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## Prediction of OH stretching frequencies for intramolecular OH $\cdots$ O linkages

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### *Keywords*

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Hydrogen-bonding

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VPT2 perturbation theories

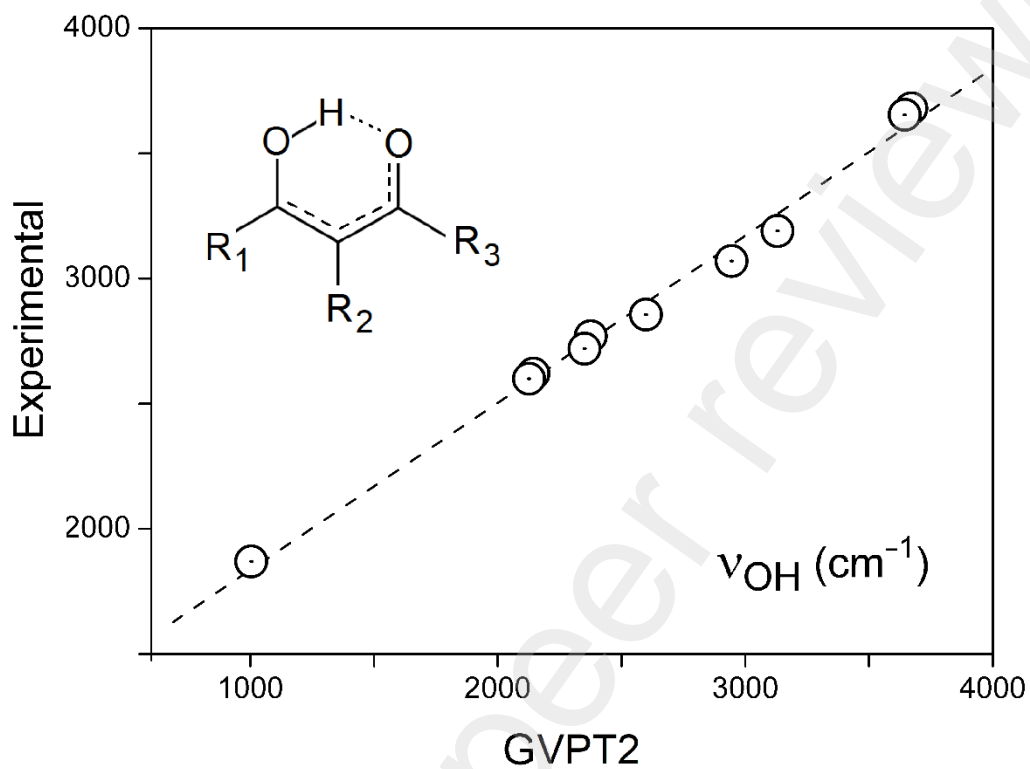
Density functional theory (DFT)

### ABSTRACT

The OH stretching frequencies for a series of compounds with intramolecular OH $\cdots$ O hydrogen bonds are computed with the DVPT2 and GVPT2 anharmonic models of Barone and associates using B3LYP-D3 density functional theory. The anharmonic models systematically underestimate the observed OH stretching wavenumbers for systems with medium to strong hydrogen-bonding, apparently due to the inability of approaches based on 2nd-order perturbation theory (PT2) to account accurately for the properties of large-amplitude vibrational motions. Nevertheless, the computed wavenumbers correlate linearly with the observed values. But it is noteworthy that the wavenumbers obtained with standard harmonic analyses lead to even better correlations than those computed with the expensive anharmonic models, resulting in linear regression equations of great predictive value (standard deviations close to 20 cm<sup>-1</sup>). For example, effective OH stretching wavenumbers for 2-acetylmalonamide enol and 2-cyanomalonamide enol are predicted between 2300 and 2400 cm<sup>-1</sup>. In contrast to the linear correlations observed for intramolecular OH $\cdots$ O hydrogen bonds, intramolecular NH $\cdots$ O linkages are characterized by corresponding non-linear relationships.

