

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

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**Abstract** The harmonic and anharmonic frequencies of fundamental vibrations in formaldehyde and water were successfully estimated using the B3LYP Kohn-Sham limit. The results obtained with polarization- and correlation-consistent basis sets were fitted with a two-parameter formula. Anharmonic corrections were obtained by a second order perturbation treatment (PT2). We compared the performance of the PT2 scheme on the two title molecules 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 the root mean square of harmonic and anharmonic frequency deviations from experimental values was tested. The wavenumber of formaldehyde CH<sub>2</sub> 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, we show that increasing the Pople basis set size does not always lead to improved agreement between anharmonic frequencies and experimental values.

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

## Introduction

Apart from nuclear magnetic resonance (NMR) techniques, infrared (IR) and Raman vibrational spectroscopies are the two analytical techniques most often used 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. Accurate knowledge of spectrum-molecular structure relationships is important in DNA and enzymatic studies, as well as in biochemistry and pharmacology. It is therefore 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 self-consistent field (SCF), density functional theory (DFT) and second order Møller–Plesset (MP2) levels of calculations are overestimated due to anharmonicity effects [1]. This effect is most severe (over 10%) in the case of SCF predicted C–H, N–H and O–H stretching vibrations. To date, almost 4,000 papers have cited the first study in which a simple remedy was proposed to cure the deficiency in this theory 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 experimental data (we will not discuss scaling of individual force constants here). The uncertainties of combinations of 40 methods and basis sets have been studied [5]. Estimation of empirical scaling factors from

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analysis of numerous compounds and their fundamental vibrations is very tedious work [2]. Obviously, there are still some inherent errors in the proposed scaling factors. For example, Hartree-Fock (HF)-scaled frequencies show less uncertainty than the corresponding MP2 frequencies [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 scaling for individual modes [e.g.,  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{OH})$ ,  $\nu(\text{CH})$ ].

Structural and vibrational parameters predicted by theoretical methods depend on the level of theory, inclusion of correlation effects, and the completeness of the one-electron basis set used. For practical reasons, 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 sets, though fairly old, are robust and relatively small. Sometimes they reproduce experimental parameters very well. However, there is no regular change in energy toward the complete basis set limit (CBS) calculated using Pople basis sets. Dunning and coworkers [10–13] utilized the idea of smooth and regular converging energy toward the 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 with Dunning's sets, while reproducing the calculated parameters in the SCF, DFT, MP2 and coupled cluster, singles and doubles with triples treated approximately [CCSD(T)] basis set limits [21, 22].

Several benchmark studies have been published recently 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, CC methodology is prohibitively expensive for larger molecules. However, the new, less popular but more affordable *pc-n* basis sets were not employed in these 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 the accuracy of calculated harmonic and anharmonic vibrational frequencies for water and formamide in the gas phase using Pople vs Jensen's and Dunning's basis sets, and the

convergence of individual results toward B3LYP CBS. In addition, the accuracy of the density grid in calculated harmonic and anharmonic frequencies will be tested. Water and formaldehyde were selected as simple model molecules for our study as their harmonic and anharmonic frequencies in the gas phase are well known. Several works comparing the 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 interactions. Thus, the conclusions of current study will aid further 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 results obtained with experimental and previously 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. The efficient B3LYP density functional was selected and, for comparison purposes, some calculations were also performed at restricted HF (RHF) and MP2 levels. In addition, 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 the 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 a fine grid is critical in the case of indirect spin–spin coupling constant 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 the case of Jensen’s pc- $n$  basis sets,  $X=n+2$  was assumed for graphical fitting purposes only [21, 38]. All fittings were performed with a 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) that are 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

