Estimating the carbonyl anharmonic vibrational frequency from affordable harmonic frequency calculations

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Abstract A linear correlation between harmonic and anharmonic frequencies of water calculated at B3LYP level of theory was observed with a number of basis sets. Similar relationships were found in both the gas phase and solution for several small molecules. The best correlation was found for C=O stretch mode in formaldehyde, formamide and N-methylacetamide. The average difference between B3LYP harmonic and anharmonic ν(C=O) frequencies calculated with several basis sets in these molecules was 30 cm^{-1}. The *ad hoc* correction of −30 cm^{-1}, added to harmonic frequencies of two different carbonyl groups present in a structure of a larger molecule was tested as a fast way of predicting anharmonic frequencies without elaborated calculations. The proposed approach was tested successfully on a larger molecule of E and Z isomers of N-acetyl-α,β-dehydrophenylalanine N′,N′-dimethylamide [Ac-(E/Z)-ΔPhe-NMe$_2$] and the estimated anharmonic ν(C=O) frequencies were close to directly calculated results.

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Introduction

Vibrational spectroscopy is one of the most versatile tools in analytical chemistry. For example, mid-IR spectroscopy has been shown to yield detailed structural information for peptides and proteins. In particular, the amide I band (originating mainly from C=O stretching vibration) position is most commonly used for secondary structure analysis [1, 2]. For about the last 30 years, experimental infrared (IR) and Raman studies have been supported by theoretical predictions of harmonic frequencies. However, due to the neglect of anharmonicity in the calculations, theoretical harmonic frequencies [3, 4] overestimate experimental numbers. For example, RHF overestimate CH, OH and NH stretching modes by about 5–10 % and B3LYP by 3–5%. This drawback of theory can sometimes be corrected by application of a simple scaling of the force constants or frequencies [4]. However, obtaining scaling factors requires very laborious testing of a large number of molecules for a given theoretical method and basis set. Thus, only a limited number of scaling factors are available so far [4–6].

A significantly more elegant theoretical approach is based on the calculation of anharmonic frequencies [7–17]. Several methods have been proposed, including VPT2 implemented by Barone [9, 14] in Gaussian [18, 19], VSCF [17, 20–23], VMP2 [24, 25], VCI [26–28] or VCC [29]. In particular, VPT2 is recommended as a fully automated feature of Gaussian 09 [19]. Unfortunately, these anharmonic calculations need significantly more CPU time, which has so far restricted this analysis to relatively small molecules only. The main difference in calculations of harmonic (ideal, parabolic potential energy curve) and anharmonic frequencies lie in the severe approximations in the first curve, which are valid only for very close displacements from equilibrium distance (see Fig. 1).
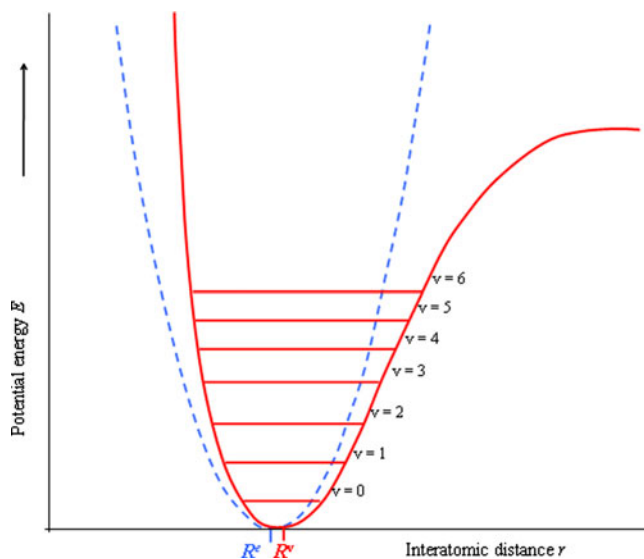
Fig. 1 Schematic representation of the potential energy surface of two interacting atoms using harmonic (*dashed line*) *vs* anharmonic (*solid line*) approximations

The results of our recent studies on anharmonicity of vibration modes in water, formaldehyde [30] and formamide [31] prompted us to compare our harmonic and anharmonic frequencies with experimental values and led to an evaluation of the performance of both types of calculations. In addition, some dependencies between these individual types of frequencies were left without analysis.

