Transferable Specific Scaling Factors for Interpretation of Infrared Spectra of Biomolecules from Density Functional Theory

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A set of transferable local scaling factors is established for assignment of infrared spectra of molecular systems of biological interest experimentally recorded under gas-phase conditions. Each scaling factor is specific for an experimentally observable vibrational mode chosen among those bringing significant structural information. Those factors are provided for harmonic calculations at the DFT B3LYP and DFT B3PW91 levels respectively with 7 and 2 different basis sets. The used training set of neutral molecules comprises nucleobases, aminoacids, peptides, sugars, and neurotransmitters. The proposed specific scaling factors usable for unambiguous conformer assignments lead to typical prediction errors ca. 10 cm^{-1} for free and moderately hydrogen-bonded group frequencies with red-shifts up to 200 cm^{-1}.

1. Introduction

Infrared spectroscopy is a powerful tool allowing the determination of structures of molecules of biological interest either in gas phase,[1−12] liquids,[13−18] matrices,[19−25] or solid state.[26,27] During recent years, a sizable number of experimental infrared spectroscopy studies have been devoted to small or rather moderate size systems that are well identified through mass spectrometry.[1,28,29] Those gas-phase studies then correspond to a nearly ideal situation because it can then be assumed that the experiments are conducted in absence of any environmental effect exactly as in the quantum chemistry calculations required for their interpretation. Infrared spectra of cold[7,30−32] or warm neutral[33] or ionic[34,35] species have been recorded by means of different infrared spectroscopic methods,[36] providing a wealth of reliable experimental data at rather good resolution (typically a few wavenumbers or better). Gas-phase Fourier-transform spectroscopy,[33,37] although restricted to neutral species, covers the whole IR spectral range. The combination of infrared laser excitation and resonant two-photon ionization (IR/R2-PI) is strikingly powerful because it provides the possibility of conformer-selection offered by the ionization process.[1,38] Infrared spectra of a sizable number of conformers have thus been separately recorded. However, this approach is mostly restricted to systems possessing suitable chromophores in the visible/UV region, although it has been recently extended to hot ionic species that do not possess this property.[34] Resonant infrared multiphoton dissociation (R-IRMPD) conducted with free-electron lasers[35,39−42] is nearly applicable to any mass-selected ionic species up to rather large sizes.[43] However, this method can suffer from the presence of small spectral shifts induced by absorption of radiation from excited species during the fragmentation process and does not provide conformer selection.

Assignments of experimental infrared spectra are performed through calculations.[44] Following a systematic or a Monte-Carlo exploration of the potential energy surface of the investigated species,[36] a set of structures corresponding to the lowest-energy tautomers or conformers supposedly populated under experimental conditions is optimized. For each tautomer or conformer, a corresponding vibrational spectrum is then predicted and compared to the experimental one. According to the size of the considered systems, semiempirical,[45,46] torsional anharmonicity,[47] density functional theory (DFT) [33,48−51]or ab initio,[4,52−55] methods are then preferentially used. Whereas the determination of the respective structural parameters and energies of conformers requires a reliable high-level of computation, typically the MP2 or RI-MP2 levels that include dispersion, most often at the ab initio level that is computationally demanding,[50,53] it turns out that simulations only conducted at the DFT level generally provide rather satisfying predictions of IR spectra[56,57] as long as electrostatic interactions can be held as the only ones responsible for hydrogen bonding. In contrast, DFT failures are observed in the case of strong hydrogen bonding and N−H$\cdots\pi$ interactions that require inclusion of dispersion terms ignored by DFT. Comparisons between computed and observed vibrational patterns are then used instead of absolute positions of spectral lines. Although different methods have been devised for taking into account the problem of the anharmonicity of vibrational modes of molecular systems of biological interest,[47,48,52,58−60] infrared spectra simulations are most usually performed within the harmonic approximation.

Scaling factors must be applied to harmonic frequencies to take into account the discarded anharmonicity terms.[26] In some exceptional cases, harmonic frequencies are identical for two different modes. Any scaling factor then cannot lift the degeneracy and a much more elaborate treatment must been used.[61] Otherwise, within the framework of a harmonic treatment, different strategies are opened. The most usual one consists in the use of uniform or broad-band scaling factors that can be applied over nearly the whole infrared spectral region.[62] Another strategy consists in the use of specific or local scaling factors that take into account the idiosyncrasy of each vibrational mode.[23,24,63−66] The use of those specific scaling factors can be restricted to a family of tautomers or conformers of a given molecular system. It can be also extended to molecules possessing the same biological function such as peptides.[5]