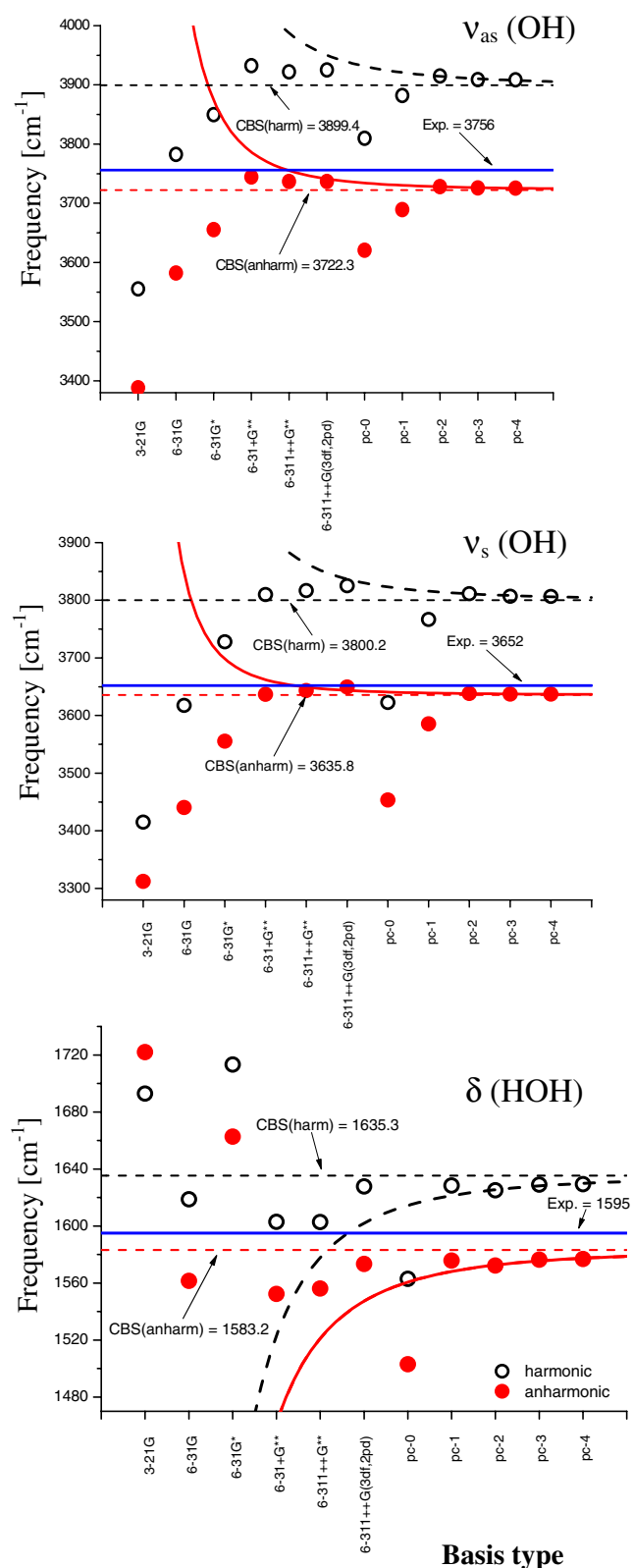
Single scaling factors were used for low and high frequencies. Three fundamental studies [2–4] on scaling factors are used in frequency and zero-point vibrational (ZPV) energy calculations. Evaluation of scaling factors is very laborious work and, therefore, despite the presence of myriad methods and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

## Results and discussion

The B3LYP-calculated harmonic and anharmonic frequencies of water modes as a function of selected Pople and

Jensen basis set size are shown in Fig. 1. For  $\delta(\text{HOH})$  mode, the wavenumbers predicted with Pople basis sets behave irregularly, and an increase in the basis set size (compare 6-31G and 6-31G\*) does not lead to better prediction of this water vibration. On the other hand, the results obtained with Jensen basis sets change more regularly. Thus, we used Eq. 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 observed a significantly lower sensitivity of wavenumber to the size and completeness of pc- $n$  basis set hierarchy than with the Pople basis sets. Moreover, one can see a significantly smaller deviation from experimental values for the estimated CBS anharmonic with respect to harmonic frequencies. For example, for the water OH asymmetric stretch mode these values are  $-34$  vs  $143 \text{ cm}^{-1}$ , respectively (Fig. 1). B3LYP-predicted formaldehyde vibrational modes show a similar dependence on basis set type and size (Fig. 2).

