1337	1160	1347	1352	1188
	6	1171	1157	1159	1153	1154	1119	1160	1150	1177
	7	1088	1064	1061	1055	1061	1061	1063	1063	1075
	8	1006	987	963	960	969	968	964	963	998
	9	676	669	629	622	622	668	630	632	670
b_2	14	3180	3056[a]	3085		3082	3079	3083	3080	3079
	15	3162	3052[a]	3056		3080	3057	3052	3041	3057
	16	1601	1556	1563	1540	1572	1563	1566	1564	1571
	17	1438	1406	1446	1408	1412	1413	1450	1401	1436
	18	1311	1284	1283	1283	1281	1281	1283	1287	1306
	19	1081	1058	1131	1112	1131	1049	1129	1113	1075
	20	1056	1039		1058	1058	1027	1032	1052	1049
	21	629	622	664	663	673	622	667	660	628
				Out-of-Plane						
b_1	22	981	962			985	987	842	986	998
	23	762	751	760	760	745	745	759	755	782
	24	370	362	369	372	369	376	370	370	375
a_2	10	1019	1002			963	1025	938	970	1039
	11	943	926			765	945	861	786	949
	12	775	763			785	729	753	775	793
	13	372	365			377	367	410	363	372

[a] Band affected by Fermi resonance.

probably not the source of the disagreement, because its unperturbed frequency at 1241 cm^{-1} resonates with $\nu_{10} + \nu_{12}$ at 1282 cm^{-1}, resulting in bands at 1237 and 1289 cm^{-1}. With the exception of these two strongly perturbed bands (ν_4 and ν_{19}), the agreement between experiment and theory can only be described as stunning for bands other than C−H stretches. For the latter, probably only a full CCSD(T) force field can resolve the assignment. Even when including ν_4 and ν_{19} (but excluding all C−H stretching frequencies), the mean absolute error for the computed values compared to the experimental data of Klots[49] is 3.6 cm^{-1} and the RMS error is 5.3 cm^{-1}; without ν_4 and ν_{19}, they are reduced to 2.7 and 3.8 cm^{-1}, respectively.

The double-harmonic infrared intensities are in good agreement with the B3LYP/cc-pVTZ values[30] and in reasonable agreement with the experimental numbers. Even here, the C−H stretches differ, probably not only because of anharmonic contributions and Fermi resonances, but also because of the poor description of these modes by DFT. Still, the excellent performance seen for benzene results is repeated for pyridine.

C. Pyridazine. Pyridazine (Figure 1c) has been of particular interest in the last couple of years.[51−53] A large body of experimental data is available, generally measured in the gas phase, but when certain modes were unavailable, the authors of refs 52 and 53 substituted their own liquid or solid-phase measurements in order to get a full complement of frequencies. All of the spectra have been assigned with the aid of scaled Hartree−Fock, MP2, BLYP, or B3LYP harmonic force fields using small basis sets. Some of them have their force fields fitted to match the experimental data. Despite the large amount of data, huge discrepancies exist, as shown in Table 4. This seems to be especially true for the out-of-plane modes where experimental assignments and values seem almost arbitrary. For ν_{11}, for example, the experimental numbers range from 765 to 949 cm^{-1}, and even the two most recent numbers appear at opposite ends of this range. These assignments have been done using different methods and scaling techniques, because no reliable theoretical data were available at the time.

The same problem with the C−H stretches that was encountered for benzene and pyridine occurs for pyridazine as well; the situation is further complicated because the experimental data differs, and thus, we cannot assign the frequencies of the experiment. Despite the discrepancies between various experimental numbers, all of the C−H stretches appear plausible within the error range of our method.

As the INS data set dramatically varies from the remainder of the experimental data, and because it did not appear to be reliable for pyridine, it was excluded from our analysis, although it is reported in Table 4 for completeness.

Because such a large amount of experimental data is available, it is best to discuss each mode separately, starting with the in-plane modes.

(i) For ν_3, all experiments except the first of ref 54 agree on an assignment to the 1570 cm^{-1} band. Our results, however, would seem to indicate that the assignment around 1555 cm^{-1} might be more plausible.

(ii) The same occurs for ν_4. Experimental values of refs 53 and 54 cluster around 1440 cm^{-1}, with refs 52 and 55 around 1415 cm^{-1}. Our calculation clearly favors the former assignment.

(iii) For ν_5, significant differences between experiments of refs 52, 54, and 55 and the computed value of 1145 cm^{-1} can be found. The experimental assignments are thus untenable in light of this huge discrepancy of more than a hundred cm^{-1}, and only ref 55 proposes an assignment of 1160 cm^{-1}, which still appears to be on the high side.

(iv) For ν_6, most experiments have assignments around the computed 1157 cm^{-1}; however, ref 53 assigned this mode to 1120 cm^{-1} because of their previous assignment. Our calculated ν_5 and ν_6 nearly coincide.

