

*Regular article*

# Vibrational analysis of small species in the liquid phase by a combined density functional theory and polarizable continuum method

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**Abstract.** The vibrational frequencies of small organic molecules and inorganic ions were predicted both in vacuum and in the liquid phase at the B3LYP/6-311G++(d,p) level of theory, within the harmonic approximation. The solvent effect was introduced as an electrostatic influence of the bulk by means of the integral equation formalism of the polarizable continuum model. The results show that the application of this continuum solvation model can reduce the overall error in the theoretical predictions. In order to improve the quality of the results, two different scaling procedures were applied. The frequencies obtained for the continuum, when compared with vacuum calculations, show a better linear correlation with experimental data, which increases the efficiency of the scaling procedures. A further reduction of the errors is obtained by partitioning the overall set of frequencies according to the nature of the normal modes and the charge of the solutes. The quality of the theoretical predictions, especially for the stretching modes of vibration of nonionic chemical species, is here noteworthy.

**Keywords:** Density functional theory – Solvent effects – Continuum – Raman spectra – Frequency scaling

## Introduction

Experimental spectroscopy is an invaluable tool to determine molecular structures, to study intramolecular and intermolecular forces or to identify reactive intermediates. Therefore, it is not surprising that prediction and interpretation of vibrational spectra have been amongst the most important applications of quantum ab initio techniques for almost the last 3 decades. In the

recent past, density functional theory (DFT) [1] became an attractive alternative to other methods traditionally used by computational chemists to predict the vibrational behavior of a wide range of molecular systems. In fact, DFT calculations have been able to incorporate electron correlation effects in the definition of molecular force fields and to show, at the same time, a competitive computational cost when compared with other post-Hartree–Fock (HF) methods [2]. In the last few years, several density functionals have been proposed and used quite routinely as computational tools [3], but Becke's three-parameter exchange–correlation hybrid functional with nonlocal correlation corrections, provided by Lee, Yang and Parr (B3LYP) [4, 5] has revealed a remarkable performance in the prediction of vibrational frequencies of a wide range of chemical species [5, 6, 7, 8, 9, 10, 11].

The implementation of analytical first and second derivatives has also played a crucial role in such success [7], but the lack of higher derivative contributions has always restricted the calculations within the harmonic approximation. Therefore, the predicted frequencies have remained affected by errors to a great extent owing to anharmonicity effects. In addition, there are other source of errors, like the inadequacy of the theoretical methods to include surrounding effects, such as the natural packing in crystal structures, the presence of counterions in ionic substances or the local and long-range interactions with the solvent when experimental data is obtained in the liquid phase. It is well known that the harmonic frequencies predicted by HF methods are systematically overestimated by about 12% when compared with experimental fundamentals [13]. The observation that the overall statistics of such errors follow approximately a systematic trend (also at other levels of theory) led several authors to propose different scaling procedures for semiempirical, HF and DFT calculations [8, 9, 10, 12, 14, 15, 16, 17, 18, 19, 20, 21, 22]. These scaling methods have proved to be successful in reproducing vibrational spectra, especially for the selected set of molecules for which they have

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been calibrated. However, transferability of the scaling factors is a major problem, even for molecules exhibiting similar structural features. One important cause for some failure in such transferability is the variability of the interactions established between the molecule and the surroundings, which may result in large and unexpected effects on the vibrational behavior. Therefore, these effects should be taken into account if improved theoretical predictions are desired.

Concerning the particular case of solvent media, some theoretical approaches have been employed over the last few decades to improve the calculation of physicochemical properties of molecular systems in liquid solution [23, 24, 25, 26, 27]. More recently, some popularity has been reached by continuum solvation methods where a solute is placed inside a cavity with appropriate shape, made in a continuous medium characterized by a dielectric constant  $\epsilon$ . The electronic distribution of the solute induces a charge density at the surface of the cavity which, in turn, creates an electric field that modifies the energy and properties of the solute. The effect of the reaction field is solved iteratively in the self-consistent-field method by the inclusion of a supplementary potential term in the solute Hamiltonian. This method has shown flexibility and accuracy enough to become a popular tool in computational chemistry, and has been successfully coupled with semi-empirical, HF and DFT Hamiltonians [23]. Recently, a vibrational analysis of the formate anion in aqueous solution was reported by our group [12], where the integral equation formulation of the solvation continuum model (integral equation formalism of the polarizable continuum model, IEF-PCM) [24, 25] was coupled with a wide range of HF, Møller–Plesset and DFT levels of calculation. In particular, the promising results obtained with the hybrid functional B3LYP [11, 12] led us to extend the study to other molecular systems.

As already mentioned, the influence of the solvent on the properties of a solute is not easy to predict and quantify without using accurate methods. The aim of this work is to present a systematic theoretical study of the vibrational behavior of several neutral and charged species in the liquid phase, using the IEF-PCM. As a first approximation only the electrostatic influence of the bulk is considered here. The inclusion of explicit solvent molecules, which we intend to carry out in future work, is expected to improve the description of the solvation model by taking into account important local interactions with the solute. In order to reduce the errors in the predictions, without significant increase in computational effort, the calculated harmonics were corrected using two different and simple scaling procedures, which are referred to in the next section.