One might expect that, in the case of numerical calculations of anharmonic frequencies, the quality of the results could be influenced by the accuracy of the density grid, as in the case of the 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 Tables 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 root mean square (RMS) deviation values are shown. The top of Table 1 gathers the results obtained for default optimization and frequency conditions (keywords OPT, Freq=anharm), and compare them with results calculated using a very accurate density grid [keywords OPT=tight, Freq=anharm, SCF=tight, INT (GRID=150590)]. Thus, the upper half of Table 1 lists results for selected Pople basis sets, and 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 the accuracy of water frequency prediction for either Pople or Jensen’s basis sets. However, in the case of high frequency formaldehyde anharmonic vibrations [ $\nu_{\text{asym}}(\text{CH}_2)$  in Table 2], grid size has a significant impact on the 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, a more accurate density grid is important for improving formaldehyde anharmonic frequency accuracy.



**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 complete basis set limit (CBS) (2,3,4) estimated

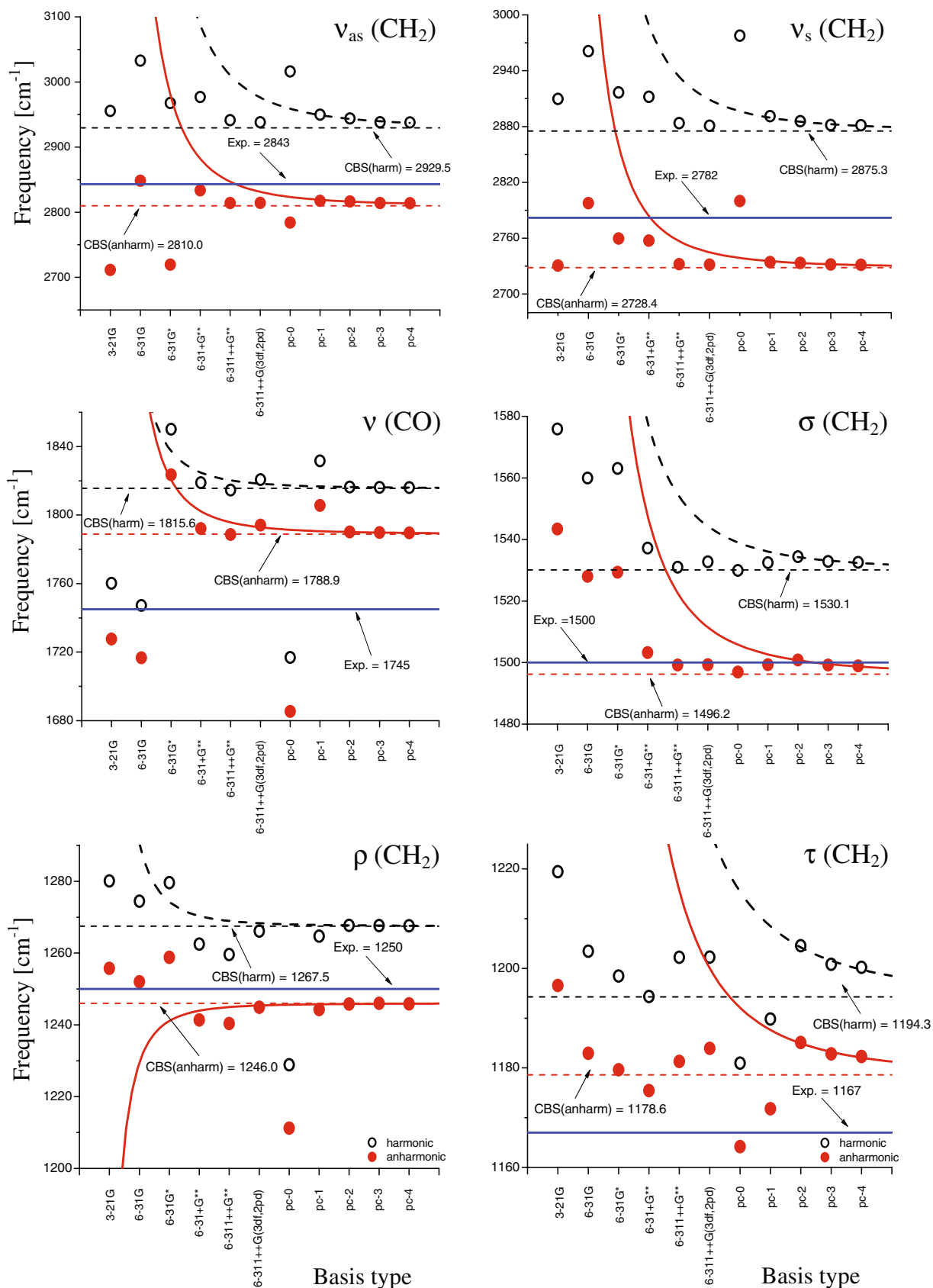
On the contrary, formaldehyde harmonic frequencies do not change upon changing grid size.