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### Graphical Abstract

#### Highlights

- DVPT2 and GVPT2 underestimate OH stretching wavenumbers for OH $\cdots$ O linkages
- Observed and predicted OH stretching wavenumbers are linearly correlated
- OH stretching wavenumbers predicted for 2-substituted malonamide enols

## 1. Introduction

Hydrogen-bonding is an important factor in many areas of chemistry and biology and the nature of this non-covalent interaction has been an issue of interest for decades [1-9]. The formation of hydrogen bonds may lead to molecular vibrational wavenumber shifts of several hundreds of  $\text{cm}^{-1}$ , indicating the strength of the interaction [10]. Infrared (IR) absorption spectroscopy thus plays a central role in the study of hydrogen-bonding effects. But many compounds with medium to strong intramolecular  $\text{OH}\cdots\text{O}$  hydrogen-bonding exhibit broad and diffuse OH stretching bands, and the assignment of a representative OH stretching wavenumber is frequently problematic.

The possibility to support the assignment by theoretical predictions is thus of great interest. Most calculations of the vibrational structure of molecules are based on the harmonic approximation [11], but the standard harmonic analysis tends to fail for strongly hydrogen-bonded systems because of substantial anharmonic effects [12-15]. Proper full-scale anharmonic treatments demand a tremendous computational effort and is generally a matter for theoretical experts. However, great progress has been made in recent years by development of the fully automated anharmonic VPT2 (2nd-order Vibrational Perturbation Theory) procedure by Barone and associates [16-24]. The procedure is readily available with commercial software packages such as Gaussian [25] and the application is straight forward. But the original VPT2 procedure has been shown to underestimate the OH stretching wavenumbers for strongly hydrogen-bonded  $\text{OH}\cdots\text{O}$  linkages, a situation which has occasionally lead researchers astray [12-15].

Subsequently, the VPT2 model has been improved by the inclusion of proper treatments of resonance effects, resulting in procedures such as DVPT2 (Deperturbed 2nd-order Vibrational Perturbation Theory) and GVPT2 (Generalized 2nd-order Vibrational Perturbation Theory) [20-24]. GVPT2 is the default anharmonic model in the current version of the Gaussian software package [25]; it is similar to DVPT2, but the removed terms are treated variationally in a second step. The

aim is the quantitative reproduction of the vibrational spectra of molecular systems with an adequate account of “the variety of intra- and intermolecular interactions” [21].

The purpose of the present study is to investigate the performance of the improved models DVPT2 and GVPT2 for a series of compounds with intramolecular OH...O linkages (Scheme 1). The compounds are selected from the much larger series considered in our investigation published in 2011 [12], with the addition of 1,3-Butanediol (3) [26]. Methanol (1) and phenol (2) represent systems with “free” OH groups unaffected by intramolecular hydrogen-bonding, but the remaining species 3 - 14 form intramolecular OH...O linkages closing 6-membered pseudo-rings, ranging from weakly to strongly hydrogen-bonded systems. The selection in Scheme 1 includes preferentially those species for which the wavenumber of the band center is reasonably well established on the basis of experimental and theoretical criteria [12]. The IR spectra of 2-acetylmalonamide enol (12) and 2-cyanomalonamide enol (13) have apparently not been published, but 12 and 13 are included in the present calculations because strong intramolecular hydrogen-bonding is expected for these systems [27,28]. Relative to our earlier VPT2 investigations [12,13], the present DVPT2 and GVPT2 calculations use a larger basis set and include dispersion effects. Additional information is provided as Supplementary data, referred to in the ensuing text as S1 - S15.

## 2. Calculations

Quantum chemical calculations were performed with the Gaussian 16 software package [25] using B3LYP [29,30] Density Functional Theory (DFT) and the 6-311++G(d,p) basis set [25], considering molecules in the gas phase. This level of theory has proved efficient in the description of vibrational transitions for this class of compound, see for example the analysis of results for malonaldehyde enol (6) [31]. Dispersion interactions were approximated by Grimme’s D3 empirical correction [32] (empirical dispersion = gd3bj [25]). Molecular equilibrium geometries were optimized with tight convergence criteria (opt = verytight [25]), and vibrational frequencies were

computed within the harmonic approximation and with the anharmonic models DVPT2 and GVPT2 using default parameters [25]. The optimized nuclear coordinates and the vibrational harmonic and GVPT2 anharmonic wavenumbers are provided as Supplementary Information (S1-S14); the GVPT2 calculation for 1,3-butanediol (**3**) failed, for this species the DVPT2 results are given (S3). In addition, a series of calculations were performed without dispersion interactions (S15). The computed OH stretching wavenumbers are collected in Table 1. The VPT2, DVPT2, and GVPT2 calculations require large computing time, easily amounting to several cpu days for a medium sized species. For this reason, the use of other functionals and basis sets was not explored in the present study. But for comparison, Table 1 lists results previously obtained with B3LYP/6-31G(d) [12].

