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Extrapolation of water and formaldehyde harmonic and anharmonic frequencies to the B3LYP/CBS limit using the polarization consistent basis sets

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Abstract

Formaldehyde and water harmonic and anharmonic frequencies of fundamental vibrations were successfully estimated in the B3LYP Kohn-Sham limit. The obtained results with polarization- and correlation-consistent basis sets were fitted with two-parameter formula. Anharmonic corrections have been obtained by a second order perturbation treatment (PT2). On the title two molecules we compare the performance of PT2 scheme using SCF, MP2 and DFT (BLYP, B3LYP, PBE and B3PW91 functionals) methods combined with polarization consistent pc-n ($n = 0, 1, 2, 3, 4$) basis sets, Dunning's basis sets (aug)-cc-pVXZ where X=D, T, Q, 5, 6 and Pople's basis sets up to 6-311++G(3df,2pd). The influence of SCF convergence level and density grid size on RMS of harmonic and anharmonic frequency deviations from experimental values was tested. The wavenumber of formaldehyde CH₂ anharmonic asymmetric stretching mode is very sensitive to grid size for large basis sets, this effect is not observed for harmonic modes. BLYP calculated anharmonic frequencies consistently underestimate observed wavenumbers. On the basis of formaldehyde anharmonic frequencies it is shown that sometimes the increase of Pople basis set size does not warrant improved agreement of anharmonic frequencies with experimental values.

Keywords Harmonic · Anharmonic · Complete basis set limit · CBS · IR and Raman theoretical spectra

Introduction

Apart from NMR technique, IR and Raman vibrational spectroscopies are the two most often used analytical techniques for chemical characterization of small, medium and large size chemicals and their mixtures. In addition, changes in vibrational frequencies are used to study strong and weak inter- and intramolecular interactions (hydrogen bonds, association and aromatic stacking) and chemical reactions. For example, accurate knowledge of spectrum-molecular structure relationship is important in DNA and enzymatic studies, as well as in biochemistry and pharmacology. It is obvious that theoretical predictions should provide reliable frequencies and band intensities in order to support analysis of observed vibrational spectra.

Vibrational frequencies (wavenumbers) predicted theoretically at SCF, DFT and MP2 levels of calculations are overestimated due to anharmonicity effect [1]. This effect is most severe (over 10%) in case of SCF predicted C-H, N-H and O-H stretching vibrations. To date, almost 4000 papers cite the first study, in which a simple remedy proposed cured the theory deficiency by the use of scaling factors [2]. Thus, scaled theoretical wavenumbers [2-4] are used to reliably compare predicted IR and Raman spectral numbers with experiment (we will not discuss here scaling of individual force constants). The uncertainties of combinations of 40 methods and basis sets have been studied [5]. Estimation of empirical scaling factors from analysis of numerous compounds and their fundamental vibrations is a very tedious work [2]. Obviously, there are still some inherent errors in the proposed scaling factors. For example, HF scaled frequencies show less uncertainty than the corresponding MP2 ones [5, 6]. The most often used approach is based on a single scaling factor while more sophisticated studies use individual scaling of low and high frequencies, as well as for individual modes (for example $\nu(\text{C}=\text{O})$, $\nu(\text{OH})$, $\nu(\text{CH})$).

Structural and vibrational parameters predicted by theoretical methods depend on the level of theory, inclusion of correlation effect and the completeness of the used one-electron basis set. For practical reasons, density functional theory, DFT [7-9] including some degree of electron correlation is the best compromise between accuracy and size of the molecular system studied and B3LYP is a typical choice of density functional.

Among the high number of basis sets available, the so-called Pople ones, though fairly old, are robust and relatively small. Sometimes, they reproduce very well experimental

parameters. However, there is no regular change of energy toward the complete basis set limit (CBS) calculated with the Pople basis sets. Dunning and coworkers [10-13] utilized the idea of smooth and regular converging energy toward the complete basis set limit (CBS) for constructing correlation-consistent basis set hierarchies ((aug)-cc-pVXZ, where X = D, T, Q, 5 and 6). Thus, the CBS energy, and some other structural and spectral parameters were estimated using simple 2- and 3-parameter formulas. Obviously, the most accurate results were obtained for larger X (Q, 5 and 6). Later, Jensen [14-19], and also Jorge [20] designed other families of converging basis sets. In particular, Jensen's polarized-consistent basis sets pc-n, where n = 0, 1, 2, 3 and 4 seem to converge faster than Dunning's ones, while reproducing the calculated parameters in the SCF, DFT, MP2 and CCSD(T) basis set limits [21, 22].

There were several recent benchmark studies on coupled cluster (CC) predicted geometry and vibrational frequencies of selected small molecules using the correlation-consistent basis sets [23-25]. In fact, the frequencies of water [25, 26] and formaldehyde [25] have been very well reproduced using high level calculations. Unfortunately, the CC methodology is prohibitively expensive for larger molecules. However, the new, less popular and more affordable pc-n basis sets were not employed in such benchmark tests. Besides, there is an open question about Kohn-Sham limiting values of vibrational frequencies obtained using harmonic and anharmonic models.

In this study we will address the problem of accuracy of water and formamide calculated harmonic and anharmonic vibrational frequencies in the gas phase using Pople vs. Jensen's and Dunning's basis sets and the convergence of individual results toward B3LYP complete basis set limit. In addition, the accuracy of density grid on calculated harmonic and anharmonic frequencies will be tested. Water and formaldehyde were selected as simple model molecules for our study. Their harmonic and anharmonic frequencies in the gas phase are well known. Several works comparing theoretical and experimental vibrational spectra of these molecules have been published [25-29]. Moreover, their structural and vibrational parameters are modified by intermolecular interactions, including solute-solvent ones. Thus, the conclusions of current studies will be helpful in our detailed studies on amides and small polypeptides in the gas phase and solution.

Therefore, in this work we will test the performance of a typical, easy to compute harmonic model, and a more computationally demanding anharmonic method. Both methods are

available in Gaussian 09 [30] and other software packages. We will also apply an empirical (single or global) scaling factor to harmonic frequencies and compare the obtained results with experimental and earlier reported wavenumbers.