(v) For ν_7, all experimental data sets are in agreement with each other and our calculations. Considering the generally small anharmonicities for this type of vibrations, the discrepancy of 40 cm^{-1} between the computed ω_8 and the observed ν_8 seems to be a bit on the large side. The experimental assignment may have been complicated by the band's position in an IR band envelope going from 960 to 980 cm^{-1}.[53]

(vi) As with ν_5, the experimental assignment for ν_9 of Vazquez et al.[53] differs from the other obtained fundamentals and is the only one that can be confirmed by our calculations.

(vii) For ν_{16}, only refs 52 and 54 differ from the computed values, whereas for ν_{17}, the experimental assignment of Stidham and Tucci[55] both in the IR and the Raman phase appear doubtful. ν_{18} agrees nicely with all experiments.

(viii) For ν_{19} and ν_{20}, the same assignment problems that we experienced for ν_5 and ν_6 seem to have occurred; while most experiments assign values above 1100 cm^{-1} to ν_{19}, only Vazquez et al.[53] seem to give the correct assignment. This results, however, in the value of ν_{20} thus ending up a bit on the low side, and only the value of ref 55 ends up close to our calculated number. The same seems to have happened to ν_{21}, where only ref 53 is in line with our calculations. Hence, for the in-plane modes, the data set of Vazquez et al.[53] appears to be most reliable, excluding ν_3 and ν_6 (which appear to be dubious assignments) and perhaps ν_8 and ν_{20}.

(ix) For the out-of-plane modes, the experimental assignment appears to be even more problematic. For ν_{22}, all experiments differ by 20 cm^{-1} and are either found at ~986 or 842 cm^{-1}. Both assignments appear to be unlikely, because the harmonic B97-1 frequency is at 981 cm^{-1}, which would put the fundamental too low for ~986 and definitely way too high for assignment to the 842 cm^{-1} band.

(x) For ν_{23}, all experimental assignments are around the computed 751 cm^{-1}, whereas for ν_{24}, all of the experiments appear to yield assignments higher than our computed fundamental of 362 cm^{-1}.

(xi) Based on our data, all of the a_2 symmetry modes (ν_{10} through ν_{13}) should probably be reexamined, because several experimental datasets differ drastically from each other and from our calculations. A discussion of these modes is almost impossible, and with the exception of refs 53 and 54 for ν_{13}, all experimental assignments lie beyond the likely error bars of the theoretical values.

On the whole, the pyridazine vibrational spectra definitely merit further investigation, as the many experimental and theoretical datasets available are considerably at variance with each other. Thus, it is impossible to give an error estimate for the method used based on this molecule. However if our computational results prove to be as accurate as for benzene and pyridine, the experimental spectra have to be reexamined. Based on this study, one might wonder whether the addition of more nitrogens or the N−N bond is causing the deterioration of the calculated values.

D. Pyrimidine. Pyrimidine (Figure 1d), has been studied less in recent years. Notable are the IR experiments compiled by IRM,[29] the IR experiments of Billes et al.,[52] and the inelastic neutron scattering work of Navarro et al.[56] Here, we compare mainly to the IR experiments, since the INS data for neither pyridine nor pyridazine agree well with our computed values and the other experiments, for reasons outlined above. Nevertheless, for pyrimidine, the INS data seem a lot closer to the IR data than for the previous two azabenzenes (Table 5). The values for the a_1 C−H stretches are in agreement with experiment, although this seems fortuitous. Otherwise, all in-plane modes are within 8 cm^{-1} of experiment, with the sole exception of ν_{17}. Interestingly, both ν_7 and ν_9 undergo strong Fermi type 1 (overtone-fundamental) and Fermi type 2 (combination-fundamental) resonances; their resonance matrices are displayed in Table 6 with their respective eigensolutions. For ν_7, very small changes in the unperturbed fundamentals would result in the value ending up not at 1071 cm^{-1} but at the experimental assignment of 1065 cm^{-1}. The assignment of the two resonating modes appears to be purely arbitrary. As for ν_9, the resonating overtone of ν_{24} matches the experimental number exactly. Because both modes are in resonance, the overtone might have "borrowed intensity" (as described in ref 57) from ν_9, and thus the assignment.