### 3. Results and Discussion

Calculated OH stretching frequencies are compared with experimentally estimated values in Table 1. Basheer et al. [27,28] studied the structure of 2-substituted malonamides, including 2-acetylmalonamide enol (**12**), 2-cyanomalonamide enol (**13**), and 2-nitromalonamide enol (**14**). They concluded that the 2-acetyl derivative (**12**) is enolized preferentially in the acetyl group with the most stable conformation indicated in Scheme 1 [27]. The GVPT2 calculation for 1,3-butanediol (**3**) failed because of inability to find a satisfactory overlap between the deperturbed DVPT2 states and the new variational GVPT2 states (S3). No anharmonic model gave reasonable results for 2,4,6-triacetylphloroglucinol (**11**), this system is evidently a challenge for the perturbation theoretical approach (S11).

DVPT2 and/or GVPT2 perform well for the stretching wavenumbers of free or weakly hydrogen-bonded OH groups, such as in the case of methanol (**1**), phenol (**2**), and 1,3-butanediol (**3**) (Table 1). But the anharmonic procedures systematically underestimate the experimental wavenumbers for more strongly hydrogen-bonded linkages. For example, GVPT2 underestimates the experimental value for malonaldehyde enol (**6**) by about  $260\text{ cm}^{-1}$ , and for dibenzoylmethane

enol (**9**) and 2-nitromalonamide enol (**14**) the deviations are close to 480 and 870  $\text{cm}^{-1}$ , respectively. The situation is thus similar to the one observed with the original VPT2 model [12,13]. This is most likely due to the basic inability of 2nd-order perturbation theoretical models to describe accurately the properties of large-amplitude vibrational motions [23,24]. There is probably no real substitute for a full-scale treatment. For instance, advanced molecular dynamics calculations provided adequate predictions for systems like **9** [33] and **14** [34].

But in spite of the substantial complexity of the vibrational structure of these molecules, the experimental wavenumbers correlate well with those predicted with DVPT2 and GVPT2, as demonstrated by the linear regression analyses shown in Figs. 1 and 2. The RMS Standard Deviation obtained for DVPT2,  $\text{SD} = 79 \text{ cm}^{-1}$  (Fig. 1), is significantly larger than that for GVPT2,  $\text{SD} = 50 \text{ cm}^{-1}$  (Fig. 2). This is mainly because malonaldehyde enol (**6**) is an “outlier” in the case of DVPT2; for this compound, the variational procedure in GVPT2 improves the correlation. An even more successful correlation with  $\text{SD} = 27 \text{ cm}^{-1}$  is obtained with the harmonic wavenumbers as indicated in Fig. 3. Corresponding wavenumbers computed without dispersion effects yield  $\text{SD} = 24 \text{ cm}^{-1}$  (S15). The best correlation is actually obtained with B3LYP/6-31G(d), yielding  $\text{SD} = 20 \text{ cm}^{-1}$ , in spite of the much smaller basis set (Fig. 4). These regression analyses are not all strictly comparable because of different numbers of data points available, but the main trend seems clear.

Evidently, the relative shifts in OH stretching wavenumber through the series is well accounted for already at the harmonic level (Figs. 3 and 4, S15). It is noteworthy that the harmonic analysis requires orders of magnitude less computer time than the anharmonic VPT2, DVPT2, and GVPT2 procedures. A similar correlation was previously established for harmonic wavenumbers obtained with B3LYP/6-31G(d) considering a series of 32 compounds with intramolecular OH $\cdots$ O linkages, yielding  $\text{SD} = 0.74 \text{ cm}^{-1}$  [12]. The present B3LYP/6-31G(d) regression shown in Fig. 4 has a much lower  $\text{SD} = 20 \text{ cm}^{-1}$ , which can be explained by the circumstance that the previous

study covered a larger variety of molecular architectures and included some species where the experimental assignment of a representative OH stretching wavenumber was problematic [12].

In a practical sense, these regression equations have predictive value. For example, application of the regression equation in Fig. 4 suggests effective OH stretching wavenumbers close to  $2360\text{ cm}^{-1}$  for 2-acetylmalonamide enol (12) and  $2315\text{ cm}^{-1}$  for 2-cyanomalonamide enol (13). Different tautomers may contribute to the spectrum of 12 [27], this interesting compound may thus require a more detailed investigation.