Theoretical calculations

All calculations were performed using the Gaussian 09 program [30] and some results were confirmed using Gaussian 03 [31].

Basis sets and density functionals

Pople's 3-21G, 6-31G, 6-31G*, 6-311++G** and 6-311++G(3df,2pd), Jensen's pc-n polarized-consistent, and Dunning's (aug)-cc-pVXZ basis sets were used. Efficient B3LYP density functional was selected, and for comparison purposes, some calculations were also performed at RHF and MP2 levels. Besides, several other common DFT methods were selected (BLYP, B3PW91 and PBE). The pc-n basis sets were downloaded from EMSL [32].

Geometry

Fully optimized geometries of water and formaldehyde in the gas phase were obtained using default and very tight convergence criteria for each method and basis set selected. All positive harmonic vibration frequencies were obtained ensuring ground state structures.

Harmonic and anharmonic vibration calculations

The calculations were carried out in the gas phase (vacuum) using the VPT2 method as implemented by Barone [33, 34] in Gaussian program package. In several cases the finest DFT integration grid was selected by using in the command line SCF=tight and Int(Grid=150590) instead of Int(Grid=ULTRAFINE) keyword. The use of such fine grid is critical in case of indirect spin-spin coupling constants calculations with tailored basis sets [35, 36].

CBS calculations

The harmonic and anharmonic frequencies, $Y(x)$, were calculated using polarization-consistent pc-n basis sets, where $n = 0, 1, 2, 3$ and 4 , and the correlation-consistent (aug)-cc-pVXZ basis sets, where $X = D, T, Q, 5$ and 6 , and subsequently extrapolated to the B3LYP CBS limit, $Y(\infty)$, by fitting the results to two-parameter functions [37]:

$$Y(X) = Y(\infty) + A/X^3 \quad (1)$$

The extrapolated value $Y(\infty)$ corresponds to the best estimate of the predicted property for infinite zeta (or cardinal number “X”), where A and $Y(\infty)$ are fitted parameters. In case of Jensen’s pc-n basis sets, $X = n + 2$ for graphical fitting purposes only was assumed [21, 38]. All the fittings were performed with two-parameter formula (Eq. 1), in several cases enabling exact fitting of only two data points. Since smaller values of “X” and “n” yield results (frequencies in this study) more corrupted by errors due to basis set imperfections, the CBS values are often estimated using higher cardinal numbers. For example, CBS(4,5,6) indicates estimation using $X = Q, 5$ and 6 , or $n = 2, 3$ and 4 , respectively.

Scaling factors

Single scaling factors were used for low and high frequencies. There are three fundamental studies [2-4] on scaling factors used in frequency and ZPV calculations. Evaluation of scaling factors is a very laborious work and therefore, despite the presence of myriads of methods and basis sets, only several scaling factors are available in the literature. In particular, scaling of results obtained with recently introduced Jensen’s basis sets and very large Dunning’s basis sets are lacking. Thus, in several cases we arbitrary used the values for similar basis sets. For the convenience of the reader, all the used scaling factors in our work are collected in one table (Table S1 in the supporting material).

Results and discussion

In Fig. 1 are shown B3LYP calculated harmonic and anharmonic frequencies of water modes as function of selected Pople and Jensen basis set size. For $\delta(\text{HOH})$ mode the wavenumbers predicted with Pople basis sets behave irregularly and the increase of the basis set size

(compare 6-31G and 6-31G*) does not warrant better prediction of this water vibration. On the other hand, the results obtained with Jensen basis sets change more regularly. Thus, we used formula 1 to fit the results of both harmonic and anharmonic frequencies for $n = 2, 3$ and 4 toward the basis set limit. The limiting values (CBS(harm) and CBS(anharm)) are shown in Fig. 1 as straight dashed lines and compared with experimentally observed results in the gas phase (straight solid line). Usually we observe a significantly less sensitivity of wavenumbers on the size and completeness of pc-n basis set hierarchy as compared to Pople basis sets. Moreover, one can notice a significant smaller deviation from experiment for CBS estimated anharmonic with respect to harmonic frequencies. For example, these values for water OH asymmetric stretch mode are -34 vs. 143 cm^{-1} , respectively (Fig. 1). B3LYP predicted formaldehyde vibrational modes show similar dependence on the basis set type and size (Fig. 2).

One could expect that in case of numerical calculations of anharmonic frequencies, the quality of results could be influenced by the accuracy of density grid, similarly as for indirect spin-spin coupling constant [36, 39]. Detailed analysis of water and formaldehyde B3LYP frequency deviation from experimental values [40, 41], calculated with Pople and polarization-consistent basis sets, is shown in Table 1 and 2 respectively. Both harmonic and anharmonic deviations of water individual stretching and deformation modes are compared with deviations from simple scaling of harmonic values for different basis sets. In addition, as some general measure of calculation accuracy, the standard deviation values (RMS) are shown. In the top of Table 1 the results obtained for default optimization and frequency conditions are gathered (keywords OPT, Freq=anharm) and compared with results calculated using very accurate density grid (keywords OPT=tight, Freq=anharm, SCF=tight, INT(GRID=150590)). In the upper half of Table 1 we gathered the results for selected Pople basis sets, and in the bottom half the corresponding values obtained with Jensen's basis sets and the final CBS values. Similar results obtained for formaldehyde are presented in the same way in Table 2. First, it is evident from Table 1 that there is no impact of grid size on accuracy of water frequency prediction for both Pople and Jensen's basis sets. However, in case of high frequency formaldehyde anharmonic vibrations ($\nu_{\text{asym}}(\text{CH}_2)$ in Table 2) this has a significant impact for two largest Pople (6-311++G** and 6-311++G(3df,2pd)) and Jensen's basis sets ($n = 1, 2, 3$ and 4 as well as CBS). Thus, more accurate density grid is important for improving formaldehyde anharmonic frequency accuracy. On the contrary, the formaldehyde harmonic frequencies do not change upon changing grid size.