TABLE 5: Computed and Observed Fundamental Frequencies (cm^{-1}) of Pyrimidine[a]

		calculated		experiment		
		B97-1/TZ2P		IR		INS
	mode	harmonic	fundamental	IRM[29]	ref 52	ref 56
			In-Plane			
a_1	1	3194	3074[b]	3074	3082	3074
	2	3161	3045[b]	3052	3053	3052
	3	3147	3025[b]	3038	3053	3038
	4	1607	1565	1570	1572	1580
	5	1433	1404	1398	1465	1390
	6	1160	1139	1147	1155	1139
	7	1077	1071[b]	1065	1065	1080
	8	1004	989	991	969	972
	9	691	685[b]	678	679	665
b_2	12	3151	3040[b]	3086	3047	3086
	13	1605	1562	1568	1569	1565
	14	1494	1464	1466	1411	1470
	15	1393	1365	1370	1356	1376
	16	1252	1225	1225	1224	1225
	17	1211	1173	1159	1158	1136
	18	1091	1072	1071	1071	1021
	19	630	623	623	621	628
			Out-of-Plane			
b_1	20	1026	1006	980	1033	1070
	21	981	962	955	980	980
	22	822	809	811	804	826
	23	736	723	721	719	722
	24	347	340	344	347	344
a_2	10	1001	982	[927]	960	1020
	11	404	396	399	398	344
B97-1	RMS deviation experiment-theory			5.3	21.2 (9.9[c])	

[a] All RMS deviations exclusive of C−H stretches and ν_{20} (see text). [b] Band affected by Fermi resonance. [c] Additionally excluding ν_5 and ν_{14}.

TABLE 6: Fermi Resonances of Pyrimidine

Resonance Matrices (cm^{-1}) of Pyrimidine

deperturbed	ν_7	$\nu_{23}+\nu_{24}$
	1060.0	
	10.9	1060.1

deperturbed	ν_9	$2\nu_{24}$
	682.7	
	3.7	680.0

Eigensolutions

perturbed	ν_7	$\nu_{23}+\nu_{24}$
coefficient of	1049.2	1070.9
ν_7	−0.7085	−0.7057
$\nu_{23}+\nu_{24}$	−0.7057	−0.7085

perturbed	ν_9	$2\nu_{24}$
coefficient of	677.4	685.3
ν_9	−0.5760	0.8175
$2\nu_{24}$	0.8175	−0.5760

TABLE 7: Computed and Observed Fundamental Frequencies (cm^{-1}) of Pyrazine[a]

		calculated		experiment			
		B97-1/TZ2P		IR			INS
	mode	harmonic	fundamental	IRM[29]	ref 52	ref 59	ref 61
			In-Plane				
a_g	1	3168	3043[b]	3055	3053	3054	3054
	2	1612	1567	1580	1579	1574	1571
	3	1251	1233	1233	1235	1230	1240
	4	1037	1020	1016	1015	1015	1015
	5	607	598	602	601	596	602
b_{3g}	11	3147	3024[b]	3040	3062	3040	3040
	12	1576	1533	1525	1522	1529	1529
	13	1372	1342	1346	1353	1343	1359
	14	715	706	704	698	701	698
b_{1u}	15	3148	2990[b]	3012	3017	3018	3018
	16	1513	1481	1483	1484	1482	1485
	17	1163	1136	1130	1135	1135	1062
	18	1030	1013	1018	1020	1020	1007
b_{2u}	19	3162	3055[b]	3069	3069	3069	3069
	20	1440	1413	1411	1413	1416	1427
	21	1214	1174	1149	1337	1146	1146
	22	1084	1061	1063	1063	1062	1131
			Out-of-Plane				
a_u	6	1002	982	[960]		[997]	1065
	7	347	338	[350]		[422]	350
b_{1g}	8	946	927	927	925	919	940
b_{2g}	9	987	968	983	976	983	983
	10	775	762	756	755	754	754
b_{3u}	23	804	791	785	785	786	818
	24	429	421	418	417	420	414
B97-1		RMS deviation experiment-theory		6.9 (5.3[c])	7.1 (6.7[c])	6.5 (5.5[c])	

[a] All RMS deviations exclusive of C−H stretches and ν_{21}. [b] Band affected by Fermi resonance. [c] Additionally excluding ν_9.

When looking at the out-of-plane modes in Table 5, only ν_{10} and ν_{20} yield different results compared to the first set of experimental results. Both discrepancies have been mentioned before by the harmonic-only study,[30] and ν_{20} has a very small intensity. Moreover, by using scaled HF frequencies, Wiberg[58] has suggested that the assignment for ν_{10} might also be incorrect. The IRM[29] assignments for modes 5, 6, 13, and 21 appear more plausible than from ref 52. Neglecting the problematic modes 10 and 20 and reassigning mode 9 to 677 cm^{-1}, the errors, including the C−H stretches, are 6.3 (mean absolute) and 11.4 cm^{-1} (RMS), and without them are 4.1 and 5.3 cm^{-1}, respectively. Thus, this method again appears to be very reliable for predicting fundamental frequencies.