In this short study we will show that a linear correlation exists between anharmonic and harmonic frequencies of water in the gas phase as well as in solution modeled using the polarized continuum model (PCM approach [32]). We demonstrate the existence of similar correlations for the different vibrations of formaldehyde, formamide (FMA) and N-methylacetamide (NMA). Finally, we propose a simple way to estimate the anharmonic ν(C=O) frequency of E and Z isomers of Ac-(E/Z)-ΔPhe-NMe$_2$ from significantly computationally less expensive harmonic frequencies. The proposed model molecules are α,β-dehydrophenylalanine derivatives and belong to a group of nonstandard peptides with a double bond between the C$^\alpha$ and C$^\beta$ atoms. The α,β-dehydroamino acids have unique conformational properties and form the subject of our recent studies [33, 34].

Computational methods

All calculations were performed using the Gaussian 03 [18] and 09 programs [19]. Density functional theory with the popular hybrid functional B3LYP [35–38] and basis sets of small, medium and large size (3-21G and 6-31G*, Dunning aug-cc-pVXZ, where X=D, T, Q, 5 and 6 [39–42] and Jensen pc-n [43–48], where n=0, 1, 2, 3 and 4) were

selected. Full structure optimisation with default parameters and the INT(GRID=150590) keyword in the gas phase and in solution (using the PCM model [32]) was performed. Frequency analysis was carried out to verify the nature of the minimum state of all the stationary points obtained. The anharmonic vibration calculations were carried out in vacuum and in solution using the VPT2 method as implemented by Barone [9, 14] in the Gaussian program package [18, 19]. Fermi resonances were handled in all calculations by default settings in the G09 anharmonic calculations.

Four model molecules, for which accurate experimental IR data are available from the literature, were selected: water [49], formaldehyde [50], formamide (FMA) [17, 51] and N-methylacetamide (NMA) [23, 52, 53]. The number of basis set used depended on the size of molecule studied and the necessary computational time. For the smaller systems—water, formaldehyde and formamide—the largest number of basis sets was used in the calculation of their vibrational frequencies in the gas phase (see basis sets No. 1–21 in Table 1), while NMA in the gas phase was calculated using only basis sets No. 1–10. The harmonic frequencies of water, formaldehyde and formamide were calculated using the PCM method in eight solvents (*n*-hexane, CCl$_4$, CHCl$_3$, acetone, acetonitrile, DMSO, water, formamide) with basis sets No. 1–11, while for NMA calculations were carried out only for water and chloroform as solvents and with the basis sets No. 1–10.

To validate the performance of our estimation scheme of carbonyl anharmonic frequency, the E and Z isomers of Ac-ΔPhe-NMe$_2$ [34] were selected. Full geometry optimization of the tested diamides was performed with the B3LYP/6–311++G(p,d) method and both harmonic and anharmonic frequencies were calculated.

FTIR measurements

Analytical grade CHCl$_3$ was dried and purified following standard methods and stored over freshly prepared 0.4-nm molecular sieves. The IR spectra of E and Z isomers of Ac-ΔPhe-NMe$_2$ in CHCl$_3$ were recorded at 20°C using a Nicolet Nexus spectrometer equipped with DTGS detector and flushed with dry nitrogen during the measurements. All spectra were recorded at 1 cm^{-1} resolution and averaged using 100 scans. Solvent spectra obtained under identical conditions were subtracted from the sample spectra. The thickness of the KBr liquid cell was 2.86 mm and the concentration was varied between 8.6×10^{-3} and 1.7×10^{-2} mol l^{-1}. The spectra were analyzed with the GRAMS AI spectroscopy software suite [54]. The number and position of component bands were obtained from second derivatives and by Fourier self-deconvolution techniques as an "initial guess". Next, the