There is no clear dependence of Pople basis set size on RMS deviations of harmonic and anharmonic frequencies. For example, the 6-31G basis set predicts relatively well water harmonic frequencies, as opposed to anharmonic ones. In contrary, a reversed performance of the same basis set (6-31G) is observed in case of formaldehyde. Thus, we should treat such behavior as result of accidental error cancelation. In other words, vibrational analysis using small basis sets is unreliable due to basis set incompleteness. For larger Pople basis sets an improvement in prediction of water anharmonic frequencies is observed. Thus, for 6-311++G(3df,2pd) basis set the corresponding anharmonic and harmonic RMS deviations of 17 vs. 139 cm^{-1} are observed. This is also clearly visible in Fig. 1. In case of Jensen's basis set, starting from $n = 2$, water anharmonic frequencies are predicted significantly better than harmonic ones (RMS deviations of 23 vs. 129 cm^{-1} for pc-2). Moreover, the RMS values for anharmonic water frequencies predicted with Pople basis sets (except for 6-311++G(3df,2pd)) are larger than with pc-n basis set.

The use of simple harmonic frequency scaling leads to fairly accurate water wavenumbers. The accuracy of scaled water wavenumbers is similar to anharmonic results for the studied Pople and Jensen's basis sets (Table 1), and for formaldehyde scaled harmonic frequencies are often even closer to the experimental values than the anharmonic ones (Table 2).

Next, water and formaldehyde harmonic and anharmonic wavenumbers were calculated with Dunning's cc-pVXZ and aug-cc-pVXZ basis sets. The results are very similar to those obtained earlier with Jensen's basis sets (see Figs. S1 – S4 in the supplementary material), and the corresponding deviations from experimental values are gathered in Table S2 and S3. Similarly to results in Table 1, there is no dependence of grid size on water frequencies predicted with both Dunning's basis set series (Table S2). However, in case of formaldehyde, similarly to results obtained with Jensen's basis set family (Table 2), the improvement of grid size used in conjunction with larger Dunning's basis sets (cc-pVXZ for $X = 5$ and 6, and aug-cc-pVXZ for $X = T, Q$ and 5) leads to over twofold improvement of RMS of anharmonic frequencies, mainly due to better description of CH_2 asymmetric stretching. Moreover, in all cases the scaled harmonic frequencies for formaldehyde are significantly closer to experiment than the corresponding anharmonic values (Table S3) and are comparable for water (Table S2).

The CBS values obtained with Jensen's and Dunning's basis set families are very similar for both molecules. However, it is important to note that Jensen's basis sets allow significantly

faster calculations than Dunning ones. The dependence of CPU time necessary for VPT2 calculations with pc-n, cc-pVXZ and aug-cc-pVXZ basis sets in case of formaldehyde is presented in Fig. 3. For example, the CPU time for formaldehyde anharmonic calculations using cc-pV6Z and pc-4 basis sets with the same computer resources and configuration was 16 vs. 2.5 days, respectively. Similar patterns of CPU timing are observed for water (Fig. S5). In addition, the advantage of using polarization- instead of correlation-consistent basis sets is getting more important for larger molecules.

In the next step we tested the performance of several methods (RHF, MP2, B3LYP, BLYP, B3PW91 and PBE) in predicting anharmonic frequencies of water and formaldehyde at different Jensen's basis set sizes (pc-2 and pc-4) and compared with two often used Pople's basis sets (6-31G and 6-311++G**). The obtained results for water harmonic and anharmonic frequency deviations from experiment are shown in Table 3 and similar data for formaldehyde in Table 4. Contrary to earlier discussed formaldehyde anharmonic results obtained from B3LYP calculations, there was no influence of grid size on water and formaldehyde anharmonic deviations at BLYP, B3PW91 and PBE level. Therefore, only results for large grid and tight SCF convergence criteria are presented in Tables 3 and 4. However, for the sake of comparison, all results are presented in Tables S4 – S7.

In case of RHF calculations, both harmonic and anharmonic frequencies (these are considerably better) obtained with both Pople and Jensen's basis sets significantly overestimate experimental water and formaldehyde frequencies. MP2 anharmonic values obtained for 6-31G basis set for water and formaldehyde are not very accurate and the increase of basis set size significantly improves the results. On the other hand, the MP2 calculations are extremely expensive and feasible for very small molecules only. Water harmonic values obtained at BLYP/6-31G level underestimate experimental frequencies and anharmonic calculation using PT2 method leads to their severe underestimation. Accidental error cancellation leads to very accurate BLYP calculated water harmonic frequencies but the corresponding anharmonic values are too low (Table 3). In case of formaldehyde, harmonic frequencies calculated at BLYP level using larger basis sets are fairly accurate while the corresponding anharmonic values are too small. Hence, paradoxically, formaldehyde anharmonic vibrations calculated at BLYP level with larger basis sets show worse RMS values. In case of B3PW91 and PBE density functionals similar improvements to those, observed for B3LYP are obtained in case of formaldehyde anharmonic frequencies for larger basis sets (Table 3 and 4). However, one has to notice that contrary to B3LYP, very good

anharmonic results for formaldehyde are obtained by using the default grid size with B3PW91 and PBE density functionals (see Tables S6 and S7). This makes B3LYP a more expensive DFT method of anharmonic calculations for some molecules. Therefore, to get a more general insight, similar studies on accuracy and reliability of VPT2 method in predicting fundamental vibrations for a larger set of model molecules are planned.

Conclusions

In this paper, for the first time, we showed the convergence of harmonic and anharmonic (calculated using VPT2 method) water and formaldehyde frequencies toward the B3LYP/pc-n and B3LYP/(aug)-cc-pVXZ complete basis set limits.