E. Pyrazine. As with pyrimidine, only few experiments have been done for pyrazine (Figure 1e). The vibrational assignments are displayed in Table 7. In ref 52, assignments were done in the gas phase for the IR active modes and in a melt for the Raman spectrum. Overall, the agreement is again very good for modes other than C−H stretches. If the previously mentioned tendency to underestimate the C−H stretches is taken into account, all assignments appear plausible, with the possible exception of the assignment of ν_{11} from ref 52. It should be noted that all of the C−H stretches are perturbed by Fermi resonances. For the in-plane modes, especially, ν_{21} appears to lie beyond the error bars of our method. It has been mentioned by the harmonic-only study in ref 30 that this “Kekulé mode” is problematic and it was concluded that this mode has significant multireference character, because it corresponds to the dissociation into 2HCN + C_2H_2. However, hybrid density functionals are usually capable of describing nondynamical correlation to a certain extent, because for example the atomization energy of ozone is reasonably well reproduced. For this mode, the assignment of ref 52 appears to be implausible.

For all of the other modes, most of the experiments are scattered only by about 5 cm^{-1}, with this agreement suggesting that their assignments and values are pretty accurate. The out-of-plane modes are generally quite well described by theory. Note that the two a_u modes are not, because they are neither IR nor Raman active; for this reason, they are not assigned in ref 52. The INS values are somewhat disappointing for both frequencies, because the chief advantage of this method is the ability to reveal such bands. Another discrepancy is for the first b_{2g} mode (ν_9), although the value of ref 52 is the one closer to our values.

This leads to mean absolute and RMS errors compared to ref 52 (ref 59) of 7.8 (7.9) and 10.4 (11.1) cm^{-1}, including the C−H stretches, and of 5.4 (5.1) and 6.9 (6.5) cm^{-1} when excluding them. If the problematic ν_2 and ν_9 are excluded, the mean absolute and RMS errors for the non C−H stretches reduce to 4.1 (4.1) and 5.4 (5.5) cm^{-1}, respectively. Thus, the general RMS discrepancy of 5 to 7 cm^{-1} is obtained for pyrazine as well.

F. 1,3,5-Triazine (*s*-Triazine). 1,3,5-Triazine (Figure 1f) is the only azabenzene with a degenerate point group symmetry (D_{3h}). Because of this, the a_2' modes (ν_4 and ν_5) are both IR and Raman inactive. The INS[60] value for ν_4 coincides exactly with our calculation (Table 8); the discrepancy of 124 cm^{-1} for ν_5 is outlandish even for the INS data and this band is probably misassigned. The inelastic neutron scattering data[50,51,56,61,60] are clearly inferior to the other experimental data sets. This is hardly surprising as this method relies on fitting and scaling a harmonic force field which is obtained from DFT in small split-valence basis sets. Already for the harmonics, this introduces errors on the order of about 50 cm^{-1}. The error for the C−H stretches is expected to be even larger. It would be interesting to reanalyze their data based on the present anharmonic force fields, although this still would not resolve the

TABLE 8: Computed and Observed Fundamental Frequencies (cm^{-1}) of 1,3,5-Triazine[a]

		calculated		experiment		
		B97−1/TZ2P		IR,Raman		INS
	mode	harmonic	fundamental	ref 80	IRM[29]	ref 60
		In-Plane				
a'_1	1	3164	3025[b]	3082	3042	3042
	2	1156	1137	1130	1137	1125
	3	1005	989	989	989	991
a'_2	4	1400	1375	[1556]		1375
	5	1168	1124	[1381]		1000
e'	8	3159	3034[b]	3081	3059	3056
	9	1594	1545	1560	1556	1555
	10	1439	1405	1404	1410	1414
	11	1194	1167	1168	1173	1165
		Out-of-Plane				
a''_2	6	947	932		925	940
	7	755	740		737	732
	13	1043	1043		1034	1030
	14	345	338		399	333
B97-1	RMS deviation experiment-theory				7.5 (5.0[c])	

[a] All RMS deviations exclusive of C−H stretches. [b] Band affected by Fermi resonance. [c] Additionally excluding ν_{13}.

problems associated with the C−H stretches, for which large basis set coupled cluster frequencies would be desirable. The experimental IR/Raman data of Daunt et al.[62] and Lancaster et al.[63] are very similar to those of IRM[29] and are not listed in Table 8. With the exception of the first *e''* ν_{12} and the C−H stretches, which are again underestimated, all computed values are within 11 cm^{-1} of experiment. Again, the errors are similar to the other azabenzenes; including the C−H stretches, the mean absolute error is 7.6 cm^{-1} and the RMS error 11 cm^{-1}. Excluding the stretches (and ν_{12}), these numbers reduce to 5.1 (3.4) and 7.5 (5.0) cm^{-1}, respectively.

G. 1,2,3-Triazine. For 1,2,3-triazine (Figure 1g), only one IR and Raman spectrum in KBr has been experimentally determined:[64] the assignment was assisted by scaled MP2/6-31G* harmonic frequencies. The spectrum looks very similar to that of pyrimidine; even the same Fermi resonances are present.