## Methods

A quite heterogeneous set of 23 chemical species was studied in this work, both in the gas phase and in aqueous solution or organic solvents. The molecular systems and the corresponding surround-

ing media considered for the calculations are listed in Table 1. This particular set of compounds was obtained by restricting ourselves to the cases for which accurate data from liquid Raman experiments are available [33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46], and to those solvents for which a previous calibration has already been implemented in software packages.

All the calculations in this work used the Gaussian 98 package of programs [28]. The energy minimizations were carried out without any geometry constrictions, and the B3LYP functional was used within the DFT method. The frequency calculations were performed at the same level of quantum theory and under the harmonic approximation.<sup>1</sup> The basis set of atomic functions employed throughout this work was the expanded triple-zeta basis set 6-311 + + G(d,p), with diffusion and polarization functions added to all the atoms. This choice was based on the good compromise expected between computation time and accuracy of the calculations in such diverse molecular systems which include highly charged anions and atoms of the third row of the periodic table. The integral equation formalism of the polarizable continuum model, IEF-PCM [24, 25] was employed to include the electrostatic influence of the solvent. Each solute was inserted in a cavity with an appropriate shape based on interlocking spheres centered on its non-hydrogen atoms, as defined by the united atom topology model (UATM) [29]. The surface of each sphere was subdivided into 60 triangular tesseræ resulting from the projection of the faces of an inscribed pentakisdodecahedron. The cavity was inserted in a continuum medium characterized by a different dielectric constant  $\epsilon$  for each solvent (Table 1). The energy minimizations were carried out within the PCM starting from the geometries previously optimized in the gas phase. The harmonic frequency calculations were then performed at exactly the same level of theory, i.e. B3LYP/6-311 + + G(d,p).

The statistical analysis of the errors was based on the root-mean-square (rms) error,

$$\text{rms} = \sqrt{\frac{\sum_i^N \left( \frac{\omega_i^{\text{calc}} - \omega_i^{\text{expt}}}{\omega_i^{\text{expt}}} \right)^2}{N}}, \quad (1)$$

where  $\omega_i^{\text{calc}}$  and  $\omega_i^{\text{expt}}$  stand for the calculated harmonic frequencies and the experimental fundamentals, respectively, and the summation is extended to all the  $N$  vibrations analyzed. The use of adimensional relative errors seems more suitable for comparisons between different methods and molecular systems.

In order to improve the predicted frequencies, two different scaling procedures were used. One is the uniform scaling method, where a single linear factor is defined,  $\lambda_k$ , which scales the calculated harmonic frequencies as

$$\omega_i^{\text{sc1}} = \lambda_k \omega_i^{\text{calc}}. \quad (2)$$

For each particular set of vibrations analyzed in this work, an error function was considered with the relative deviations between  $\omega_i^{\text{expt}}$  and  $\omega_i^{\text{sc1}}$ . A least-squares fitting procedure was used to minimize such error functions and resulted in the following expression for the scaling factor [12]:

$$\lambda_k = \frac{\sum_i^N \frac{\omega_i^{\text{calc}}}{\omega_i^{\text{expt}}}}{\sum_i^N \left( \frac{\omega_i^{\text{calc}}}{\omega_i^{\text{expt}}} \right)^2}. \quad (3)$$

The other procedure is the wavenumber linear scaling (WLS) method [21], where a frequency-dependent scaling factor is obtained by least-squares fitting, assuming a linear relationship between  $\omega_i^{\text{expt}}/\omega_i^{\text{calc}}$  and  $\omega_i^{\text{calc}}$ .

<sup>1</sup>Traditionally, spectroscopists have used the term frequency instead of wavenumber to indicate a quantity expressed in units of reciprocal centimeters. This convention will be used throughout this work

**Table 1.** The 23 chemical species and respective media considered for the calculations. The experimental spectroscopy data, taken from references, are indicated for each case

Species	Medium	$\epsilon$	Species	Medium	$\epsilon$
C <sub>6</sub> H <sub>6</sub>	Vacuum[31]	2.247	H <sub>2</sub> O	Vacuum[33]	78.39
	Benzene [35]			Water[35]	
BrC <sub>3</sub> OH	Vacuum[32]	2.247	HCOO <sup>-</sup>	Vacuum[38]	78.39
	Benzene [43]			Water[44]	
ClC <sub>3</sub> OH	Vacuum[32]	2.247	NO <sub>2</sub> <sup>-</sup>	Vacuum [39]	78.39
	Benzene[43]			Water[45]	
C <sub>2</sub> H <sub>3</sub> N	Vacuum[33]	36.64	S <sub>4</sub> <sup>2-</sup>	Vacuum[40]	78.39
	Acetonitrile[33]			Water [40]	
CH <sub>3</sub> CONHCl	Vacuum[34]	36.64	BrO <sub>4</sub> <sup>-</sup>	Vacuum [41]	78.39
	Acetonitrile[34]			Water[46]	
CHCl <sub>3</sub>	Vacuum[33]	4.9	ClO <sub>4</sub> <sup>-</sup>	Vacuum[31]	78.39
	Chloroform[35]			Water [46]	
CH <sub>3</sub> OH	Vacuum[35]	32.63	NO <sub>3</sub> <sup>-</sup>	Vacuum[39]	78.39
	Methanol[35]			Water [47]	
CCl <sub>4</sub>	Vacuum[35]	2.228	CS <sub>3</sub> <sup>2-</sup>	Vacuum[42]	78.39
	Carbon tetrachloride [33]			Water [42]	
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	Vacuum [35]	10.36	SO <sub>4</sub> <sup>2-</sup>	Vacuum[31]	78.39
	1,2-Dichloroethane[35]			Water [46]	
CH <sub>3</sub> COCH <sub>3</sub>	Vacuum[33]	20.7	PO <sub>4</sub> <sup>3-</sup>	Vacuum [31]	78.39
	Acetone[35]			Water [46]	
CH <sub>3</sub> NO <sub>2</sub>	Vacuum[36]	38.2	PS <sub>4</sub> <sup>3-</sup>	Vacuum[42]	78.39
	Nitromethane[35]			Water [42]	
CH <sub>3</sub> OCONH <sub>2</sub>	Vacuum[37]	4.9			
	Chloroform[37]				