In the present work, we propose a set of specific scaling factors that can be used in the interpretation of gas-phase studies

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TABLE 1: Scaling Factors $a_{scal}^{\nu,L}$ for the B3LYP Functional

basis set	3−21 g	3−21 g**	3−21+g*	6−31 g*	6−31+g*	6−311++g**	SVP
ν (OH) free	1.0498	0.9814	1.0375	0.9752	0.9733	0.9533	0.9586
ν (OH) bound	1.1687	1.0231	1.1188	0.9656	0.9602	0.9391	0.9581
ν (NH_2)	0.9778	0.9456	0.9745	0.9615	0.9605	0.9576	0.9593
ν (NH)	0.9783	0.9418	0.9788	0.9596	0.9606	0.9588	0.9598
ν (CO)	0.9946	0.9969	1.0611	0.9608	0.9774	0.9831	0.9542
ν (NH2)	0.9427	0.9580	0.9459	0.9626	0.9653	0.9781	0.9942
ν (NH)	0.9910	0.9748	0.9782	0.9635	0.9665	0.9764	0.9724

TABLE 2: Scaling Factors $a_{scal}^{\nu,L}$ for the B3PW91 Functional

basis set	6−31 g*	6−31+g*
ν (OH) free	0.9664	0.9656
ν (OH) bound	0.9728	0.9685
ν (NH_2)	0.9548	0.9545
ν (NH)	0.9542	0.9554
ν CO)	0.9507	0.9654
ν (NH2)	0.9639	0.9662
ν (NH)	0.9591	0.9623

involving molecular systems. Those specific scaling factors are provided for widely used DFT vibrational spectra calculations. The here used calculations have been performed with the *Gaussian 03* package.[67] The training set is chosen among molecules possessing biological functions such as sugars, peptides, nucleobases, or neurotransmitters that have been experimentally studied in the gas-phase. Our goal is to evaluate the degree of confidence and transferability it is possible to expect from those proposed factors according to the used functional and basis set.

2. Determination of Specific Scaling Factors

Molecular systems of biological interest are characterized by the presence of several functional groups (O−H, N−H, C═O, etc.) that allow them to become engaged in hydrogen bonds with other molecules and provide them crucial molecular recognition properties. In isolated systems, the existence of different tautomers is possible. In a nucleobase such as guanine, a large number of imino or amino forms as well as keto or enol forms can be present.[68,69] Functional groups can also engage into intramolecular hydrogen bonds between themselves leading to different conformers. Both improvements of the tunability of high-power infrared lasers and developments of sources for setting biomolecular systems in the gas-phase coupled to supersonic beams[70] or ultracold ionic cells[7] that provide very low rotational temperatures have occurred during the last years. This has led to the availability of a sizable number of highly resolved experimental infrared spectra available in the literature. The assignment of observed transitions to individual configurations or conformations represents a challenging task because the structural differences can be subtle. In gas-phase infrared spectroscopy, typical resolutions are in between 10−20 cm^{-1} in the case of free-electron lasers down to 1 cm^{-1} and better in the case of optical parametric oscillators (OPO). With the spread of quantum chemistry packages and availability of computer power among experimentalists, conformer-selective or tautomer-selective experimental spectra are most usually interpreted by means of DFT simulations of vibrational spectra within the harmonic approximation. Among functionals, the hybrid functional B3LYP[71] is the most popular. It presents the remarkable ability to allow the simulation of vibrational spectra nearly over the whole available range of tunability of pulsed infrared lasers that extends from 600 to 3700 cm^{-1}. Other functionals such as the B3PW91 functional provides fair results for interpretation of IR spectra.[72] In the present work, we restrict our investigation to the DFT B3LYP and DFT B3PW91 functionals and we evaluate the predicting performances of widely used different basis sets. The choice of a basis set is the result of a compromise between prediction performances and computer-time requirement. Among the most widely popular basis sets used for the interpretation of infrared spectra of molecules of biological interest, one generally finds basis sets with a size comprised in between that of the 6−31G* basis set up to that of the 6−311 ++ G** set.[73] The low-level 3−21G ensemble of basis-set is no longer used in the case of molecules possessing a number of atoms smaller than 100. However, rather well-resolved infrared spectra of larger and larger molecular systems are now recorded.[41,74] A need for fast and reasonably accurate predictions of infrared spectra thus seems to appear. In that spirit, we thus wish to here evaluate the ability of not only the large basis-sets but also the low-level basis sets of the 3−21G family to more or less correctly simulate infrared spectra.