1. The convergence of harmonic and anharmonic frequencies with respect to basis set size shows that pc-n basis sets consistently perform better than Pople ones. Both correlation-consistent and polarization consistent basis sets enable obtaining essentially the same CBS values of harmonic and anharmonic frequencies. However, the CPU time for calculations using cc-pVXZ basis sets is significantly longer than with the corresponding pc-n ones. The deviations of CBS values for harmonic frequencies are significantly larger than the corresponding anharmonic numbers (RMS of 119 vs. 24 cm^{-1} in case of water frequencies calculated using B3LYP/pc-n, and 62 vs. 32 cm^{-1} in case of formaldehyde frequencies). However, RMS deviations after simple scaling of harmonic frequencies are in most cases smaller and easier to obtain (39 and 16 cm^{-1} , for water and formaldehyde respectively). On the other hand, there are no available scaling factors for Jensen's basis set yet. Thus, only arbitrary scaling factors were used for harmonic frequencies calculated with polarization-consistent basis sets.
2. There is no point of using VPT2 method in conjunction with RHF and BLYP methods (first values are far too high and for the second method the anharmonic frequencies are too low).
3. The optimization criteria and density grid size has negligible effect on harmonic frequencies of water and formaldehyde, but it could significantly influence the corresponding anharmonic vibrations. For example, in more demanding calculations (OPT=very tight, SCF=tight and INT(GRID=150590), the B3LYP calculated formaldehyde anharmonic frequencies with large basis sets are significantly closer to experimental values.

The anharmonic frequencies depend on many points on the PES away from the equilibrium and the applied method of calculation should produce very smooth PES (with constant errors). Therefore it could explain the high sensitivity of formaldehyde anharmonic frequencies to grid size in contrary to harmonic vibrations. In case of default grid size (sparse points) energy variations are not smooth and could lead to significant changes in anharmonic frequencies. On the basis of the results obtained in this study we want to stress the need of future studies in this field.

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Supporting material

Additional figures (convergence of water and formaldehyde harmonic and anharmonic frequencies as well as CPU timing for water) and tables (applied scaling factors and the influence of grid size and SCF convergence criteria on harmonic and anharmonic frequency deviations) are gathered in supporting material. This material is made available free of charge via the Internet at <http://pubs.acs.org>.

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Tables

Table 1 Deviations of water B3LYP harmonic (Δ_{harm}), anharmonic (Δ_{anh}) and scaled harmonic (Δ_{scal}) frequencies [cm^{-1}] calculated with selected Pople and Jensen's basis sets from the experimental values

mode	exp. ^a	3-21G			6-31G			6-31G*			6-31+G**			6-311++G**			6-311++G(3df,2pd)		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
computation criteria: opt freq=anharm																			
$\nu_{\text{as}}(\text{OH})$	3756	-200	-373	-338	25	-173	-121	93	-102	-56	175	-6	37	166	-18	43	169	-18	46
$\nu_{\text{s}}(\text{OH})$	3657	-242	-351	-374	-41	-215	-181	70	-102	-74	152	-13	18	160	-12	40	168	-6	48
$\delta(\text{HOH})$	1595	98	125	32	24	-31	-39	118	64	52	8	-41	-48	8	-39	-43	33	-22	-19
<i>RMS</i>		190	304	292	31	160	127	96	91	61	134	25	37	133	26	42	139	17	40
computation criteria: opt=tight scf=tight INT(Grid=150590) freq=anharm																			
$\nu_{\text{as}}(\text{OH})$	3756	-201	-368	-338	27	-174	-120	94	-100	-55	176	-12	38	166	-19	43	169	-19	46
$\nu_{\text{s}}(\text{OH})$	3657	-242	-345	-374	-40	-217	-180	71	-102	-73	153	-20	19	160	-13	40	168	-8	48
$\delta(\text{HOH})$	1595	98	127	32	24	-34	-39	118	68	52	8	-43	-48	8	-39	-43	33	-22	-18
<i>RMS</i>		190	300	292	31	162	127	96	91	61	135	28	37	133	26	42	139	17	40
mode	exp.	pc-0			pc-1			pc-2			pc-3			pc-4			CBS ^b		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
computation criteria: opt freq=anharm																			
$\nu_{\text{as}}(\text{OH})$	3756	50	-157	-61	126	-70	6	159	-24	38	153	-27	55	153	-27	55	144	-31	46
$\nu_{\text{s}}(\text{OH})$	3657	-37	-224	-143	110	-74	-6	154	-15	36	150	-16	55	150	-16	55	143	-18	49
$\delta(\text{HOH})$	1595	-30	-92	-75	33	-22	-17	30	-23	-20	34	-18	-7	34	-18	-6	40	-11	-1
<i>RMS</i>		40	167	99	99	60	11	129	21	33	125	21	45	125	21	45	119	22	39
computation criteria: opt=tight scf=tight INT(Grid=150590) freq=anharm																			
$\nu_{\text{as}}(\text{OH})$	3756	54	-135	-57	126	-67	6	159	-28	38	153	-30	56	153	-30	55	143	-34	46
$\nu_{\text{s}}(\text{OH})$	3657	-34	-203	-140	110	-71	-7	155	-19	37	150	-20	55	150	-20	55	143	-21	49
$\delta(\text{HOH})$	1595	-32	-92	-78	33	-19	-17	30	-23	-20	34	-19	-7	34	-18	-6	40	-12	0
<i>RMS</i>		41	151	98	98	58	11	129	23	33	125	23	45	125	23	45	119	24	39

^a from ref. [40]; ^b estimated for pc-n where n=2,3,4 using Eq. 1

Table 2 Deviations of formaldehyde harmonic (Δ_{harm}), anharmonic (Δ_{anh}) and scaled harmonic (Δ_{scal}) frequencies [cm^{-1}] calculated with selected Pople and Jensen's basis sets from the experimental values