## Discussion

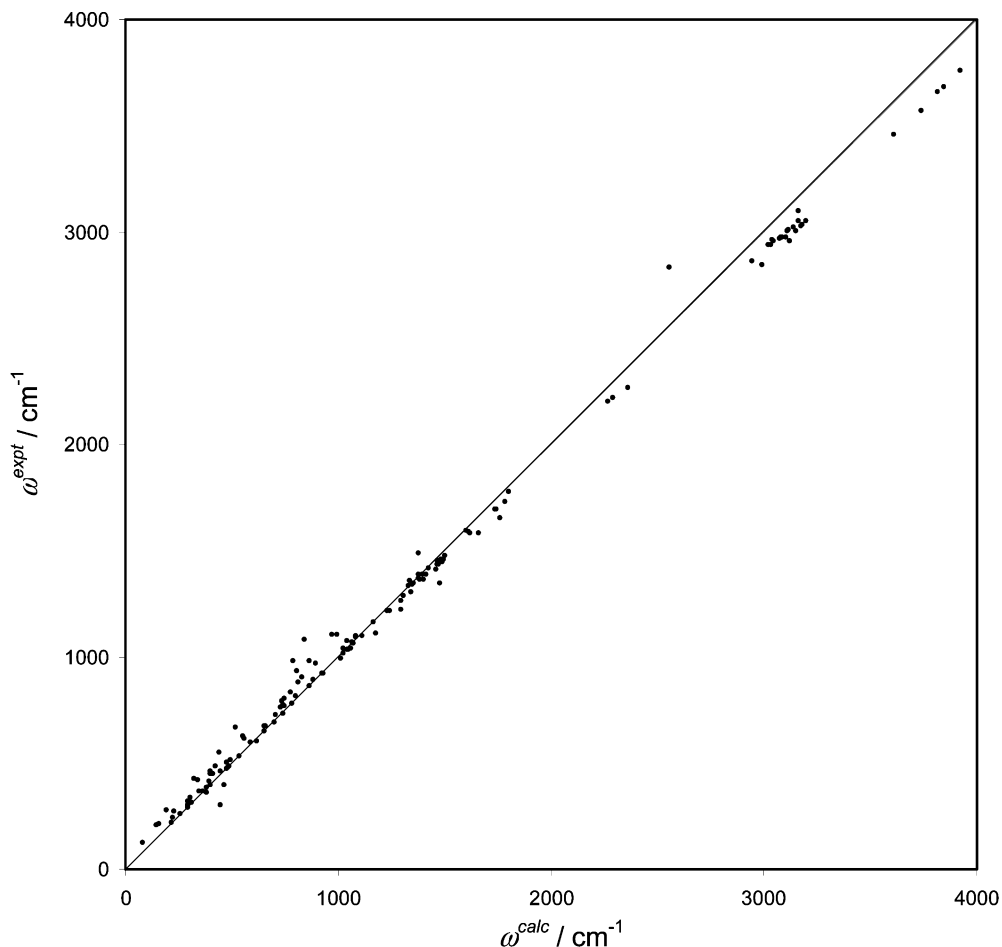
### *Analysis for a vacuum*

The geometry optimizations were started from reasonable initial structures taken from experimental data or high-level theoretical calculations (see references in Table 1). The assignment of each calculated frequency to the corresponding normal mode was established through the analysis of the displacements of the nuclei, with the use of the visualization program Molekel [30]. The predictions carried out for a vacuum were all compared with available gas-phase IR or Raman experimental data [31, 32, 33, 34, 35, 36, 37]. In the particular case of the ions, solid-phase Raman spectra were taken as references [31, 38, 39, 40, 41, 42].