Infrared spectra obtained by means of tautomer- and/or conformer-selective gas-phase experiments have been chosen as the training set of molecular systems. The goal being oriented toward transferability, the training set here used has been chosen to include several biological functions. The training set comprises nucleobases, a model of the amide bond, aminoacids, dipeptides, mono- and disaccharides, and a β-blocker. The list of corresponding references is provided as Supporting Information. The structures of the 45 different tautomers and/or conformers belonging to 23 molecules (see the list in the Supporting Information) have been optimized at the DFT B3LYP and DFT B3PW91 level with different Gaussian basis sets ranging from the most economical 3−21G set up to today widely used and computer-time-consuming 6−311++G** set. We also include the SVP basis set[75,76] as an example of basis set outside the basis set ensemble established by Pople et al.

The vibrational frequency spectra have then been simulated and each tautomer and/or conformer published assignment has then been carefully checked. In gas-phase experiments, the density of infrared absorbing species is extremely low, several orders of magnitude less than for liquid- or solid-phase recorded spectra. The consequence is that the only observable vibrational modes are those possessing large intensities. In contrast with vibrational spectra obtained from Fourier-transform spectroscopy in the condensed phase, assignments presented in gas-phase experimental works, thus only concern rather restricted numbers of vibrational modes. In practice, the assigned spectral features mostly correspond to the O−H, N−H, symmetric and asymmetric N−H_2^s and N−H_2^{as} bond stretches in the 3200−3600 cm^{-1} range and to the C═C stretch and to the N−H and N−H_2 γ bending modes in the 1500−1700 cm^{-1} range.

For each level of theory (DFT functional and basis set), L and each of the preceding vibrational modes υ, individual scaling factors $a_{scal}^{i,j,\nu,L}$ have been simply obtained by dividing the experimental value $\nu_{exp}^{i,j,\nu}$ published in the literature for molecule i in a given conformation or configuration j by the corresponding

TABLE 3: Mean Error $\varepsilon_{v,L}$ in cm^{-1} (Text) for the Different Levels of Calculation[a]

functional	B3LYP	B3LYP	B3LYP	B3LYP	B3LYP	B3LYP	B3LYP	B3PW91	B3PW91
basis set	3−21 g	3−21 g**	3−21+g*	SVP	6−31 g*	6−31+g*	6−311++g**	6−31 g*	6−31+g*
ν (OH) free	36.4	33.0	13.7	6.5	6.1	3.1	2.8	7.9	4.8
ν (OH) bound	32.8	30.9	9.9	22.8	19.6	10.3	12.5	18.1	10.1
ν (NH_2)	26.0	30.4	26.0	10.6	10.1	10.8	10.9	9.7	12.5
ν (NH)	11.3	18.1	10.2	7.0	6.3	5.8	5.9	5.9	5.7
ν (CO)	13.6	11.3	6.7	6.5	6.0	4.3	4.8	6.4	4.8
ν (NH2)	11.6	11.1	7.1	5.3	5.0	3.6	4.3	4.3	3.8
ν (NH)	11.3	15.8	17.8	3.8	3.5	4.7	4.5	3.4	3.3
all	22.8	25.1	16.0	8.2	7.6	6.6	6.7	7.7	7.5

[a] In this table, the free ν (OH) values include totally free and weakly hydrogen-bonded (with red shifts less than 150 cm^{-1}) frequencies. The bound ν (OH) values correspond to much larger red shifts.

TABLE 4: Mean Error Dispersion $\sigma_{v,L}$ in cm^{-1} (Text) for Different Vibrational Modes and Levels of Calculation L[a]

functional	B3LYP	B3LYP	B3LYP	B3LYP	B3LYP	B3LYP	B3LYP	B3PW91	B3PW91
basis set	3−21 g	3−21 g**	3−21+g*	SVP	6−31 g*	6−31+g*	6−311++g**	6−31 g*	6−31+g*
ν (OH) free	48.6	41.3	21.7	8.1	7.3	4.3	4.0	9.9	6.1
ν(OH) bound	45.4	36.0	13.3	26.4	22.7	12.1	14.6	21.1	11.7
ν (NH_2)	38.1	43.3	34.9	13.7	12.0	13.3	12.6	11.3	14.8
ν (NH)	17.9	34.0	17.2	9.3	9.0	7.9	8.2	8.3	7.0
ν (CO)	8.1	8.8	8.2	4.8	4.9	5.0	4.5	7.3	5.0
ν (NH2)	17.7	13.7	10.7	8.4	7.4	5.3	6.4	7.4	5.6
ν (NH)	14.5	19.6	29.4	3.1	2.7	3.4	3.1	2.4	2.9
all	34.2	35.7	24.3	10.6	9.6	9.1	8.8	9.7	9.8

[a] In this table, the free ν (OH) values include totally free and weakly hydrogen-bonded (with red shifts less than 150 cm^{-1}) frequencies. The bound ν (OH) values correspond to much larger red shifts.