Table 1 Basis sets used for calculation in the gas phase (21 basis sets) and solution[a–d] and the number of basis set functions for the studied molecules

No	Basis set	No of basis functions				
		H_2O	CH_2O	$HCONH_2$	NMA	Ac-(E,Z)-ΔPhe-NMe$_2$
1	3-21G	13	22	33	59	
2	6-31G	13	22	33	59	
3	6-31G*	19	34	51	89	
4	6-31+G**	29	48	72	130	287
5	6-311++G**	36	58	87	159	403
6	6-311++G(3df,2pd)	69	108	162	300	486
7	pc-0	13	22	33	59	
8	pc-1	24	38	57	105	
9	pc-2	58	88	132	248	
10	pc-3	132	196	294	558	
11	pc-4	235	344	516	986	
12	cc-pVDZ	24	38			
13	cc-pVTZ	58	88			
14	cc-pVQZ	115	170			
15	cc-pV5Z	201	292			
16	cc-pV6Z	322	462			
17	aug-cc-pVDZ	41	64			
18	aug-cc-pVTZ	92	138			
19	aug-cc-pVQZ	172	252			
20	aug-cc-pV5Z	287	414			
21	aug-cc-pV6Z	443	632			

[a] Water in eight solvents (n-hexane, CCl$_4$, CHCl$_3$, acetone, acetonitrile, DMSO, water, formamide) calculated with basis sets No 1–11

[b] Formaldehyde in eight solvents calculated with basis sets No 1–11

[c] Formamide in eight solvents calculated with basis sets No 1–11

[d] NMA in the gas phase and in two solvents (water and chloroform) calculated with basis sets No 1–10

accurate band positions were determined by curve-fitting procedure with a mixed Gauss-Lorentz profile. More details concerning the experimental part were described in our earlier work [34].

Results and discussion

Figure 2 shows the differences between the harmonic and anharmonic frequencies of water in the gas phase calculated using the B3LYP hybrid exchange-correlation functional and the 21 basis sets. It is apparent that the differences between harmonic and anharmonic frequencies are roughly constant. They depend on the vibration mode and not on the quality of the basis set. In fact, only the smallest basis sets (3-21G, pc-0 and cc-pVDZ) produce results that deviate significantly from this trend. Thus, the mentioned average difference (without the result from the 3-21G basis set) is 52 cm^{-1} for the δ(HOH) bending vibration, 172 and 187 cm^{-1} for symmetric and asymmetric stretching OH frequencies. These values reproduce very closely the experimental values of 53, 175 and 185 cm^{-1}, respectively [14].

A diagram of the linear correlation between the harmonic and anharmonic frequencies of the ν_{as}(OH) vibrational mode of water in vacuum, in water and in