The comparison of the overall set of calculated frequencies with the corresponding experimental fundamentals shows that, in general, DFT performs better than HF methods. This result is not surprising, and corroborates other previous studies on the performance of DFT methods in predicting vibrational frequencies [9, 10, 11, 12, 18, 19, 20]. In fact, the value of 8.93% obtained for the rms of the relative errors is significantly smaller than the typical 12% of standard HF methods. A scatter plot of experimental data against calculated values is shown in Fig. 1, and yields a reasonable Pearson correlation coefficient ( $r = 0.9976$ ) for a linear regression with the intercept at the origin. It is quite evident that the deviation from linearity is not homogeneous over all the range of frequencies; for example, for low frequencies the predictions are systematically underestimated, whereas for high frequencies a general overestimation is observed. Besides the obvious trend of the absolute deviation to increase with frequency, the

characteristics of the normal modes seem to include some perturbation in that general behavior. Therefore, a comparative statistical analysis was done in some different partitions of the overall set of frequencies. Firstly, and regarding the nature of the normal modes, three different subsets were proposed, namely stretch, bend and other. As shown in Table 2, the value of the rms decreases from 8.93 to 7.06% for stretching but an increase is observed in bending and other modes of vibration. In addition, the rms of the absolute errors,  $rms_{abs}$ , shows the opposite behavior, increasing from 77.2  $cm^{-1}$  in the overall set to 102.2  $cm^{-1}$  in stretching modes, whereas for bend and other subsets a considerable decrease to 44.0 and 43.5  $cm^{-1}$ , respectively, is observed. These results show that, though the absolute deviations are slight bigger for stretching modes, the relative errors become smaller owing to the typical high frequency of most of these modes. On the other hand, the remaining modes are predicted with smaller absolute errors, but the corresponding lower values of the frequency result in a loss of the relative accuracy.

The comparison between theoretical predictions and experimental data must be done carefully. Calculations carried out for a vacuum cannot reproduce exactly the real conditions of a gas-phase spectroscopy experiment. In particular, when comparison is made with solid-phase spectroscopy, some important environmental effects are neglected, such as the natural packing of crystal structures and/or the presence of neighboring ions in ionic substances. The overall set of 23 molecular systems includes ten anions (Table 1), for which solid-phase spectroscopy data are available [31, 38, 39, 40, 41, 42]. Therefore, the original set was partitioned into two different subsets, namely ionic and nonionic. In this case, it is observed that calculations perform better for



**Fig. 1.** Correlation between the unscaled predictions of the harmonic frequencies for a vacuum,  $\omega_i^{\text{calc}}$ , and the experimental values,  $\omega_i^{\text{expt}}$

nonionic systems (both relative and absolute rms have decreased) than for the ions. If we go further in the partition, and consider the stretch and bend subsets for both types of molecular systems, the main contribution for that different performance becomes evident. In fact, the stretching modes of the nonionic systems are predicted with lower relative errors (rms=4.31%) when compared with those of the ions (rms=11.1%). Concerning the bending modes, the results are not so encouraging, though the predictions are still worst for the ionic systems.

In order to improve the agreement between predicted frequencies and experimental fundamentals, two different scaling procedures were applied to all the subsets considered in Table 2, namely a uniform scaling method (single  $\lambda$ ) and a linear scaling method ( $\lambda$  linear). The former is an adaptation of the method proposed by Scott and Radom [18] to minimize the relative errors of the predictions [12], whereas the later is based on the WLS method of Yoshida and coworkers [21, 22], where a linear relationship between the scaling factor and the vibrational wavenumbers is assumed. The uniform scaling method has shown no efficiency for the whole set of frequencies, nor for its partition into three types of modes. However, if the partition of the original set into ionic and nonionic molecular systems is considered, the

improvement with that scaling method is evident for both subsets. In particular, the ionic systems show a considerable reduction in the relative rms (from 13.0 to 10.4%), though with some cost in the high-frequency modes (the absolute rms has increased from 91.8 to 131.6  $\text{cm}^{-1}$ ). The small error of rms=6.70% obtained in the nonionic subset is reduced to rms=6.35% by this uniform scaling method. If we partition these two subsets into stretching and bending modes (see last four rows of Table 2) we realize that the scaling can reduce the errors in all the cases. However, as far as the relative rms are concerned, the scaling seems to be more effective for the ionic systems than for the nonionic ones. The error obtained for the stretching modes of the nonionic systems, which is surprisingly small even before the scaling, is reduced to rms=3.39%.

The uniform scaling method is an attractive corrective technique because of its simplicity and general application, but the different magnitudes of  $\lambda$  presented in Table 2 show that the performance of the theoretical calculations depends on the nature of the molecular system and the type of vibrational mode. The WLS method [21, 22], on the other hand, is able to introduce some variability of the scale factor without significant increase of data processing. A scatter plot of the ratio  $\omega^{\text{expt}}/\omega^{\text{calc}}$  against  $\omega^{\text{calc}}$  is shown in Fig. 2 for the whole

**Table 2.** Statistical analysis of the theoretical predictions for a vacuum. Root mean square of the relative errors (rms) and of the absolute errors (rms<sub>abs</sub>)