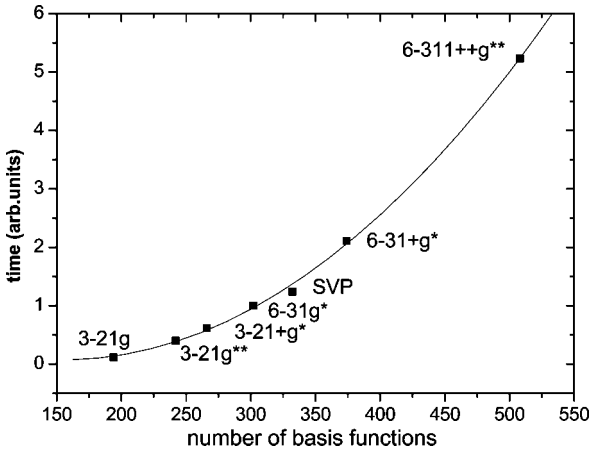

Figure 1. Computer time required for the simulation of the vibrational spectrum of a molecule (phenyl-*D*-mannose[82]) containing 34 atoms plotted as a function of the number of basis functions for different basis sets (the solid line is only a guide for the eye). The DFT functional is here the B3LYP functional.

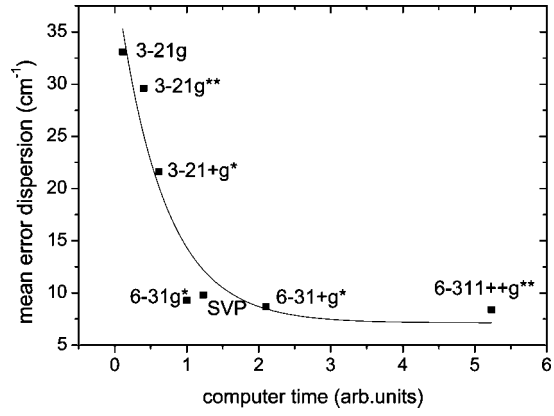

Figure 2. The mean error dispersion σ (in cm^{-1}) (text) for the prediction of vibrational frequencies of a conformer of the phenyl-*D*-mannose molecule[82] from specific scale factors is plotted as a function of the required computer time (the solid line is only a guide for the eye).

calculated value $\nu_{cal}^{i,j,v,L}$. The here proposed gas-phase transferable specific scaling factors $a_{scal}^{v,L}$ have then be obtained by simple arithmetic averaging of the individual values deduced from the training set of molecules. To evaluate the prediction capabilities and the transferability of those scaling factors, we also calculate the mean error $\varepsilon_{v,L}$ given by $\varepsilon_{v,L} = {}^{-}\nu_{predict}^{i,j,v,L} - \nu_{exp}^{i,j,v}$ and the mean error dispersion $\sigma_{v,L}$ given by $\sigma_{v,L}^2 = {}^{-}(\nu_{predict}^{i,j,v,L} - \nu_{exp}^{i,j,v})^2$. The predicted frequency values are, by definition, equal to $\nu_{predict}^{i,j,v,L} = a_{scal}^{v,L}\, \nu_{calt}^{i,j,v,L}$.

The engagement of the corresponding chemical groups into hydrogen bonds induces red-shifts $\delta\nu$ and line-broadenings. The here-proposed set of specific scaling factors cover the whole range of red-shifts encountered in the used training set ($\delta\nu \leq$ 150 cm^{-1}). However, if the specific scale factor established from free or nearly free O−H modes($\delta\nu \leq$ 150 cm^{-1}) is used for strongly H-bonded O−H groups ($\delta\nu \approx$ 300−350 cm^{-1}), we observe that errors as large as 50 cm^{-1} can be encountered. Prediction errors for those strongly red-shifted O−H modes can be reduced down to 20 cm^{-1} if another specific factor is introduced. Because the number of molecular systems in the used training set that exhibit such large red-shifted OH modes is too small, this specific scaling should be used with extremely carefully and is only introduced to emphasize the difference between nearly free and strongly hydrogen-bonded OH groups. It is worthwhile to note that differences between the two specific scaling factors can already be as large as 1%. Interpretation of larger red-shifts, corresponding to even larger anharmonicities such as those encountered in proline (530 cm^{-1})[77] would probably require different specific factors making difficult the achievement of accurate predictions.