CHCl$_3$ obtained with a different basis set is shown in Fig. 3. Similar linear correlations of the other two vibrational modes are presented in the electronic supplementary material (Fig. S1). Out of the three vibrations, δ(HOH) seems to be most sensitive to solvent effects, and the correlation is slightly worse for very low quality basis sets for this vibrational mode (Fig. S1c).
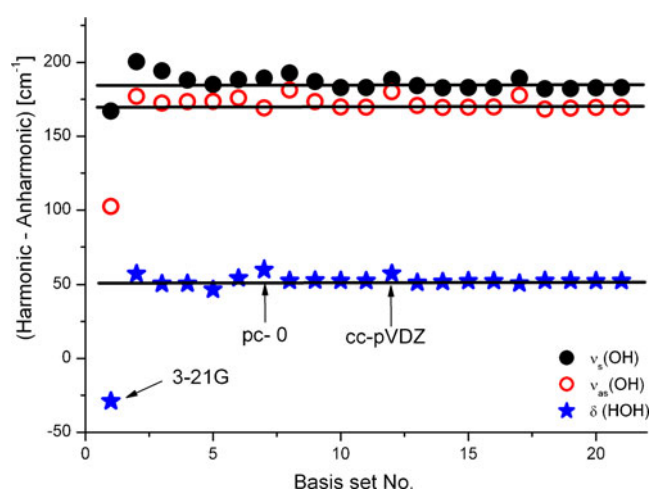
Fig. 2 Difference between water's harmonic and anharmonic frequencies calculated at B3LYP level *vs* the 21 basis set used in the gas phase (basis set numbers are explained in Table 1)
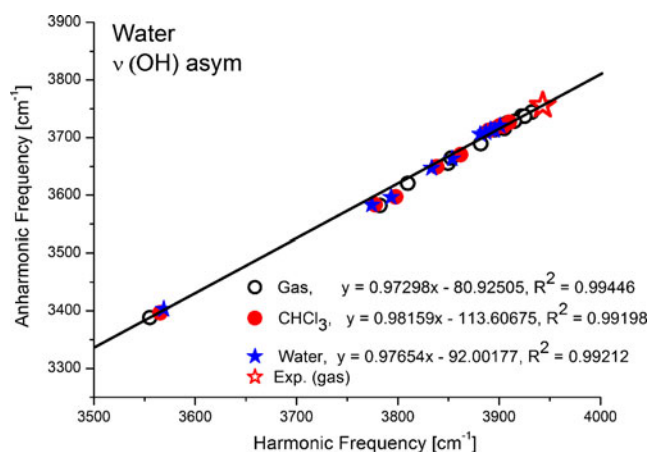
Fig. 3 Correlation between calculated harmonic and anharmonic $\nu_{as}(OH)$ frequencies of water in the gas phase and in solution calculated with the B3LYP hybrid exchange-correlation functional using 21 basis sets in vacuum and 11 in solution. The experimental value [49] is marked with an *open star* symbol

In the case of formaldehyde and formamide, linear correlations are also found between the harmonic and anharmonic frequencies of the $\nu(C=O)$ vibrational modes calculated in vacuum, and in several solvents, as shown in Figs. 4a and 5. Moreover, the experimental harmonic and anharmonic values of formaldehyde in the gas phase [50] represented by a star symbol, falls ideally on the linear least square fit line.

However, the corresponding correlation diagrams for $\nu_{as}(CH_2)$ in Fig. 4b, and $\nu_s(CH_2)$ vibrations of formaldehyde, and for $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ vibrations in formamide in Figs. S2–S4 of the supplementary material show significantly more scattered results. This is particularly the case for the smaller basis sets, as can be seen from the more detailed diagrams for the results obtained in vacuum, chloroform and water, shown in Figs. S2A–S2C, S3A–S3C and S4A–S4C. A linear least square fit was therefore not performed. Nevertheless, the experimental results for formaldehyde and formamide (marked as stars in Figs. S2A and S3A) fall on a line that can be drawn through the results obtained with the larger basis sets. A linear behavior of harmonic *vs* anharmonic frequencies for C=O stretch mode, and the lack of such a relationship for several other vibrational modes is unclear, and can probably be attributed to a specific property of the VPT2 method. Moreover, this behavior is probably not due to Fermi resonance. Vibrational analysis of formaldehyde at B3LYP/pc-4 level indicates two Fermi resonances (CH_2 sym stretch is in resonance with two combination bands). Hence, CH_2 asym stretch does not participate in Fermi resonance and shows a very irregular behavior in Fig. 4b. To the best of our knowledge this observation has not been reported previously.
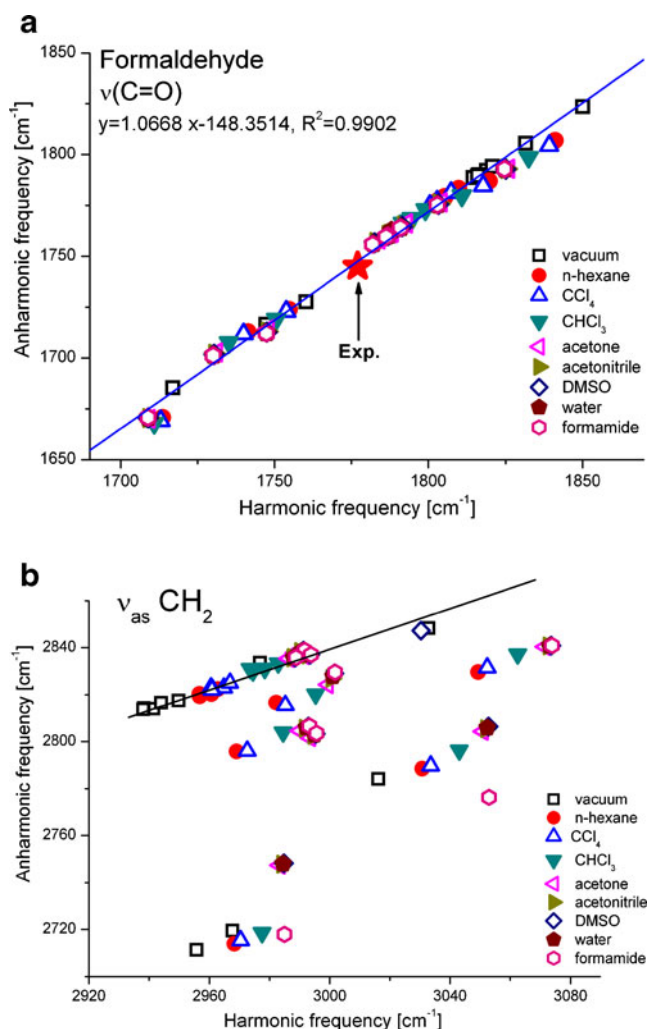