Species	Normal modes <sup>a</sup>	Without correction		Correction with single $\lambda$			Correction with $\lambda$ linear		
		rms (%)	rms <sub>abs</sub> (cm <sup>-1</sup> )	$\lambda$	rms (%)	rms <sub>abs</sub> (cm <sup>-1</sup> )	$\lambda = b + m\omega^{\text{calc}}$	rms (%)	rms <sub>abs</sub> (cm <sup>-1</sup> )
Overall (154)		8.93	77.2	1.0044	8.92	81.6	$b = 1.0817$ $m = -4.4969 \times 10^{-5}$	8.61	71.0
Overall	Stretch (73)	7.06	102.2	0.9993	7.06	101.2	$b = 1.0816$ $m = -3.8658 \times 10^{-5}$	6.16	70.6
	Bend (63)	10.5	44.0	1.0089	10.5	47.2	$b = 1.1182$ $m = -9.9503 \times 10^{-5}$	10.4	41.1
	Other (18)	9.64	43.5	1.0104	9.59	46.7	$b = 1.2848$ $m = -2.7881 \times 10^{-4}$	8.32	49.4
Ionic	Overall (43)	13.0	91.8	1.0865	10.4	131.6	$b = 1.1877$ $m = -8.3939 \times 10^{-5}$	9.04	115.3
Nonionic	Overall (111)	6.70	70.7	0.9788	6.35	44.8	$b = 1.0134$ $m = -1.7837 \times 10^{-5}$	6.35	35.4
Ionic	Stretch (22)	11.1	121.4	1.0702	8.93	158.5	$b = 1.1640$ $m = -6.0824 \times 10^{-5}$	7.30	103.3
	Bend (19)	13.6	43.1	1.0978	10.3	61.1	$b = 1.2428$ $m = -2.1609 \times 10^{-4}$	8.46	49.5
Nonionic	Stretch (51)	4.31	92.6	0.9742	3.39	41.6	$b = 1.0075$ $m = -1.4746 \times 10^{-5}$	3.09	27.0
	Bend (44)	8.87	44.3	0.9785	8.59	39.6	$b = 1.0184$ $m = -2.6344 \times 10^{-5}$	8.81	38.6

<sup>a</sup>The number of frequencies analyzed in each subset are shown in parentheses

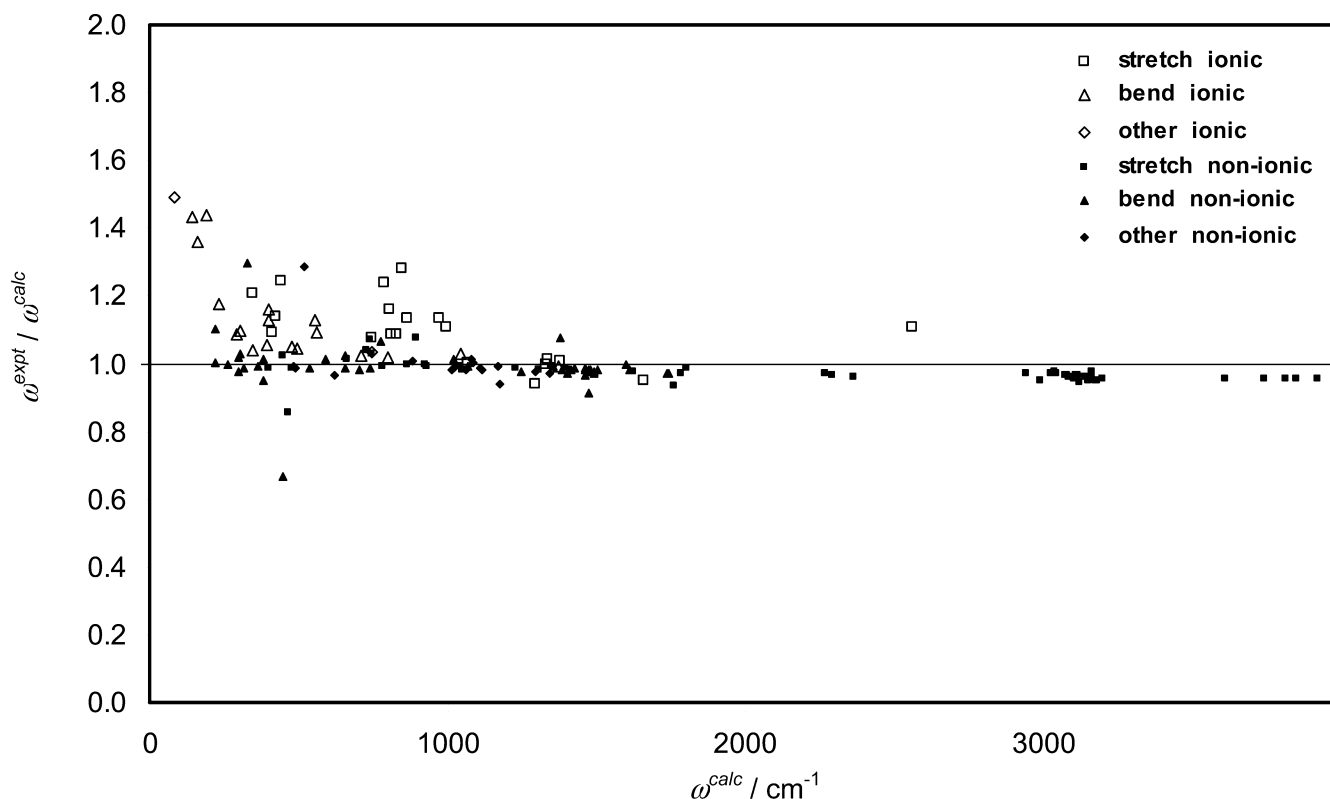
set of frequencies, grouped by charge of the molecular system and the type of normal modes. This figure shows the dependence of the ratios upon the characteristics of the normal modes and their bigger dispersion below 1,000 cm<sup>-1</sup>, which justify the trial partitions referred to earlier. The WLS linear relationship obtained by least-squares fitting for all the frequency subsets considered so far and the values of the rms obtained by the subsequent correction are shown in Table 2. In general, and as long as our sample of frequencies is concerned, the results show that this method has been more effective than the uniform scaling. Its performance over the whole set of frequencies is not very impressive (the rms has decreased from 8.92 to 8.61%), however, for the partition by modes of vibration, the improvement of the error in the prediction of stretching and other modes is clear. The results also show that ionic systems are more sensitive to this linear scaling than nonionic ones, as was already observed with the uniform scaling. In the ionic systems, the bending modes are more effectively corrected than the stretching modes, but the reverse is observed in the nonionic subset, where the small value of the relative errors obtained for the stretching modes, rms = 3.09%, is noteworthy.