mode	exp. ^a	3-21G			6-31G			6-31G*			6-31+G**			6-311++G**			6-311++G(3df,2pd)		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
computation criteria: opt freq=anharm																			
$\nu_{\text{as}}(\text{CH}_2)$	2843	114	-139	0	192	-23	75	125	-129	11	137	-12	32	99	-167	7	99	-165	6
$\nu_{\text{s}}(\text{CH}_2)$	2782	129	-60	16	182	9	67	135	-31	22	133	-31	30	102	-60	12	102	-58	11
$\nu(\text{CO})$	1745	15	-18	-53	3	-27	-65	105	78	33	74	48	10	70	44	13	77	50	19
$\sigma(\text{CH}_2)$	1500	76	42	15	60	29	0	63	29	2	37	3	-17	31	-1	-17	32	-1	-16
$\rho(\text{CH}_2)$	1250	31	4	-19	24	2	-25	30	9	-20	13	-8	-32	10	-10	-30	16	-5	-23
$\tau(\text{CH}_2)$	1167	53	26	6	36	16	-11	31	12	-15	26	8	-16	35	14	-3	34	16	-4
<i>RMS</i>		81	65	25	112	20	50	92	64	20	86	24	24	68	75	16	69	74	15
computation criteria: opt=tight scf=tight INT(Grid=150590) freq=anharm																			
$\nu_{\text{as}}(\text{CH}_2)$	2843	113	-132	-2	190	5	72	125	-124	10	134	-9	29	98	-29	6	95	-29	3
$\nu_{\text{s}}(\text{CH}_2)$	2782	128	-52	15	179	16	64	134	-23	22	130	-25	27	101	-50	11	99	-51	8
$\nu(\text{CO})$	1745	15	-17	-53	2	-28	-65	105	78	33	74	47	10	69	44	12	76	49	18
$\sigma(\text{CH}_2)$	1500	76	43	15	60	28	-1	63	29	2	37	3	-17	31	-1	-17	33	-1	-16
$\rho(\text{CH}_2)$	1250	31	6	-19	25	2	-24	30	9	-20	13	-8	-32	10	-9	-30	17	-5	-23
$\tau(\text{CH}_2)$	1167	52	29	5	36	16	-11	31	12	-15	27	8	-15	35	14	-3	35	17	-3
<i>RMS</i>		80	62	25	111	19	49	92	62	20	84	23	23	67	30	16	67	32	14
mode	exp.	pc-0			pc-1			pc-2			pc-3			pc-4			CBS		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
computation criteria: opt freq=anharm																			
$\nu_{\text{as}}(\text{CH}_2)$	2843	176	-69	88	108	-162	17	102	-163	11	96	-165	23	96	-166	23	87	-170	14
$\nu_{\text{s}}(\text{CH}_2)$	2782	198	6	111	110	-58	21	105	-58	16	101	-59	29	101	-60	29	94	-63	23
$\nu(\text{CO})$	1745	-28	-60	-78	87	60	30	72	45	16	72	45	26	72	45	26	71	44	26
$\sigma(\text{CH}_2)$	1500	30	-4	-15	32	-1	-15	34	1	-13	33	0	-5	33	-1	-6	30	-3	-8
$\rho(\text{CH}_2)$	1250	-21	-39	-56	15	-5	-24	18	-4	-21	18	-4	-14	18	-4	-14	18	-4	-14
$\tau(\text{CH}_2)$	1167	13	-5	-21	22	5	-15	37	17	0	34	16	4	33	15	3	27	11	-2
<i>RMS</i>		110	41	71	74	74	21	70	73	14	67	74	20	67	74	19	63	76	17
computation criteria: opt=tight scf=tight INT(Grid=150590) freq=anharm																			
$\nu_{\text{as}}(\text{CH}_2)$	2843	173	-59	85	107	-25	16	101	-26	10	95	-29	22	95	-29	22	87	-33	14
$\nu_{\text{s}}(\text{CH}_2)$	2782	196	18	109	109	-48	20	103	-49	14	99	-51	28	99	-51	27	93	-54	22
$\nu(\text{CO})$	1745	-28	-60	-78	87	61	30	71	45	15	71	45	26	71	44	26	70	44	25
$\sigma(\text{CH}_2)$	1500	30	-3	-15	32	-1	-15	34	1	-13	33	-1	-5	32	-1	-6	30	-4	-8
$\rho(\text{CH}_2)$	1250	-21	-38	-57	15	-5	-24	18	-4	-21	18	-4	-13	18	-4	-14	18	-4	-14
$\tau(\text{CH}_2)$	1167	14	-3	-21	22	4	-14	37	18	0	33	15	4	33	15	3	27	11	-3
<i>RMS</i>		108	38	70	74	33	21	69	30	14	66	31	19	66	31	19	62	32	16

^a from ref. [41]; ^b estimated for pc-n where n=2,3,4 using Eq. 1

Table 3 Deviations of water harmonic (Δ_{harm}), anharmonic (Δ_{anh}) and scaled harmonic (Δ_{scal}) frequencies [cm^{-1}] calculated with different methods and Pople or Jensen's basis sets from the experimental values