Fig. 4 Correlation between calculated harmonic and anharmonic (**a**) $\nu(C=O)$ and (**b**) $\nu_{as}(CH_2)$ frequencies of formaldehyde in the gas phase and several solvents calculated with the B3LYP hybrid exchange-correlation functional using 21 basis sets in vacuum and 11 in solution. The experimental values [50] are marked with a *closed star* symbol

Turning to a larger amide molecule like N-methylacetamide (NMA [23, 52]), one observes also for this amide a linear correlation for the calculated harmonic and anharmonic frequencies of the $\nu(C=O)$ vibrational mode in vacuum (1,707 cm^{-1} observed in vacuum, see ref. [23, 52]), and in eight solvents as apparent from Fig. 6.

The results for the three molecules suggest that a very good linear correlation exists for the $\nu(C=O)$ mode between harmonic and anharmonic frequencies calculated at the DFT/B3LYP level in the gas phase and in solution. The average difference between harmonic and anharmonic frequency of C=O for formaldehyde, formamide and NMA in the gas phase, chloroform and water calculated using several basis sets is 30 cm^{-1} (Fig. 7). Thus, the anharmonic frequency of $\nu(C=O)$ vibration is on average 30 cm^{-1} lower than the harmonic vibration, and significantly closer

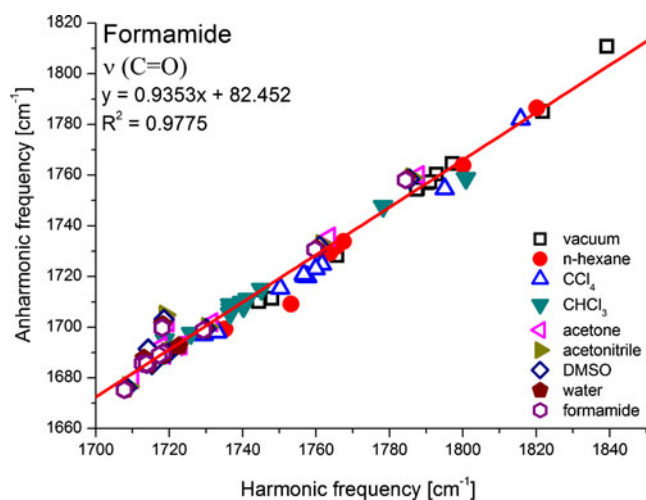**Fig. 5** Correlation between calculated harmonic and anharmonic ν(C=O) frequencies of formamide in the gas phase and several solvents calculated with the B3LYP hybrid exchange-correlation functional using 21 basis sets in vacuum and 11 in solution

to experimental values. A similar correlation is not observed or is significantly worse for other vibration modes and gets worse in the case of more polar solvents.