TABLE 9: Computed and Observed Fundamental Frequencies (cm^{-1}) of 1,2,3-Triazine[a]

		calculated		experiment		
		B97-1/TZ2P		IR	Raman	IR
	mode	harmonic	fundamental	ref 64	ref 64	reassigned
		In-Plane				
a_1	1	3195	3032[b]	3107	3110	3046
	2	3165	3028		3045	
	3	1589	1548	1597	1594	1546
	4	1384	1347	1336	1329	1336
	5	1136	1122	1080	1088	1124
	6	1092	1081[b]	1069	1064	1080
	7	1006	985	979	977	979
	8	675	667	660	660	660
b_2	14	3171	3042[b]	3046		3046
	15	1584	1538	1545	1547	1545
	16	1438	1410	1410		1410
	17	1219	1199	1195	1198	1195
	18	1101	1078	1124	1127	1080
	19	974	929	935		935
	20	662	659[b]	653		660
		Out-of-Plane				
b_1	10	1017	998			
	11	824	811	819		819
	12	783	769	769		769
	13	302	296	[318]		
a_2	8	992	973			
	9	358	350		365	
B97-1	RMS deviation experiment-theory			22.1		5.2

[a] All RMS deviations exclusive of C−H stretches. [b] Band affected by Fermi resonance.

TABLE 10: Fermi Resonances (cm^{-1}) of 1,2,3-Triazine

Resonance Matrices of 1,2,3-Triazine

deperturbed	ν_6	$\nu_{12} + \nu_{13}$
	1074.5	
	10.6	1061.4

deperturbed	ν_{20}	$\nu_9 + \nu_{13}$
	655.1	
	−6.3	647.6

Eigensolutions

perturbed	ν_6	$\nu_{12} + \nu_{13}$
coefficient of	1055.5	1080.7
ν_6	−0.4804	−0.8770
$\nu_{12} + \nu_{13}$	0.8770	−0.4804

perturbed	ν_{20}	$\nu_9 + \nu_{13}$
coefficient of	644.0	658.7
ν_9	0.4939	−0.8695
$\nu_9 + \nu_{13}$	0.8175	0.4939

At first glance at the spectra in Table 9, the agreement between theory and experiment is disappointing. For very few of the modes is there agreement between the spectra. However, the authors did not consider *any* Fermi resonances in the lower spectrum (although they noted that one might exist, involving ν_{17}), and simply assumed the ordering of the fundamentals to be identical to that of the MP2/6-31G* harmonics. This however leads to obvious misassignments. For example, ν_6 and ν_{18} lie almost on top of each other, whereas $\nu_{12} + \nu_{13}$ borrows intensity from ν_6 because of the Fermi resonance, as can be seen in Table 10. If the resonance were not as strong as computed, specifically, if the unperturbed fundamental were shifted only a few cm^{-1} toward higher values, the perturbed $\nu_{12} + \nu_{13}$, presently calculated at 1056 cm^{-1}, might easily correspond to the band at 1064 cm^{-1}, assigned to ν_6 in ref 64. The same actually applies to ν_{20}, which has a strong Fermi resonance with $\nu_9 + \nu_{13}$, that has, however, been calculated at a lower value of 644 cm^{-1}. We have also reassigned the first a_1 C−H stretch (mode 1), because the discrepancy between experiment and theory appears too high even for a C−H stretch. Needless to say, this mode also has a strong Fermi resonance with the $2\nu_{15}$ overtone, which has its largest component for the eigenvector with the associated eigenvalue at 3100 cm^{-1}, again explaining the experimental value perfectly. The only other value which is still in question would be a small peak at 1597 cm^{-1}, which might correspond to an impurity; a band was found that was assigned to acetylene, a fragmentation product of 1,2,3-triazine. The value of 318 cm^{-1}, which has been reported for ν_{13}, is actually just a scaled Hartree−Fock harmonic frequency.

Therefore, a dramatic change in the errors is obtained by reassigning the experimental spectrum. Including the C−H stretches in the error analysis, the mean absolute error decreases from 17.7 to 4.7 cm^{-1} and the RMS error from 27.9 to 6.1 cm^{-1}. By excluding the C−H stretches, the mean absolute and RMS errors improve from 14.6 and 22.1 cm^{-1}, respectively, to 4.1 and 5.2 cm^{-1}. Thus, accuracy consistent with the preceding azabenzenes can be obtained following some reassignments in the experimental spectrum. This also corroborates our conclusion concerning pyridazine that neither substitution of C−H by N nor N−N bonds seem to be responsible for the discrepancies between experimental and computed vibrational spectra.