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 water harmonic frequencies relatively well compared to anharmonic ones. In contrast, the same basis set (6-31G) gives the opposite result in the case of formaldehyde. Thus, we should treat such behavior as the result of accidental error cancellation. In other words, vibrational analysis using small basis sets is unreliable due to basis set incompleteness. Larger Pople basis sets are associated with an improvement in prediction of water anharmonic frequencies. Thus, for the 6-311++G (3df,2pd) basis set, corresponding anharmonic and harmonic RMS deviations of 17 vs 139  $\text{cm}^{-1}$  are observed. This is also clearly visible in Fig. 1. In the case of Jensen's basis set, starting from  $n=2$ , water anharmonic frequencies are predicted significantly better than harmonic frequencies (RMS deviations of 23 vs 129  $\text{cm}^{-1}$  for pc-2). Moreover, the RMS values for anharmonic water frequencies predicted with Pople basis sets [other than 6-311++G(3df,2pd)] are larger than with the 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 the anharmonic results for the studied Pople and Jensen's basis sets (Table 1), and, for formaldehyde, scaled harmonic frequencies are often even closer to experimental values than the anharmonic frequencies (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 were very similar to those obtained earlier with Jensen's basis sets (see Figs. S1–S4 in the electronic supplementary material), and the corresponding deviations from experimental values are listed in Tables S2 and S3. Similarly to the results in Table 1, there is no dependence on grid size of water frequencies predicted with both Dunning's basis set series (Table S2). However, in the case of formaldehyde, similarly to results obtained with Jensen's basis set family (Table 2), the improvement in 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 an improvement in RMS of anharmonic frequencies of more than twofold, due mainly to a better description of  $\text{CH}_2$  asymmetric stretching. Moreover, in all cases the scaled harmonic frequencies for formaldehyde are significantly closer to experimental values 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 basis



**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

**Table 1** Deviations of water B3LYP harmonic ( $\Delta_{\text{harm}}$ ), anharmonic ( $\Delta_{\text{anh}}$ ) and scaled harmonic ( $\Delta_{\text{scal}}$ ) frequencies ( $\text{cm}^{-1}$ ) calculated with selected Pople and Jensen's basis sets from experimental values

Mode	exp. <sup>a</sup>	3-21G			6-31G			6-31G*			6-31+G**			6-311+G**			6-311++G(3df,2pd)		
		$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
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
RMS		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
RMS		190	300	292	31	162	127	96	91	61	135	28	37	133	26	42	139	17	40
Computation criteria: opt=tight scf=tight INT(Grid=150590) 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
RMS		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
RMS		41	151	98	98	58	11	129	23	33	125	23	45	125	23	45	119	24	39

<sup>a</sup> From [40]

<sup>b</sup> Estimated for pc-*n* where *n*=2,3,4 using Eq. 1



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

Mode	exp. <sup>a</sup>	3-21G			6-31G			6-31G*			6-311++G**			6-311++G(3df,2pd)					
		$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$			
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
RMS		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
RMS		80	62	25	111	19	49	92	62	20	84	23	23	67	30	16	67	32	14
Computation criteria: opt=tight scf=tight INT(Grid=150590) 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
RMS		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
RMS		108	38	70	74	33	21	69	30	14	66	31	19	66	31	19	62	32	16