It is interesting to compare with the corresponding results for systems with intramolecular  $\text{NH}\cdots\text{O}$  hydrogen bonds [35]. For a large series of amines with experimentally estimated NH stretching wavenumbers ranging from  $3400$  to  $2600\text{ cm}^{-1}$ , the correlations between experimental and calculated values were found to be non-linear [35]. At the same time, a pronounced non-linearity was found for the correlation between experimental NH stretching wavenumbers and NH proton chemical shifts [35]. The non-linearity of these relationships was unexpected in view of the results for  $\text{OH}\cdots\text{O}$  systems, which are characterized by corresponding linear relationships [12,13].

A deeper analysis of the present results, and of the origin of the different correlations observed for  $\text{OH}\cdots\text{O}$  and  $\text{NH}\cdots\text{O}$  systems, requires further theoretical studies going beyond the harmonic approximation and the perturbation theoretical approach, probably requiring full-scale anharmonic procedures. Molecular dynamics simulations seem a promising starting point [15,33,34,36], but such studies are considered outside the scope of the present investigation.

#### 4. Concluding remarks

This and previous investigations [12-15] demonstrate that the VPT2, DVPT2, and GVPT2 anharmonic models underestimate the OH stretching wavenumbers for systems with medium to strong intramolecular  $\text{OH}\cdots\text{O}$  hydrogen bonds. Most of the molecules considered in this study are characterized by large-amplitude OH stretching motions; see for example the recent treatise by



Dean et al. [37]. Hence, a major reason for the present failure of the VPT2 models seems to be the inherent inability of approaches based on low-order perturbation theory to account accurately for the properties of large-amplitude vibrational motions [23,24]. On the other hand, in spite of the vibrational complexity associated with these OH...O linkages, the calculated wavenumbers correlate well with the observed values. This leads to the derivation of linear regression equations of predictive value, as demonstrated above for 2-acetylmalonamide enol (12) and 2-cyanomalonamide enol (13). It is noteworthy that the standard harmonic analyses lead to linear regressions that are superior to those of the expensive anharmonic procedures, offering a practical way to the prediction of OH stretching frequencies for this class of compounds.

#### **Competing interests**

The author declares no competing interests.

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#### **Appendix A. Supplementary data**

Supplementary data to this article can be found online at . . .