mode	exp. ^a	RHF/6-31G			RHF/6-311++G**			MP2/6-31G			MP2/6-311++G**			B3LYP/6-31G			B3LYP/6-311++G**		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$v_{\text{as}}(\text{OH})$	3756	389	200	-45	489	316	95	77	-131	-137	247	62	74	27	-174	-120	166	-19	43
$v_{\text{s}}(\text{OH})$	3657	332	160	-86	486	324	102	0	-189	-205	228	50	60	-40	-217	-180	160	-13	40
$\delta(\text{HOH})$	1595	142	75	-40	131	81	-29	68	6	-25	34	-17	-37	24	-34	-39	8	-39	-43
<i>RMS</i>		<i>306</i>	<i>154</i>	<i>61</i>	<i>405</i>	<i>265</i>	<i>82</i>	<i>59</i>	<i>133</i>	<i>143</i>	<i>195</i>	<i>47</i>	<i>59</i>	<i>31</i>	<i>162</i>	<i>127</i>	<i>133</i>	<i>26</i>	<i>42</i>
B3PW91/6-311++G**																			
mode	exp.	BLYP/6-31G			BLYP/6-311++G**			B3PW91/6-31G			B3PW91/6-311++G**			PBE/6-31G			PBE/6-311++G**		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$v_{\text{as}}(\text{OH})$	3756	-147	-349	-169	23	-169	21	74	-126	-90	202	18	65	102	-96	53	231	49	211
$v_{\text{s}}(\text{OH})$	3657	-212	-386	-233	17	-163	15	4	-173	-153	194	21	60	33	-144	-14	222	51	202
$\delta(\text{HOH})$	1595	-3	-57	-12	-24	-70	-25	27	-32	-43	10	-36	-46	34	-25	13	15	-31	7
<i>RMS</i>		<i>149</i>	<i>302</i>	<i>166</i>	<i>21</i>	<i>142</i>	<i>20</i>	<i>45</i>	<i>125</i>	<i>106</i>	<i>162</i>	<i>26</i>	<i>57</i>	<i>65</i>	<i>101</i>	<i>33</i>	<i>185</i>	<i>44</i>	<i>169</i>
B3LYP/pc-2 and B3LYP/pc-4																			
mode	exp.	RHF/pc-2			RHF/pc-4			MP2/pc-2			MP2/pc-4			B3LYP/pc-2			B3LYP/pc-4		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$v_{\text{as}}(\text{OH})$	3756	483	305	108	475	302	99	235	45	65	215	31	66	159	-28	38	153	-30	55
$v_{\text{s}}(\text{OH})$	3657	481	316	114	473	313	106	210	33	46	189	15	44	155	-19	37	150	-20	55
$\delta(\text{HOH})$	1595	149	92	-6	153	97	-2	43	-12	-26	42	-13	-19	30	-23	-20	34	-18	-6
<i>RMS</i>		<i>403</i>	<i>259</i>	<i>91</i>	<i>397</i>	<i>258</i>	<i>84</i>	<i>184</i>	<i>33</i>	<i>48</i>	<i>167</i>	<i>21</i>	<i>47</i>	<i>129</i>	<i>23</i>	<i>33</i>	<i>125</i>	<i>23</i>	<i>45</i>
B3LYP/pc-2 and B3LYP/pc-4																			
mode	exp.	BLYP/pc-2			BLYP/pc-4			B3PW91/pc-2			B3PW91/pc-4			PBE/pc-2			PBE/pc-4		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$v_{\text{as}}(\text{OH})$	3756	16	-178	13	11	-179	9	195	9	57	187	6	50	221	37	201	214	34	194
$v_{\text{s}}(\text{OH})$	3657	11	-168	9	9	-167	7	188	16	54	182	13	48	214	44	194	209	41	188
$\delta(\text{HOH})$	1595	-1	-53	-2	3	-49	2	32	-21	-25	36	-16	-20	35	-17	27	40	-12	32
<i>RMS</i>		<i>11</i>	<i>144</i>	<i>9</i>	<i>8</i>	<i>144</i>	<i>7</i>	<i>157</i>	<i>16</i>	<i>48</i>	<i>152</i>	<i>12</i>	<i>42</i>	<i>179</i>	<i>35</i>	<i>162</i>	<i>174</i>	<i>32</i>	<i>157</i>

^a from ref. [40]

Table 4 Deviations of formaldehyde harmonic (Δ_{harm}), anharmonic (Δ_{anh}) and scaled harmonic (Δ_{scal}) frequencies [cm^{-1}] calculated using different methods and Pople or Jensen's basis sets from the experimental values

mode	exp. ^a	RHF/6-31G			RHF/6-311++G**			MP2/6-31G			MP2/6-311++G**			B3LYP/6-31G			B3LYP/6-311++G**		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$\nu_{\text{as}}(\text{CH}_2)$	2843	457	262	111	326	210	32	263	144	89	204	21	73	191	-15	74	98	-29	7
$\nu_{\text{s}}(\text{CH}_2)$	2782	426	272	90	315	182	28	238	71	69	193	45	65	181	18	66	101	-50	11
$\nu(\text{CO})$	1745	165	135	-35	251	226	66	-65	-107	-159	17	-14	-59	3	-27	-64	69	44	13
$\sigma(\text{CH}_2)$	1500	173	141	-2	150	120	-3	15	-10	-69	59	26	-8	60	28	0	31	-1	-17
$\rho(\text{CH}_2)$	1250	124	103	-20	113	96	-13	34	11	-38	29	8	-26	24	2	-25	10	-9	-29
$\tau(\text{CH}_2)$	1167	162	143	22	169	150	45	30	8	-37	39	19	-13	36	15	-11	35	14	-3
<i>RMS</i>		285	188	61	235	171	37	148	79	87	119	25	48	112	20	50	67	30	16
mode	exp.	BLYP/6-31G			BLYP/6-311++G**			B3PW91/6-31G			B3PW91/6-311++G**			PBE/6-31G			PBE/6-311++G**		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$\nu_{\text{as}}(\text{CH}_2)$	2843	63	-149	46	-13	-260	-15	204	0	73	107	-20	5	228	27	190	128	-1	113
$\nu_{\text{s}}(\text{CH}_2)$	2782	68	-101	51	3	-157	1	192	30	64	109	-40	9	212	52	175	127	-21	112
$\nu(\text{CO})$	1745	-61	-93	-71	-10	-37	-11	13	-17	-62	89	64	25	29	-1	6	107	82	97
$\sigma(\text{CH}_2)$	1500	13	-19	4	-11	-43	-12	63	30	-4	29	-2	-24	69	37	50	32	1	24
$\rho(\text{CH}_2)$	1250	-14	-37	-21	-28	-48	-29	26	4	-29	9	-9	-35	31	9	15	13	-6	6
$\tau(\text{CH}_2)$	1167	-8	-29	-15	-10	-32	-11	37	18	-14	36	15	-6	45	25	30	41	20	35
<i>RMS</i>		46	85	42	15	128	15	119	20	49	75	33	21	133	30	108	88	36	78
mode	exp.	RHF/pc-2			RHF/pc-4			MP2/pc-2			MP2/pc-3			B3LYP/pc-2			B3LYP/pc-4		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$\nu_{\text{as}}(\text{CH}_2)$	2843	321	208	41	312	203	31	233	42	102	216	31	101	101	-26	10	95	-29	22
$\nu_{\text{s}}(\text{CH}_2)$	2782	312	179	38	304	173	30	216	66	89	199	51	87	103	-49	14	99	-51	27
$\nu(\text{CO})$	1745	249	224	72	249	224	72	21	-11	-54	20	-12	-47	71	45	15	71	44	26
$\sigma(\text{CH}_2)$	1500	154	122	8	151	119	4	57	24	-9	47	14	-12	34	1	-13	32	-1	-6
$\rho(\text{CH}_2)$	1250	123	102	1	122	102	0	31	9	-23	26	4	-22	18	-4	-21	18	-4	-14
$\tau(\text{CH}_2)$	1167	174	156	55	170	153	51	45	25	-6	35	17	-11	37	18	0	33	15	3
<i>RMS</i>		235	171	44	230	168	40	134	35	60	123	26	59	69	30	14	66	31	19
mode	exp.	BLYP/pc-2			BLYP/pc-4			B3PW91/pc-2			B3PW91/pc-4			PBE/pc-2			PBE/pc-4		
		Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}	Δ_{harm}	Δ_{anh}	Δ_{scal}
$\nu_{\text{as}}(\text{CH}_2)$	2843	-10	-257	-12	-14	-258	-15	106	-22	3	100	-26	-2	125	-5	109	119	-9	103
$\nu_{\text{s}}(\text{CH}_2)$	2782	6	-154	4	3	-154	2	108	-42	7	103	-44	3	123	-25	108	119	-27	104
$\nu(\text{CO})$	1745	-6	-33	-7	-8	-34	-9	89	63	25	89	61	25	105	80	95	105	79	95
$\sigma(\text{CH}_2)$	1500	-7	-42	-8	-9	-43	-10	30	-4	-24	28	-7	-26	32	0	24	30	-3	22
$\rho(\text{CH}_2)$	1250	-20	-43	-21	-20	-43	-21	15	-7	-29	15	-7	-29	18	-4	11	17	-4	11
$\tau(\text{CH}_2)$	1167	-9	-29	-9	-13	-32	-14	35	16	-7	31	12	-11	41	22	35	37	19	30
<i>RMS</i>		11	126	12	12	127	13	74	33	19	71	33	19	86	35	76	83	35	73