#### Analysis for the liquid phase

The aim of the study presented in this section was to investigate the effect of the surrounding liquid medium on the geometries and frequencies of all the 23 molecular systems. The solvent effect was introduced by means of the IEF-PCM [24, 25] at the B3LYP/6-311++G(d,p) level of calculation. The energy minimizations carried

out in the liquid phase (Table 1 for the solvent considered for each chemical species) were all started from the optimized structures previously obtained for a vacuum. The presence of the solvent did not change significantly the structures of the solutes. The mean of the absolute deviations between vacuum- and continuum-optimized structures was 0.0072 Å for the bond lengths and 0.65° for the bond angles. The most extreme case was found to be the S<sub>4</sub><sup>2-</sup> anion, which shows a variation of -3.8° in the S-S-S angles and a variation of -12.7° in its dihedral angle (more details about these structures can be provided upon request). In spite of the absence of variability in the optimized structures, some changes were observed in the calculated frequencies (these data are available upon request). The errors reported in this section were based on the comparison between the predicted frequencies and the experimental data obtained by liquid-phase Raman techniques [33, 34, 35, 37, 40, 42, 43, 44, 45, 46, 47]. Apart from the small increase of the error for the stretching modes of the nonionic systems, the results compiled in Table 3 show that the IEF-PCM improved the theoretical predictions even before any correction was applied. If the partition by type of vibration is considered, it is observed that the bending modes are much more affected by the inclusion of the continuum solvent; on the other hand, the nonionic systems are shown to be more sensitive to this effect than the ionic ones. In fact, the last partition presented in Table 3 shows that the bending modes of the nonionic systems decrease the value of the relative rms by 5.01 when compared with the gas-phase values, and this is the biggest reduction observed in all the partitions.

In general, for all the 23 solutes, the application of either correction method leads to the same conclusion



**Fig. 2.** Correlation between  $\omega_i^{\text{calc}}$  and the ratios of  $\omega_i^{\text{expt}}$  to the  $\omega_i^{\text{calc}}$  frequencies. The results are grouped by charge of the molecular system and type of vibrational mode

about the effect of the polarizable continuum over the vibrational modes. A scatter plot of the ratio  $\omega^{\text{expt}}/\omega^{\text{calc}}$  against  $\omega^{\text{calc}}$  for the whole set of frequencies calculated in the continuum is shown in Fig. 3. If a comparison is made with the vacuum calculations (Fig. 2), it is observed that the dispersion of the ratio values, though not satisfactory, is reduced to some extent; the overall linear correlation coefficient changed from  $r=0.43321$  to  $r=0.49173$ . The worst predictions appear in the low-frequency region, but even excluding the points which could be treated as outliers, no significant improvement in the linear regression is obtained. Those few special cases correspond to the overestimated value of the *N*-chloroacetamide N–Cl stretching mode (with a  $\omega^{\text{expt}}/\omega^{\text{calc}}$  ratio around 0.85, Fig. 3), and the three modes exhibiting a ratio above 1.3, namely the S–S–S torsion and bending modes of the  $\text{S}_4^{2-}$  anion, and the torsion mode of  $\text{PS}_4^{3-}$ . Compounds containing halogen atoms or having linear molecular structures were already referred to as being special cases of poor theoretical prediction [21, 22]. In the particular case of *N*-chloroacetamide in acetonitrile, a side calculation was performed in order to evaluate the influence of the UATM on the prediction of the N–Cl stretching mode. A new cavity to lodge the solute molecule was defined with spheres also centered on the hydrogen atoms; however, the calculated harmonic frequency showed only a small change from 466.0 to 461.8  $\text{cm}^{-1}$ .