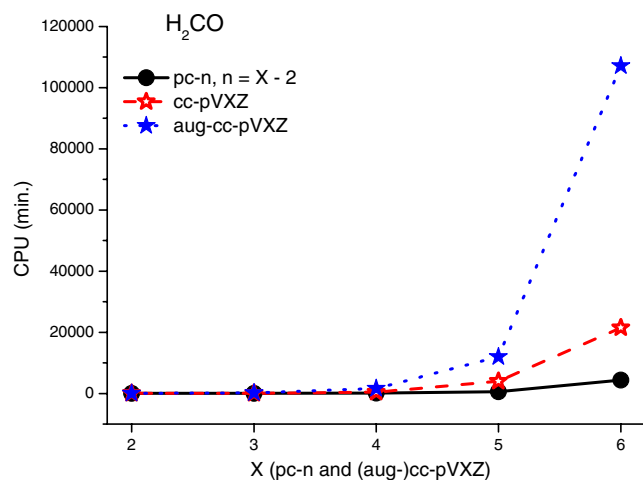
<sup>a</sup> From [41]

<sup>b</sup> Estimated for pc-*n* where *n*=2,3,4 using Eq. 1

sets. The dependence of CPU time necessary for VPT2 calculations with *pc-n*, *cc-pVXZ* and *aug-cc-pVXZ* basis sets in the 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 becomes 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 the results with those from two often used Pople's basis sets (6-31G and 6-311++G\*\*). The results obtained for water harmonic and anharmonic frequency deviations from experiment are shown in Table 3; similar data for formaldehyde are shown in Table 4. Contrary to formaldehyde anharmonic results obtained from B3LYP calculations discussed earlier, there was no influence of grid size on water and formaldehyde anharmonic deviations at BLYP, B3PW91 and PBE level. Therefore, only results for large grids 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 the case of RHF calculations, both harmonic and anharmonic (although these are considerably better) frequencies obtained with both Pople and Jensen's basis sets significantly overestimate experimental water and formaldehyde frequencies. The MP2 anharmonic values obtained with the 6-31G basis set for water and formaldehyde are not very accurate, but increasing the size of the basis set significantly improves the results. On the other hand, MP2 calculations are extremely expensive and feasible for very



**Fig. 3** CPU time (min) dependence on the type and size of basis set for formaldehyde VPT2 calculation with *pc-n*, *cc-pVXZ* and *aug-cc-pVXZ* basis sets

small molecules only. Water harmonic values obtained at the BLYP/6-31G level underestimate experimental frequencies, and anharmonic calculation using the 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 the 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 the BLYP level with larger basis sets exhibit worse RMS values. In the 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 (Tables 3, 4). However, it should be noted that, contrary to B3LYP, very good anharmonic results are obtained for formaldehyde by using the default grid size with B3PW91 and PBE density functionals (see Tables S6, S7). This makes B3LYP a more expensive DFT method for anharmonic calculations of some molecules. Therefore, to gain a more general insight, similar studies on the accuracy and reliability of the VPT2 method in predicting fundamental vibrations for a larger set of model molecules are planned.

## Conclusions

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

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 basis sets. Both correlation-consistent and polarization-consistent basis sets enable essentially the same CBS values of harmonic and anharmonic frequencies to be obtained. However, the CPU time for calculations using *cc-pVXZ* basis sets is significantly longer than with the corresponding *pc-n* sets. The deviations in CBS values for harmonic frequencies are significantly larger than the corresponding anharmonic numbers (RMS of 119 vs 24  $\text{cm}^{-1}$  in the case of water frequencies calculated using B3LYP/*pc-n*, and 62 vs 32  $\text{cm}^{-1}$  in the 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  $\text{cm}^{-1}$ , for water and formaldehyde, respectively). On the other hand, there are as yet no available scaling factors for Jensen's basis