The proposed scaling factors are given in Tables 1 and 2 respectively for the DFT B3LYP and DFT B3PW91 functionals with different basis sets. The corresponding mean errors $\varepsilon_{v,L}$ and mean error dispersions $\sigma_{v,L}$, averaged over the molecules

of the used training set, are respectively given in Tables 3 and 4 for different vibrational modes.

The ν NH_2 ($\approx$ 3300−3500 cm^{-1}) stretching mode[78] can possibly be in Fermi resonance with the 2γ NH_2 bending modes (1600 cm^{-1}) and the symmetric and asymmetric vibrational modes may be influenced differently. Interestingly, the largest mean error and mean error dispersion are found for the NH_2 stretching mode (except for the bound OH mode as explained above) independently of the functional or the basis set. We have thus been led to investigate if the prediction capability is improved or not if a distinction is made between the symmetric NH_{2s} and asymmetric NH_{2as} stretch modes. As shown in the Supporting Information, we observe an improvement in the prediction performances for some basis sets. To simplify the simulation of infrared spectra, it is reasonable in a first stage to ignore the distinction between symmetric and asymmetric NH_2 stretch modes. Similarly, the distinction between NH and NH_2 bending modes can of course be avoided. This is particularly true for the B3LYP functional with the three 6−31G*, 6−31+G*, and 6−311++G** basis sets where the two scaling factors do not differ by more than 0.2%, whereas for others basis sets and functional, the discrepancy gets larger at the expanse of prediction performances and ease of assignment.

In the comparison between performances of the different levels of computation, it is interesting to take into account both the improvement of prediction capability brought by the increase of the number of basis set functions and the corresponding increase of required computer time. As a typical example, Figure 1 presents the computer time required for the simulation of the vibrational spectrum of a conformer of the phenyl-*D*-mannose molecule[9] plotted as a function of the number of basis functions for different basis sets. Figure 2 presents the mean error dispersion σ (in cm^{-1}) for the prediction of vibrational frequencies of a conformer of the same molecule plotted as a function of the required computer time when using the specific scale factors provided in Table 1. Both curves are given for the B3LYP functional.

As can be expected, the required computer time increases steadily with the number of basis functions. The prediction performances first rapidly increase with the size of the used basis set but levels off above the 6−31+G* basis set. For the small 3−21G basis sets, the inclusion of polarized and diffuse functions brings a sizable improvement, in particular for nearly free and hydrogen-bonded OH stretches. The same holds to obtain a good prediction of the O−H stretch frequencies from larger basis sets. On the contrary, we observe that the addition of diffuse functions strongly increases the computer time but surprisingly does not bring any sizable improvement of the prediction capability. We also compare the two widely used functionals B3LYP and B3PW91. Those two functionals provide equivalent results, although for O−H stretches, B3LYP is slightly more accurate while B3PW91 performs better for N−H and N−H_2 bends.

3. Conclusion

DFT calculations offer an excellent compromise between speed and prediction performances. From a practical point of view, the use of a large basis set such as 6−311++G** does not bring any sizable improvement with respect to the less computer-time demanding 6−31G* and 6−31+G* basis sets. Moreover, except for O−H stretches that require the use of diffuse functions, the 6−31G* basis set provides prediction accuracies as good and possibly even better than basis sets including diffuse functions.

The present local scaling factors are here established from tautomer- or conformer-selective experimental spectra obtained for neutral molecular systems. We here include local scaling factors for low-level basis sets. These basis sets are no longer used for molecular systems containing less than typically 100 to 200 atoms. However, high-resolution experimental infrared spectra are now obtained for rather large biomolecular systems such as decapeptides[79] or gramicidins,[80] and their interpretation can be conducted through different approaches such as the use of a low-level of calculation such as the B3LYP 3−21+G* level or QM/MM.[81] The prediction capability is then slightly twice lower than the one obtained with the B3LYP 6−31G* level but the computer time and memory requirement are sizably reduced.

Supporting Information Available: Table of the mean error $\varepsilon_{v,L}$, mean error dispersion $\sigma_{v,L}$, and scaling factors $a_{scal}^{v,L}$ for the different levels of calculation L when the distinction between symmetric and asymmetric NH_2 stretches is established; and a bibiography of frequency and scale factor calculations for different functionals and basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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