We also noticed that a very similar difference of about 30 cm^{-1} between harmonic and anharmonic ν(C=O) frequencies could be calculated from results obtained earlier. Thus, in the case of VPT2 calculations on formamide using the MP2/aug-cc-pVTZ and B3LYP/6-31+G** methods, we calculated differences of 32.99 cm^{-1} (see Table 1 in ref. [17]) and 33.7 cm^{-1} (see Table 1 in [53]) from the original data. In case of NMA, the differences are 28 cm^{-1} (see Table 1 ref. [23] and 30.2 cm^{-1} (see Table 1 in [53]), respectively.
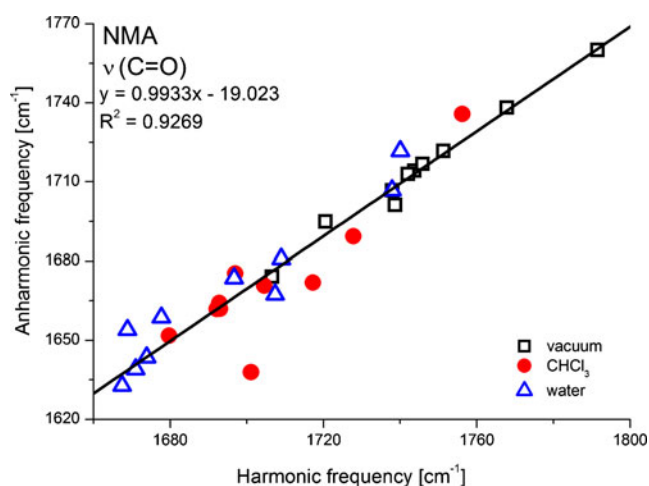

Fig. 6 Correlation between calculated harmonic and anharmonic ν(C=O) frequencies of N-methylacetamide (NMA) in the gas phase and two solvents calculated with the B3LYP hybrid exchange-correlation functional using 11 basis sets
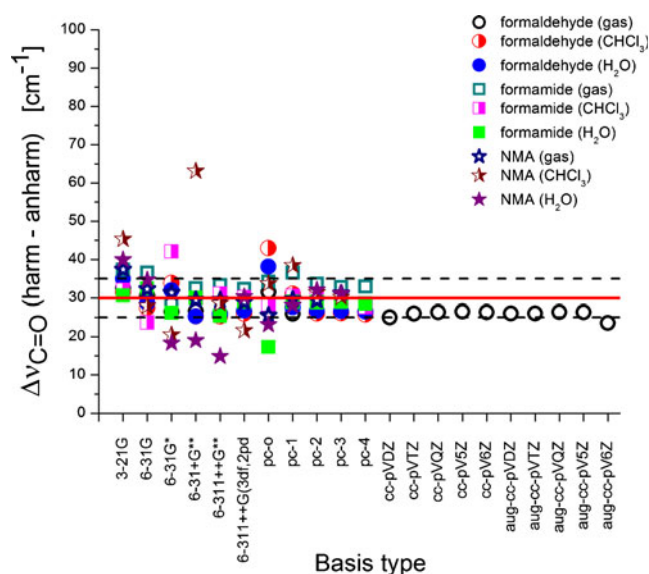

Fig. 7 Difference between formaldehyde, formamide and NMA harmonic and anharmonic frequencies of ν$_{(C=O)}$ calculated in the gas phase, chloroform and water vs the basis set quality used. The average difference of 30 cm^{-1} is represented by a *solid line* and most points are within ±5 cm^{-1} (*dashed lines*)