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

Mode	exp. <sup>a</sup>	RHF/6-31G			RHF/6-311++G**			MP2/6-31G			MP2/6-311++G**			B3LYP/6-31G			B3LYP/6-311++G**		
		$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{OH})$	3756	389	200	-45	489	316	95	77	-131	-137	247	62	74	27	-174	-120	166	-19	43
$\nu_{\text{s}}(\text{OH})$	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
RMS		306	154	61	405	265	82	59	133	143	195	47	59	31	162	127	133	26	42
		BLYP/6-31G			BLYP/6-311++G**			B3PW91/6-31G			B3PW91/6-311++G**			PBE/6-31G			PBE/6-311++G**		
Mode	exp.	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{OH})$	3756	-147	-349	-169	23	-169	21	74	-126	-90	202	18	65	102	-96	53	231	49	211
$\nu_{\text{s}}(\text{OH})$	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
RMS		149	302	166	21	142	20	45	125	106	162	26	57	65	101	33	185	44	169
		RHF/pc-2			RHF/pc-4			MP2/pc-2			MP2/pc-4			B3LYP/pc-2			B3LYP/pc-4		
Mode	exp.	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{OH})$	3756	483	305	108	475	302	99	235	45	65	215	31	66	159	-28	38	153	-30	55
$\nu_{\text{s}}(\text{OH})$	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
RMS		403	259	91	397	258	84	184	33	48	167	21	47	129	23	33	125	23	45
		BLYP/pc-2			BLYP/pc-4			B3PW91/pc-2			B3PW91/pc-4			PBE/pc-2			PBE/pc-4		
Mode	exp.	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{OH})$	3756	16	-178	13	11	-179	9	195	9	57	187	6	50	221	37	201	214	34	194
$\nu_{\text{s}}(\text{OH})$	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
RMS		11	144	9	8	144	7	157	16	48	152	12	42	179	35	162	174	32	157

<sup>a</sup> From [40]

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

Mode	exp. <sup>a</sup>	RHF/6-31G			RHF/6-311++G**			MP2/6-31G			MP2/6-311++G**			B3LYP/6-31G			B3LYP/6-311++G**		
		$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{CH}_2)$	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
RMS		285	188	61	235	171	37	148	79	87	119	25	48	112	20	50	67	30	16
		BLYP/6-31G			BLYP/6-311++G**			B3PW91/6-31G			B3PW91/6-311++G**			PBE/6-31G			PBE/6-311++G**		
Mode	exp.	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{CH}_2)$	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
RMS		46	85	42	15	128	15	119	20	49	75	33	21	133	30	108	88	36	78
		RHF/pc-2			RHF/pc-4			MP2/pc-2			MP2/pc-3			B3LYP/pc-2			B3LYP/pc-4		
Mode	exp.	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{CH}_2)$	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
RMS		235	171	44	230	168	40	134	35	60	123	26	59	69	30	14	66	31	19
		BLYP/pc-2			BLYP/pc-4			B3PW91/pc-2			B3PW91/pc-4			PBE/pc-2			PBE/pc-4		
Mode	exp.	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$	$\Delta_{\text{harm}}$	$\Delta_{\text{anh}}$	$\Delta_{\text{scal}}$
$\nu_{\text{as}}(\text{CH}_2)$	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
RMS		11	126	12	12	127	13	74	33	19	71	33	19	86	35	76	83	35	73

<sup>a</sup> From [41]

set. Thus, arbitrary scaling factors were used for harmonic frequencies calculated with polarization-consistent basis sets.

- There is no point in using the VPT2 method in conjunction with the RHF and BLYP methods (the former values are far too high, and for the second method the anharmonic frequencies are too low).
- Optimization criteria and density grid size have a negligible effect on the harmonic frequencies of water and formaldehyde, but 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 potential energy surface (PES) away from the equilibrium, and the method of calculation applied should produce very smooth PES (with constant errors). This could explain the high sensitivity of formaldehyde anharmonic frequencies to grid size, in contrast to harmonic vibrations. With the 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 here, we would stress the need for further study in this field.

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