TABLE 11: Computed and Observed Fundamental Frequencies (cm^{-1}) of 1,2,4-Triazine[a]

		calculated		experiment	
		B97-1/TZ2P		IR	hires-IR
	mode	harmonic	fundamental	ref 65	refs 66 and 67
		In-Plane			
a′	1	3178	3051[b]	3090	
	2	3175	3075[b]	3060	
	3	3150	3007[b]	3035	
	4	1596	1556	1560	
	5	1563	1524	1529	
	6	1470	1438	1435	
	7	1401	1376	1380	
	8	1314	1286	1295	
	9	1179	1171[b]	1163	
	10	1139	1107	1136	
	11	1096	1067[b]	1113	
	12	1063	1044	1050	1043.5
	13	1011	989	955	
	14	726	717	713	
	15	632	629[b]		
		Out-of-Plane			
a″	16	1014	1001		
	17	990	976		
	18	862	853	851	
	19	791	779	768	768.7
	20	379	372		367.9
	21	316	308		311.3
B97-1	RMS deviation experiment-theory			16.1 (5.8[c])	

[a] All RMS deviations exclusive of C−H stretches. [b] Band affected by Fermi resonance. [c] Additionally excluding ν_{11}; 1113 cm^{-1} band reassigned to ν_{10}.

H. 1,2,4-Triazine. Because 1,2,4-triazine (Figure 1h) is highly unstable, only one "full" experimental spectrum has been measured as a liquid film,[65] although more recently two high-resolution IR spectra have been recorded for four frequencies.[66,67] For the C−H stretches (Table 11), possibly ν_1 and ν_2 may have been swapped, because they both take part in a large resonance matrix block. Overall, 10 frequencies and combination bands interact forming this large resonance block that include modes 1−3. Hence, it is not surprising that a correct assignment based merely on experimental data would be problematic. With this swap, all three C−H stretches are underestimated by the usual 10−30 cm^{-1}. Only ν_{11} appears questionable in view of our results. However, ν_9 has a Fermi resonance with the combination of ν_{17} and ν_{21}, and the resonance, eigenvector, and eigenvalue matrixes are displayed in Table 12. The Fermi resonances displayed in these tables are similar to pyrimidine, 1,2,3-triazine, and 1,2,4-triazine. Assuming that both of the Fermi resonances are slightly stronger than predicted, because ν_{21} is underestimated by 3 cm^{-1} compared to the high-resolution IR data, the new $\nu_{17} + \nu_{21}$ could well end up lower than the predicted 1143 cm^{-1}, explaining the value of 1136 cm^{-1} that would then not be assigned to any mode. The assignment of ν_{11} in the experiment would then correspond to ν_{10}, in agreement with the calculated spectrum. The assignment of ν_{13} also appears to be incorrect.

Of the four modes obtained by high-resolution IR, the newer data for ν_{12} validates our computational value of 1044 cm^{-1} rather than the 1050 cm^{-1} predicted by the older experiment. On the other hand, the low-resolution IR value of 769 cm^{-1} for mode 19 is closer to the hi-res data compared to our predicted 779 cm^{-1}. These new experiments show the usefulness of the theoretical value, because its resolution is apparently even comparable to that obtained by low-resolution IR data.

TABLE 12: Fermi Resonances (cm^{-1}) of 1,2,4-Triazine

Resonance Matrices of 1,2,4-Triazine		
deperturbed	ν_{11}	$\nu_{17} + \nu_{21}$
	1160.4	
	−13.7	1153.4
deperturbed	ν_{15}	$2\nu_{21}$
	622.8	
	8.4	617.7
Eigensolutions		
perturbed	ν_{11}	$\nu_{17} + \nu_{21}$
coefficient of	1142.7	1171.0
ν_{11}	0.6136	−0.7896
$\nu_{17} + \nu_{21}$	0.7896	0.6136
perturbed	ν_{15}	$2\nu_{21}$
coefficient of	611.4	629.0
ν_9	−0.5949	0.8038
$2\nu_{21}$	0.8038	−0.5949

TABLE 13: Harmonic Frequencies (cm^{-1}) of 1,2,4,5-Tetrazine

	CCSD	CCSD(T)				B3LYP	B97-1
	ref 25	Full[25]	frozen-core			ref 30	
	6-311G**			cc-pVTZ	ANO-4321	cc-pVTZ	TZ2P
	In-Plane						
a_g	3253	3223	3221	3223	3226	3196	3192
	1524	1456	1452	1455	1457	1472	1473
	1059	1018	1018	1025	1025	1050	1047
	758	741	740	747	745	756	751
b_{1u}	3251	3222	3218	3222	3225	3199	3191
	1250	1212	1210	1218	1216	1232	1231
	1109	1088	1088	1096	1098	1099	1096
b_{2u}	1505	1471	1465	1472	1470	1479	1478
	1167	1137	1134	1138	1137	1151	1147
	845	908	905	932	927	964	969
b_{3g}	1611	1558	1552	1561	1561	1559	1560
	1345	1321	1319	1323	1323	1330	1325
	648	637	635	640	640	656	650
	Out-of-Plane						
a_u	344	257	319	344	346	354	344
b_{2g}	985	947	957	998	996	1011	999
	803	772	783	816	816	837	829
b_{3u}	930	896	904	919	921	940	930
	297	228	270	276	270	258	250