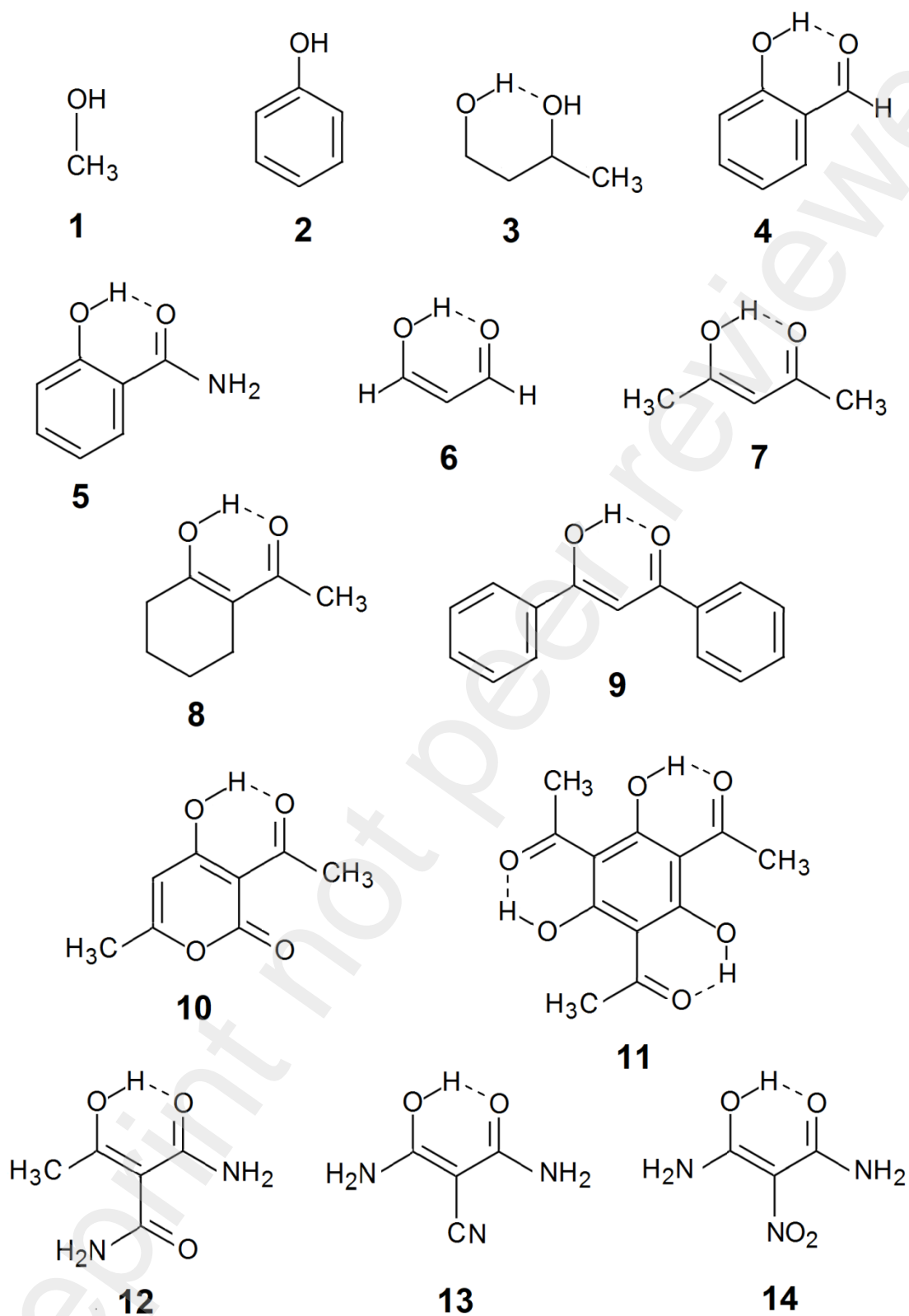
**Table 1.**

Calculated and observed OH stretching wavenumbers ( $\text{cm}^{-1}$ ). The experimentally estimated values are taken from the collection in Ref. [12], except for those of 1,3-butandiol (**3**) which are quoted from Ni et al. [26].

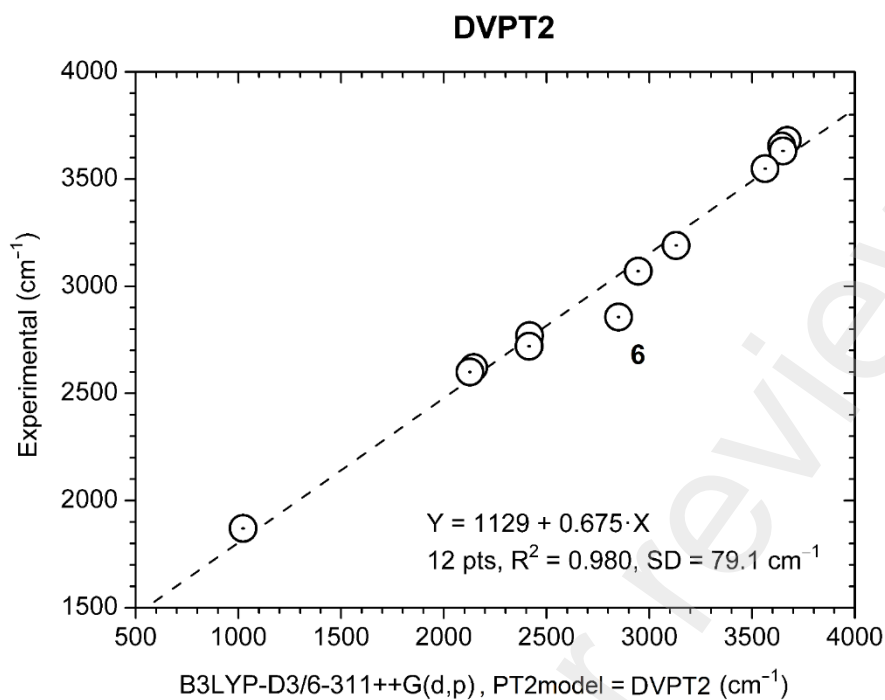
#	Compound	B3LYP/6-31G(d)		B3LYP-D3/6-311++G(d,p)			Expt.	
		Harm	VPT2	Harm	DVPT2	GVPT2		
1	Methanol	3752	3575	3847	3671	3671	3681	
2	Phenol	3749	3548	3836	3644	3644	3655	
3	1,3-Butanediol	3	3749	3545	3838	3650	(a)	3631
		1	3681	3497	3756	3563	(a)	3549
4	Salicylaldehyde	3344	3063	3412	3130	3130	3190	
5	Salicylamide	3271	2914	3313	2946	2945	3070	
6	Malonaldehyde enol	3105	2649	3148	2850	2599	2856	
7	Acetylacetone enol	3025	2460	3058	2417	2376	2770	
8	2-Acetylcyclohexanone enol	2975	2378	3000	2415	2351	2720	
9	Dibenzoylmethane enol	2903	2208	2916	2145	2144	2620	
10	Dehydracetic acid	2864	2209	2857	2127	2126	2600	
11	2,4,6-Triacetylphloroglucinol	<i>e'</i>	2719	-	2707	(3066)	(3065)	2440
		<i>a'</i>	2703	-	2691	(3707)	(3713)	-
12	2-Acetylmalonamide enol ( <i>b</i> )	2678	1720	2734	1840	1834	-	
13	2-Cyanomalonamide enol	2641	1712	2649	1654	1648	-	
14	2-Nitromalonamide enol	2286	1013	2279	1023	1004	1870	