It is therefore worthwhile to test the applicability of such a correlation for the prediction of anharmonic frequencies of ν(C=O) vibrational modes in amides and similar compounds from the, significantly computationally less expensive, harmonic frequency calculations. Such an approach could improve the accuracy of diagnostic carbonyl vibration in amides and peptides. To test this hypothesis, the IR spectrum of E and Z isomers of Ac-(E/Z)-ΔPhe-NMe$_2$ [34] (see chemical formula and atom numbering in Fig. 8) in chloroform was measured and harmonic frequency calculations performed.

The measured ν(C=O) bond stretching vibrational frequencies of the two different carbonyl groups present in the test compounds are compared in Table 2 with calculated harmonic and scaled harmonic frequencies, as well as calculated VPT2 and estimated anharmonic frequencies, where the latter were obtained using the *ad hoc*
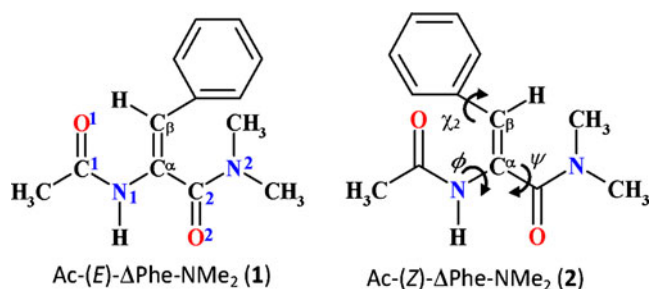

Fig. 8 General formula, atom numbering and selected torsion angles for the studied test compounds

Table 2 Performance of scaled and anharmonic vibrations in the gas phase for predicting carbonyl stretching mode: ν(C=O) harmonic and anharmonic frequencies (cm^{-1}) of Ac-(E,Z)-ΔPhe-NMe$_2$ calculated at B3LYP/6-311++G** level versus experimental values in chloroform. Total averaged deviations from experimental values are also shown

Amide I mode	harm	harm[a]	anharm	anharm[b]	exp[c]
	Isomer E				
$\nu_1(C_1{=}O_1)$	1751	1697	1721	1722	1692
$\nu_2(C_2{=}O_2)$	1699	1646	1669	1669	1640[d]
$\nu_1 - \nu_2$	53	51	52	53	52
	Isomer Z				
$\nu_1(C_1{=}O_1)$	1752	1697	1720	1722	1693
$\nu_2(C_2{=}O_2)$	1708	1654	1676	1678	1650[d]
$\nu_1 - \nu_2$	44	43	44	44	43
Aver. dev.[e]	59.0	4.8	27.8	29.0	

[a] Scaling factor 0.9686 from [4]

[b] $\nu_{anharm} \approx \nu_{harm} - 31$ cm^{-1}

[c] From experimental spectrum in CHCl$_3$

[d] Values obtained by curve fitting

[e] $1/4 \, \Sigma(\nu_{calc} - \nu_{exp})$

correlation between harmonic and anharmonic frequencies, i.e., by subtracting 30 cm^{-1} from the former ones. It is apparent from Table 2 that the theoretically predicted harmonic frequencies of four carbonyl bands overestimate the experimental values by about 60 cm^{-1}. However, the experimental separations ($\nu_1 - \nu_2$) of two different carbonyl bands of 52 and 43 cm^{-1} for isomer E and Z are well reproduced at all levels of calculations. The anharmonic frequencies show significantly better agreement with experimental values than the harmonic frequencies. The anharmonic frequencies obtained by simple subtraction of

the 30 cm^{-1} correction term from the harmonic frequencies are virtually identical with those obtained from the very demanding anharmonic calculations using the VPT2 approach.