Without making any reassignments to the experimental spectrum, the mean absolute error from experiment is 13.6 cm^{-1}, and the RMS error is 19.2 cm^{-1} including the C−H stretches. This appears to be quite large in comparison to the other azabenzenes. With the abovementioned suggested reassignments, these errors change to 7.5 and 10.0 cm^{-1}, respectively. Excluding the C−H stretches, we once again end up with a mean absolute error of 5.1 cm^{-1} and an RMS error of 5.8 cm^{-1}.

I. 1,2,4,5-Tetrazine (*s*-Tetrazine). For 1,2,4,5-tetrazine (Figure 1i), CCSD(T) harmonic frequencies are available in the literature.[25] Unfortunately, they were calculated with all electrons correlated in a basis set (6-311G**) that is only minimal in the inner-shell orbitals. The resulting errors in harmonic frequencies can easily exceed 20 cm^{-1} for small molecules,[68] several times larger than the actual effect of neglecting core correlation (typically less than 10 cm^{-1} in HCNOF systems[69]). We have recomputed the CCSD(T)/6-311G** frequencies correlating only valence electrons (Table 13). For the in-plane modes, differences with the all-electron calculations are quite minor (6 cm^{-1} or less). The out-of-plane modes, however, are drastically affected, up to 60 cm^{-1} (Table 13, especially the a_u and the second b_{3u}

TABLE 14: Computed and Observed Fundamental Frequencies (cm^{-1}) of 1,2,4,5-Tetrazine[a]

		calculated		experiment			
	mode	B97-1	CCSD(T)/B97-1	IRM[29]	ref 81	SP[74]	FMI[76]
				In-Plane			
a_g	1	3073	3107	3010	3040	3089	3090
	2	1424	1408	1415	1489	1417[b]	1418[b]
	3	1024	1000	1009	990	1015	1017
	4	741	735	736	737	734	736
b_{1u}	11	3070	3104	3086	3070	3086	3090
	12	1204	1189	1204	1200	1204	1200
	13	1079	1081	1093	1106	1109[b]	1103[b]
b_{2u}	14	1445	1437	1448	1434	1448	1440
	15	1112[c]	1102	1108	1187	1151	
	16	927	885	883	1085	893[b]	881[b]
b_{3g}	8	1511	1511	1525	1543	1523[b]	1521[b]
	9	1294	1293	1290	1278	1302	1303
	10	645	638	640	679	649	651
				Out-of-Plane			
a_u	5	336	338	335	319	335	335
b_{2g}	6	977	974	994	925	1015	
	7	814	801	801	775	799	800
b_{3u}	17	911	902	929	890	929	904
	18	244	261	254	340	254	254
RMS dev. from ν_i(B97-1/TZ2P)				15.2[d] (15.1,14.8[e])	54.8 (57.5)	19.0 (19.4)	16.0 (15.6)
ω_i(CCSD(T)/ANO4321) + ν_i − ω_i(B97-1/TZ2P)				12.2[d] (11.3,9.4[e])	63.5 (64.5)	20.1 (20.3)	11.0 (10.2)

[a] For RMS deviations, values in parentheses are exclusive of C−H stretching frequencies. [b] These assignments swapped based on IRM and our calculations. [c] Band affected by Fermi resonance. [d] Reassigning mode 1−3090 cm^{-1}. [e] Excluding also mode 17.

frequencies). This adds yet another stanza to the long litany of rejoinders in the literature (e.g., ref 70) against the practice of correlating inner-shell electrons in basis sets unsuitable for the purpose.

We have recalculated the harmonic frequencies at the CCSD(T) level (frozen core) with basis sets of *spdf* quality, specifically Dunning's popular cc-pVTZ[71] and the Almlöf-Taylor atomic natural orbital[72] basis set used in ref 46 for benzene. The CCSD(T)/cc-pVTZ and CCSD(T)/ANO4321 frequencies (Table 13) are in excellent agreement with each other, the largest difference being 6 cm^{-1} for the lowest frequency (ω_{18}). (This is very unlike the case of benzene,[46] where the two b_{2g} modes are hypersensitive to the basis set and differ significantly even between cc-pVTZ and ANO4321.) The two corresponding modes in *s*-tetrazine display appreciable differences between 6-311G* and cc-pVTZ but barely between cc-pVTZ and ANO4321. In contrast, the CCSD(T)/6-311G** frequencies differ significantly from both data sets, particularly for the two b_{2g} modes (39 and 33 cm^{-1} wrt. ANO4321), followed by the lowest b_{2u} mode (aka 'Kekulé mode', 27 cm^{-1}) and the a_u mode (25 cm^{-1}, but a relative error of 7%). So even for a valence-only CCSD(T) calculation, the 6-311G** basis set is insufficient, and the RMS deviation from the CCSD(T)/ANO4321 results, 16.4 cm^{-1} (17.3 when excluding the C−H stretching frequencies), is comparable to that of the much more cost-effective B97-1 calculations, 18.1 (15.1) cm^{-1}.