The combined method of the IEF-PCM with the WLS correction algorithm seems to constitute a promising strategy to treat the vibrational frequencies, because of the small errors that can result, even within the harmonic approximation. For the nonionic systems the errors were quite impressive; the values of the rms for stretching and bending modes were 2.92 and 3.35%, respectively. The comparison between the calculations carried out for a vacuum and a continuum shows that, in general, the influence of the reaction field is bigger for the charged molecular systems. The 290.6  $\text{cm}^{-1}$  deviation for the C–H stretching mode of the formate anion, already studied in a previous work [12], constitutes a special example of that solvent influence. In fact, the IEF-PCM has been shown to have great success in treating the strong electrostatic contribution to the solute–solvent interactions [23]; however, a few other modes belonging to noncharged systems were also found to have deviations in the calculated values greater than 100  $\text{cm}^{-1}$ , which is the case of the symmetric and asymmetric O–H stretching modes in the water molecule (132.2 and 161.2  $\text{cm}^{-1}$ , respectively) and the 219.6  $\text{cm}^{-1}$  deviation for the symmetric O–H stretching in methanol. The relative errors of the first two predictions for a vacuum were, respectively, 4.38 and 4.44%, whereas for the continuum those errors decrease to 0.77 and 0.14%. However, the error in the symmetric O–H stretching frequency of methanol increased from 4.53% for a

**Table 3.** Statistical analysis of the theoretical predictions for the continuum. rms and rms<sub>abs</sub>

Species	Normal modes <sup>a</sup>	Without correction		Correction with single $\lambda$			Correction with $\lambda$ linear		
		rms (%)	rms <sub>abs</sub> (cm <sup>-1</sup> )	$\lambda$	rms (%)	rms <sub>abs</sub> (cm <sup>-1</sup> )	$\lambda = b + m\omega^{\text{calc}}$	rms (%)	rms <sub>abs</sub> (cm <sup>-1</sup> )
Overall (168)		6.75	70.4	1.005	6.73	76.6	$b = 1.0701$ $m = -4.0640 \times 10^{-5}$	5.98	55.5
Overall	Stretch (81)	5.56	93.7	0.9927	5.51	82.2	$b = 1.0594$ $m = -3.2262 \times 10^{-5}$	4.52	52.9
	Bend (69)	7.36	35.4	1.0170	7.17	43.6	$b = 1.1076$ $m = -9.3367 \times 10^{-5}$	6.25	33.5
	Other (18)	8.89	43.5	1.0205	8.66	43.7	$b = 1.2270$ $m = -2.1149 \times 10^{-4}$	8.43	48.2
Ionic	Overall (45)	12.3	56.6	1.0749	8.60	88.9	$b = 1.1561$ $m = -7.0790 \times 10^{-5}$	7.63	94.9
Nonionic	Overall (123)	4.19	74.8	0.9841	3.87	52.3	$b = 1.0182$ $m = -2.0553 \times 10^{-5}$	3.38	28.6
Ionic	Stretch (23)	7.70	66.5	1.0545	5.72	92.5	$b = 1.1100$ $m = -3.9550 \times 10^{-5}$	4.63	62.3
	Bend (20)	12.3	44.6	1.0904	9.10	50.4	$b = 1.2120$ $m = -1.7938 \times 10^{-4}$	7.63	49.5
Nonionic	Stretch (58)	4.43	102.6	0.9719	3.36	46.4	$b = 1.0108$ $m = -1.7199 \times 10^{-5}$	2.92	26.0
	Bend (49)	3.86	30.8	0.9923	3.78	25.9	$b = 1.0326$ $m = -3.8844 \times 10^{-5}$	3.35	22.0

<sup>a</sup>The number of frequencies analyzed in each subset are shown in parentheses

vacuum to 7.03% after the inclusion of the reaction field effect. As stressed by Cappelli et al. [48] in a study of the O–H stretching mode in water and methanol, the continuum approach with a single solute molecule inside the cavity is not appropriate to describe the strong local interactions established between the hydroxyl group and the solvent molecules. Therefore, as suggested by the authors, a reasonable description of both cases can be obtained by the inclusion of one single solvent molecule, which will be considered in future work. Besides, as pointed out by Cappelli et al. [49], the presence of explicit solvent molecules may also affect scaling procedures, implying that the treatment of the theoretical predictions should be reviewed accordingly.