This is a very pleasing result (average deviation from experimental values for two calculated anharmonic vs estimated carbonyl anharmonic frequencies in two isomers is 27.8 vs 29 cm^{-1}). On the other hand, it is necessary to point out that a simple harmonic frequency scaling (with the factor 0.9686 from [4]) leads to significantly better agreement with experimental frequencies than the result from VPT2 calculations (average deviation from experimental values of harmonic vs scaled harmonic is 59.0 and 4.8 cm^{-1}). Similar better performance of simple harmonic frequency scaling than VPT2 predicted anharmonicity corrections in the analysis of experimental IR/Raman spectra was also noted in our recent studies [30, 31]. However, the drawback of using scaling factors is their limited availability, which is restricted to a narrow range of methods and basis sets, and the lack of a rigorous theoretical background.

Another approach leading to hybrid estimation of anharmonic correction was recommended by one of the reviewers. Below we will briefly examine this idea and compare the results with our *ad hoc* 30 cm^{-1} anharmonic correction for C=O stretch mode. First, the harmonic vibrations are calculated using the basis set of the best possible quality (up to CBS), and next the anharmonic frequencies are calculated with a basis set of relatively small size, feasible for very demanding VPT2 calculations. To check this approach in Tables S2A, S2B in the Electronic Supplementary Material, and in Table 3 we collected harmonic and anharmonic frequencies of C=O stretch mode for the studied molecules. The CBS harmonic

Table 3 Deviations of C=O stretch frequency calculated using anharmonic ad hoc 30 cm^{-1} and hybrid corrections from experimental values (in cm^{-1})

Correction	Experimental	Hybrid		Ad hoc (30 cm^{-1})		
		Small[a]	Large[b]	6-31+G**	6-311++G**	CBS[a]
Formaldehyde	1745.1[c]	43.8	44.6	43.8	39.5	40.5
Formamide	1754.1[d]	−4.2	−5.2	13.0	6.2	−1.7
NMA	1728[e]		−19.6		−14.3	−20.1
Izomer E[f]						
C=O 1	1692		29.2		29.5	
C=O 2	1640		29.1		28.6	

[a] Using 6-31+G** as small basis set for obtaining anharmonic correction

[b] Using 6-311++G** as large basis set for obtaining anharmonic correction

[c] From [50]

[d] From [51]

[e] From [52], the value is very low

[f] This work, two different carbonyl bands of Ac-(E)-ΔPhe-NMe$_2$ in CHCl$_3$

frequencies (obtained with Jensen's basis sets), and those obtained with smaller ones (Pople's 6-31+G** and 6-311++G** basis set) are considered. The latter are feasible for VPT2 calculation of larger molecules and are used for obtaining anharmonic correction, which is subsequently applied to improve on "accurate" CBS harmonic frequency.

It is evident from Table 3 that the anharmonic corrections of about 30 ± 5 cm^{-1} obtained from CBS calculations and with a smaller basis set are similar (the values differ by 3% to 6 %). The hybrid approach produces a very similar anharmonic correction. Thus, this alternative approach gives a very similar value of anharmonic correction for C=O stretch mode, and the anharmonically corrected CBS harmonic frequency reproduces the experimental values with "the same accuracy". However, the hybrid approach is more expensive computationally (compare the number of basis functions in Table 1).

Conclusions

A linear correlation between the harmonic and anharmonic frequencies of water and of the carbonyl stretching modes in formaldehyde, formamide and NMA, calculated at the B3LYP level of theory was observed for a number of basis sets. The anharmonic frequency of the ν(C=O) mode in these carbonyl-group-containing systems was found to be about 31 cm^{-1} lower than the harmonic frequency. This observation was tested successfully on E and Z isomers of N-acetyl-α,β-dehydrophenylalanine N′,N′-dimethylamide [Ac-(E/Z)-ΔPhe-NMe$_2$]. We propose therefore to use an *ad hoc* correction of 30 cm^{-1} in order to obtain an estimate of the anharmonic frequencies from affordable harmonic frequency calculations for C=O group containing systems. However, in the case of methods and basis sets for which frequency scaling factors are available, this way of predicting the diagnostic feature of many compounds is even more reliable.

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