^a from ref. [41]

Figure captions

- Fig. 1** Sensitivity of water B3LYP calculated harmonic and anharmonic frequencies on selected Pople and polarization consistent basis sets size. The results for pc-n basis sets were fitted with Eq. 1 and the CBS(2,3,4) estimated
- Fig. 2** Sensitivity of formaldehyde B3LYP calculated harmonic and anharmonic frequencies on selected Pople and polarization consistent basis sets size. The results for pc-n basis sets were fitted with Eq. 1 and the CBS(2,3,4) estimated
- Fig. 3** CPU time (in minutes) dependence on the type and size of basis set for formaldehyde VTP2 calculation with pc-n, cc-pVXZ and aug-cc-pVXZ basis sets

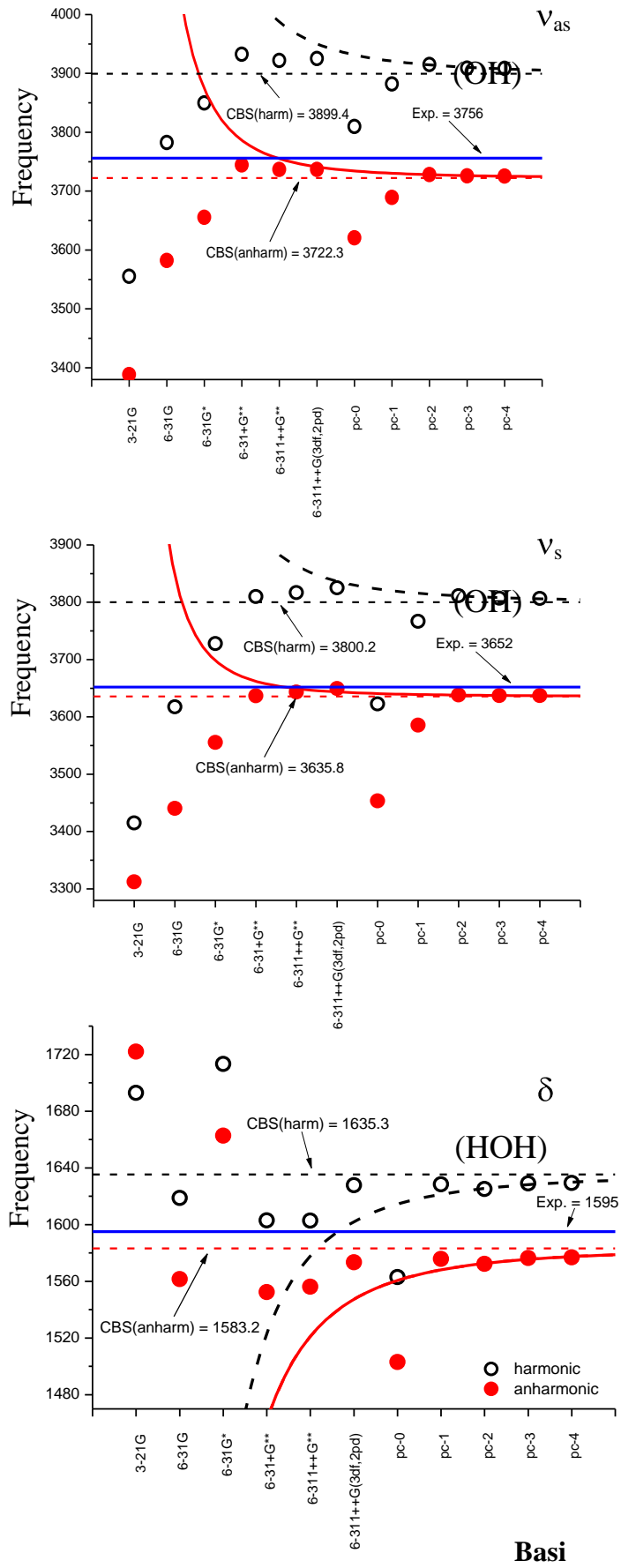


Figure 1

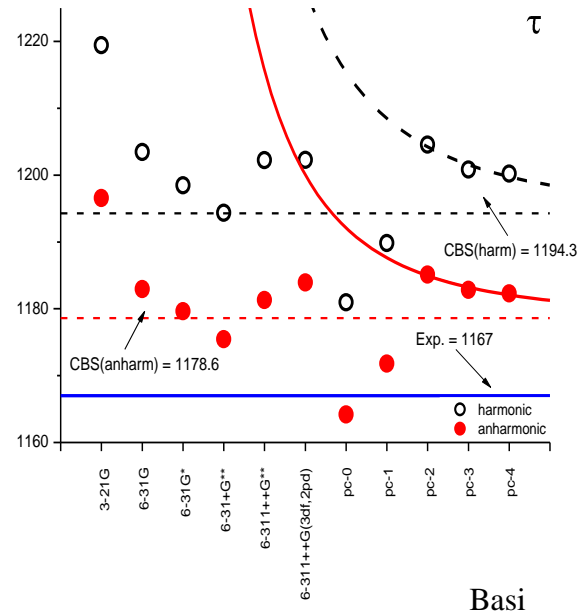
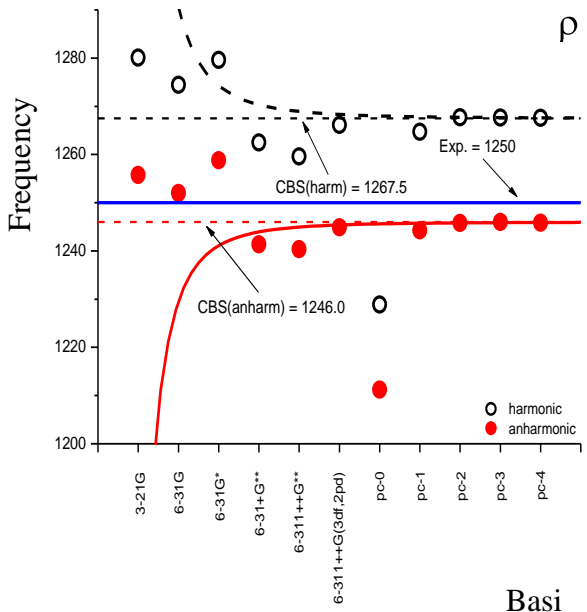
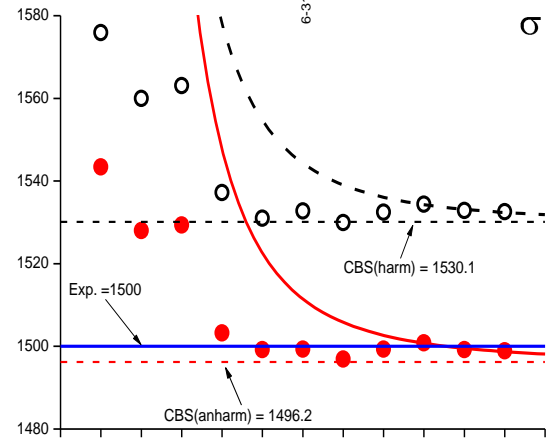
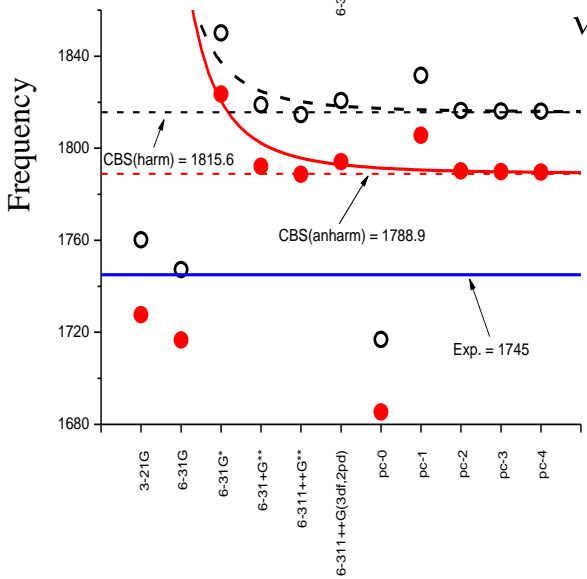
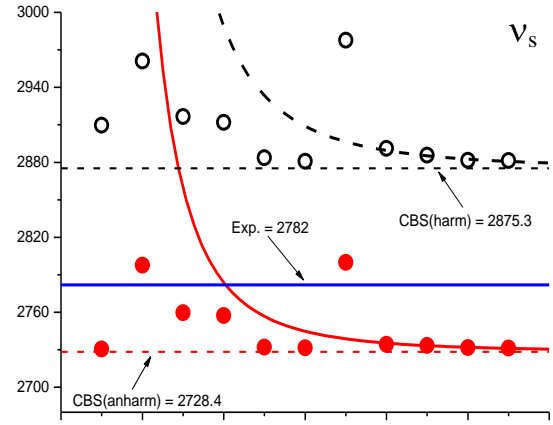
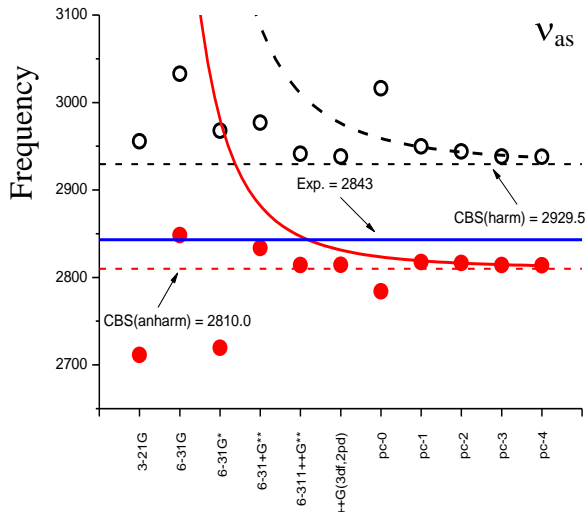


Figure 2