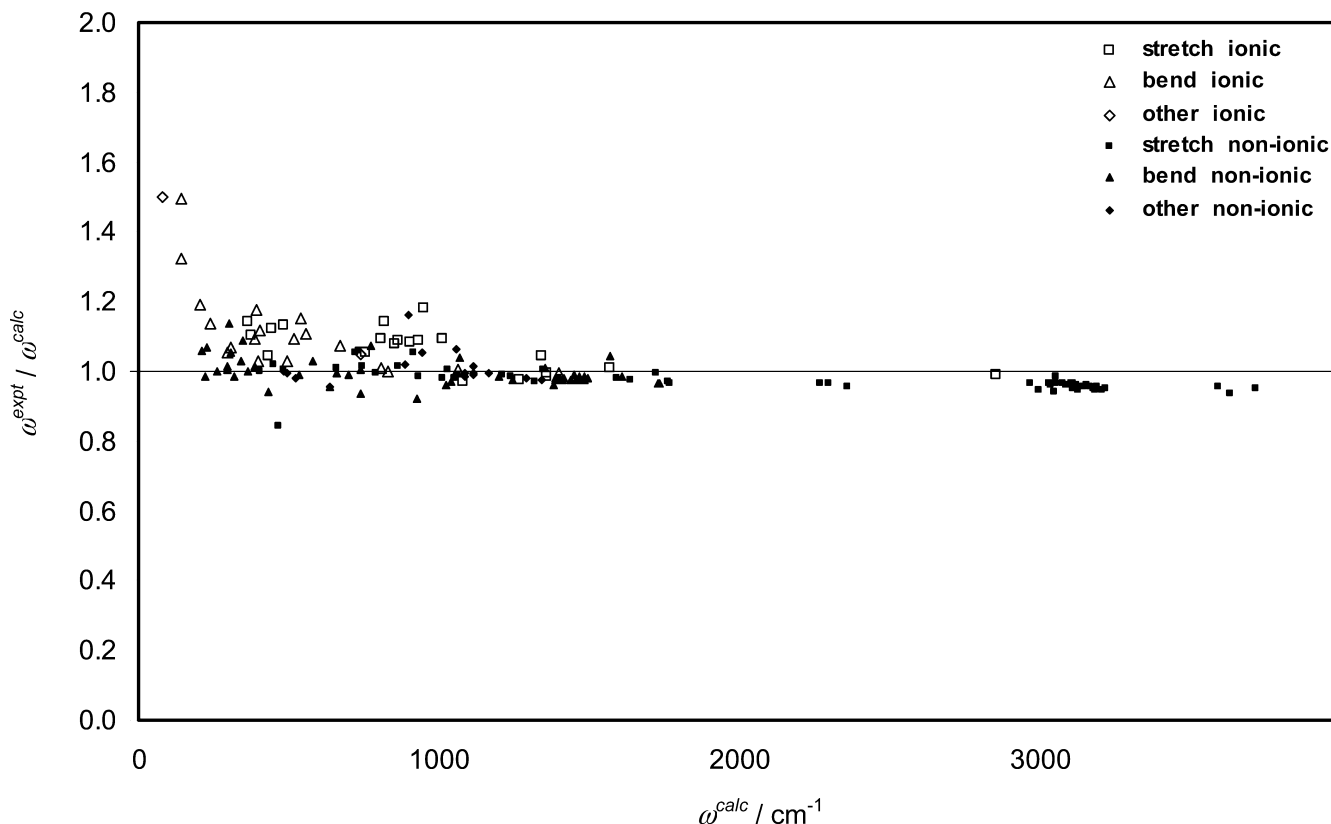
## Conclusions

The vibrations of 13 different organic molecules and 10 inorganic ions were analyzed at the B3LYP/6-311++G(d,p) level of calculation, both for the gas and the liquid phase. Concerning the gas-phase results, and as was already expected, DFT improves the quality of the predictions when compared with HF methods, even within the harmonic approximation. Comparison with gas-phase experimental results was always preferred when data were available but, especially for the ions, solid-phase spectroscopy was taken as a reference. Although the interactions felt by the molecules in gas-phase experiments could be assumed as negligible, in the condensed phase the absence of a good description of the environment is one source of error in the frequency calculations. Therefore, to take into account the solvating ambience around the solute, the IEF-PCM was employed at the same DFT level. The comparison of the

theoretical predictions with experimental data obtained from liquid-phase Raman spectroscopy techniques constitutes a good test for the polarizable continuum solvation model employed. The rms of the relative errors decreased from 8.93 to 6.75% in the overall set of 168 vibrational frequencies considered in this work. In order to reduce the errors of the theoretical predictions even further, two simple corrective procedures were employed without significant increase in computational time. The uniform scaling procedure corrects the calculated frequencies with a single optimized factor, and the WLS applied a scaling factor that varies linearly with the frequency. In general, the latter corrective method was shown to be more effective, and its application to the overall set of frequencies was able to reduce the rms of the relative errors to 8.61 and 5.98% for vacuum and liquid calculations, respectively.

The observation that the errors in the predictions do not follow the same trend led us to suggest some partitions of the overall set of frequencies into different subsets, according to the type of the normal modes and the nature of the molecular systems. The different values of the final rms obtained with this theoretical method, clearly show that the errors in the predictions greatly depend on the type of the normal mode. The small value of rms=2.92% obtained for the stretching modes of nonionic systems is noteworthy.

For molecular systems exhibiting strong solute–solvent local interactions, which is the case here of the O–H in water and methanol, the single-solute molecule approach in the continuum solvation model is not appropriate to describe their normal modes of vibration, and the addition of a few explicit solvent molecules is strongly suggested [48], which in fact should be



**Fig. 3.** Correlation between  $\omega_i^{\text{calc}}$  and the ratios of  $\omega_i^{\text{expt}}$  to the  $\omega_i^{\text{calc}}$  frequencies. The results are grouped by charge of the molecular system and type of vibrational mode

considered for future work. This theoretical method also shows a poor predictive performance for some peculiar modes, such as the overestimated value of the *N*-chloroacetamide N–Cl stretching mode (with a  $\omega^{\text{expt}}/\omega^{\text{calc}}$  ratio around 0.85, Fig. 3), and other modes exhibiting a ratio above 1.3, like the S–S–S torsion and bending modes of the  $\text{S}_4^{2-}$  anion and the rocking mode of  $\text{PS}_4^{3-}$ . The failure of predictions for compounds containing halogen atoms or having linear molecular structures has already been reported [22]. However, this combined DFT and polarizable continuum method seems to be very promising as an expedite theoretical tool to predict vibrational frequencies of small chemical species in solution. An attempt should be made in future to increase the number of molecular systems under study, and also to include a few solvent molecules around the solutes, especially in those cases where strong local interactions can be established.

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