(a) GVPT2 error, see Supplementary Information, S3.

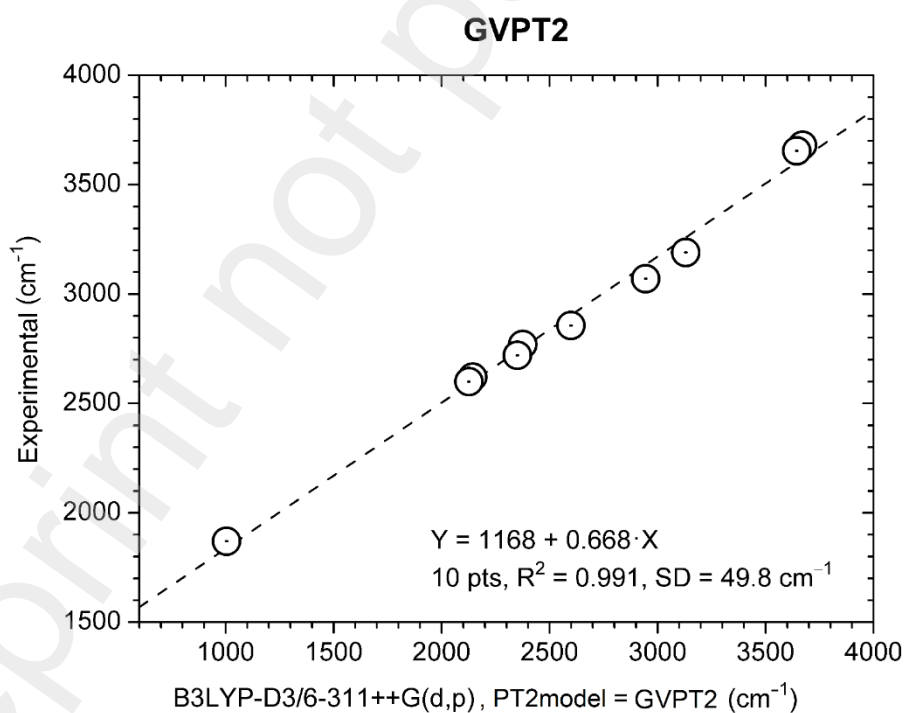
(b) Enolized on the acetyl group (Scheme 1), see Basheer et al. [27].