Turning now to the B97-1/TZ2P harmonic frequencies, the most notable differences with the CCSD(T)/ANO4321 data are for the CH stretches (underestimates of 34 cm^{-1} for both) and the Kekulé mode (overestimated by 37 cm^{-1}). Possibly, self-interaction error would adversely affect[73] the presently used functional's description of the potential surface along the Kekulé mode, and it would be interesting to see how a self-interaction corrected functional would perform. Unfortunately, no implementation of such a functional is available to the authors, let alone an implementation including analytical derivatives. Exclusive of this mode and the CH stretches, the RMS deviation between the CCSD(T)/ANO4321 and B97−1/TZ2P frequencies is about 11 cm^{-1}, compared to just 4 cm^{-1} for benzene.

As expect, agreement between B97-1/TZ2P fundamentals and experiment is likewise compromised (Table 14). We note that *s*-tetrazine is both the least stable and the most "inorganic" molecule of the series and that it has a low-lying excited state at less than 2 eV.[25] If we combine the CCSD(T)/ANO4321 harmonic frequencies with the B97-1/TZ2P anharmonic corrections, the picture brightens somewhat. Compared to the assignment of IRM,[29] the RMS deviation amounts to 9.8 cm^{-1} if the symmetric C−H stretch is excluded. The peculiarly large splitting of 76 cm^{-1} between IRM's symmetric and asymmetric CH stretches is impossible to reconcile with any of our calculations, all of which suggest a very small splitting on the order of just 3 cm^{-1}, in agreement with the earlier film IR and Raman study of Sigworth and Pace (SP).[74] (Their band origin of 3089 cm^{-1} for the symmetric CH stretch is quite compatible with our calculations: IRM's value of 3010 cm^{-1} was taken from single-vibronic-level fluorescence spectra.[75] An older gas-phase study by Franks, Merer, and Innes (FMI)[76] found both CH stretches at 3090 cm^{-1}; the symmetric one in the IR, the antisymmetric one in the Raman spectrum.) Our calculations do not reveal a resonance interaction affecting ν_1 that is severe enough to make a large CH symmetric/antisymmetric spllitting plausible. We hence conclude that ν_1 of IRM is erroneous.

One other IRM assignment which is difficult to reconcile with our best calculations concerns the highest b_{3u} mode (calculated, 902; IRM, 929 cm^{-1}) for which the FMI[76] value of 904 cm^{-1} nearly perfectly matches our calculation. It would appear that even the somewhat degraded performance, exhibited by our model for this molecule, still ought to be quite useful for resolving assignment issues or guiding high-resolution spectroscopic measurements.

IV. Conclusions

We have assessed the performance of modern density functional theory (particularly, B97-1/TZ2P) for the anharmonic vibrational spectra of a series of related medium-sized molecules. The C−H stretching frequencies are consistently underestimated by about 20−30 cm^{-1}; disregarding them, the level of agreement with experiment that can be achieved is quite astonishing (on the order of 6 cm^{-1} RMS deviation for fundamentals). Somewhat poorer accuracy is achieved for pyridazine and particularly for *s*-tetrazine. For several systems (particularly 1,2,3-triazine), our calculations strongly suggest revised assignments of the observed frequencies. For pyridazine, unfortunately, the experimental results are mutually contradictory and our analysis inconclusive. For *s*-tetrazine, basically all predicted fundamentals agree less well with experiment; the more "inorganic" character of the molecule may have adversely affected the performance of our calculations. Nevertheless, even here a RMS deviation of about 15 cm^{-1} for DFT and 10 cm^{-1} for the combined CCSD(T)/DFT results is obtained.

Overall, B97-1/TZ2P quartic force fields combined with second-order rovibrational perturbation theory shows great promise for the assignment of vibrational spectra of medium-sized organic molecules.[82]

Acknowledgment. A.D.B. is grateful for financial support from the Feinberg Graduate School. This research was supported by the Lise Meitner-Minerva Center for Computational Quantum Chemistry, of which J.M.L.M. is a member, and the Helen and Martin A. Kimmel Center for Molecular Design.

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