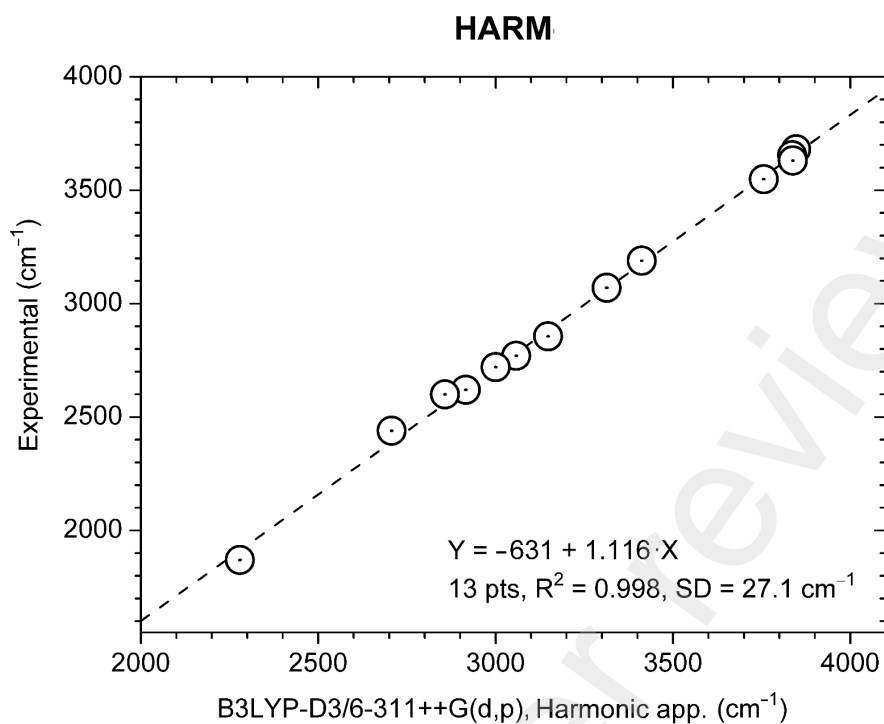
**Scheme 1.** Constitution of the 14 compounds considered in this investigation. The names of the compounds are listed in Table 1.



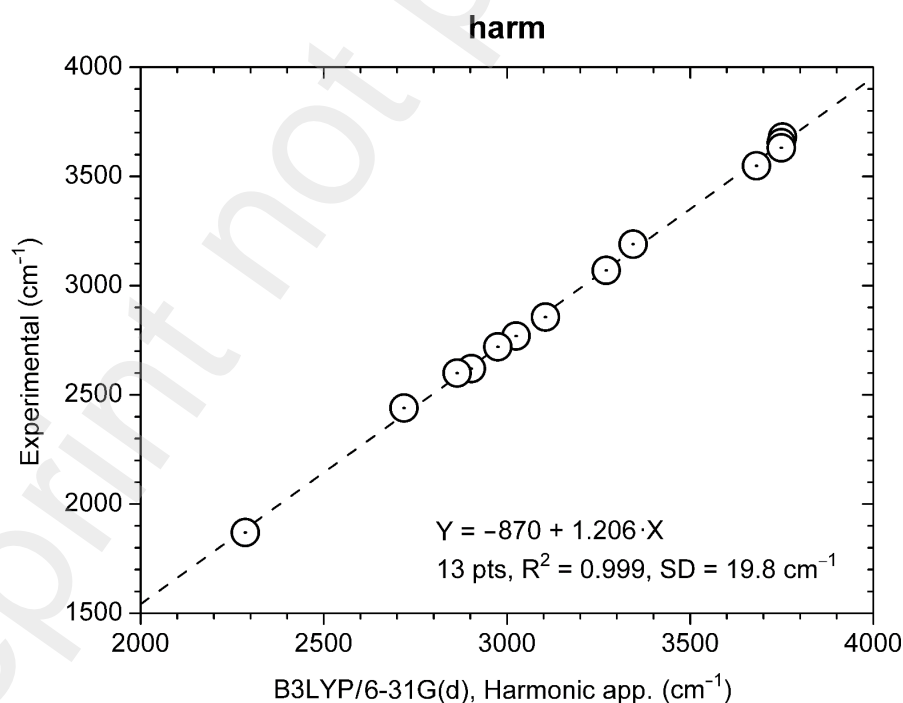
**Fig. 1.** Linear regression of experimental OH stretching wavenumbers on those predicted with B3LYP-D3/6-311++G(d,p) using the DVPT2 anharmonic model (Table 1).



**Fig. 2.** Linear regression of experimental OH stretching wavenumbers on those predicted with B3LYP-D3/6-311++G(d,p) using the GVPT2 anharmonic model (Table 1).



**Fig. 3.** Linear regression of experimental OH stretching wavenumbers on those predicted with B3LYP-D3/6-311++G(d,p) within the harmonic approximation (Table 1).



**Fig 4.** Linear regression of experimental OH stretching wavenumbers on those predicted with B3LYP/6-31G(d) within the harmonic approximation (Table 1).

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