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Is There a Simple Way to Reliable Simulations of Infrared Spectra of Organic Compounds?

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Ⓢ *Supporting Information*

ABSTRACT: To assess the ability of the quantum-chemical computations to reproduce the experimental relative intensities in the infrared (IR) spectra of both the gas- and condensed-phase systems, the hybrid DFT functional B3LYP has been applied to simulation of IR spectra for species containing from three to twelve first- or second-row atoms, both in the gas phase and in CCl_4 solutions. The results demonstrate that B3LYP, combined with the highly compact double-ζ basis set 6-31+G* and "scaled quantum mechanics" techniques, offers excellent quantitative performance in the calculations of relative IR intensities and frequencies ($\nu \leq 2200$ cm^{-1}) for the bands of vibrations of medium-size isolated molecules, whereas it produces unsatisfactory results for the solutions of the same species. Neither larger basis sets nor implicit treatment of the media effects improve the agreement of the simulated spectra with the condensed-phase experiment. At the same time, some preliminary results suggest that explicit modeling of media effects could offer better quality of the IR spectral simulations for the condensed-phase systems.
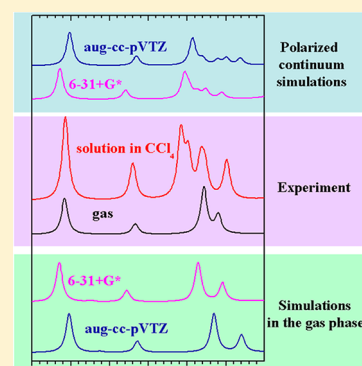
INTRODUCTION

Infrared (IR) spectroscopy is one of the most versatile means used in structural studies of organic molecules and, especially, of various materials. Quantum-chemical computations of harmonic frequencies and spectral intensities are essential for interpretation of experimental spectra, particularly for large molecules where the high density of states results in spectral complexity. As correlated ab initio methods are inapplicable to the vast majority of practically interesting systems, density functional theory (DFT) is widely used for the spectral simulations. DFT approximations, even combined with the small basis sets (6-31G*, 6-31+G*, 6-31G**) produce reasonable accuracy of fundamental frequencies, especially when scaling techniques are applied,[1,2] in the gas phase[3−7] and molecular crystals.[8−11] Evidence indicates that the problem of unsatisfactory IR intensities very often encountered in quantum-chemical spectral simulations can be solved by the appropriate choice of a basis set.[12−14] Recently, we have shown that the hybrid B3LYP functional in combination with the moderate-size Sadlej basis sets is the cost-effective method for the correct calculation of intensities of IR bands in the gas-phase spectra of small and medium-size organic molecules.[14]

In the context of the above evidence it is not quite clear why in the majority of practical cases DFT computations produce IR intensities rather poorly agreeing with the experiment. One of the possible explanations is that theoretical spectra are computed for isolated species, whereas their experimental counterparts, as a rule, are registered for condensed-phase samples. In other words, the reason for deviations between the computed and the experimental intensities is that the latter are strongly influenced by intermolecular interactions. Continuum

methods are valuable for thermodynamical calculations;[15] however, their applicability to study details of the local structure in aqueous solutions is vague. The second possible reason is a double-harmonic approximation,[16] which ignores electric anharmonicity.[17] These matters are beyond the scope of the present study. Another possibility is that the reported assessments of the quality of the intensity computations are not quite reliable because test sets of molecules used for benchmarking of the IR spectral computations are not representative enough. They include small molecules, whereas in practice spectroscopists deal with medium-sized or large species. Thus, a more thorough assessment is needed on the basis of much broader test sets of molecules of at least a medium size.

The present paper is focused on quantitative analysis of both hypotheses mentioned above. It is organized as follows: in the first part the DFT "gas-phase" computations are compared with available gas-phase experiments and high-level correlated ab initio computations for medium-size molecules; in the second part quantitative data on IR intensities in the spectra of condensed-phase systems are compared with both the "gas-phase" computations and various continuum models. As in our previous work,[14] we assess the quality of a computational method on how well it reproduces the experimental ratio of the intensities, because the relative, rather than absolute, band intensities are usually of interest for spectral simulation and interpretation. The hybrid DFT functional B3LYP was earlier

estimated as one of the best approaches to simulations of vibrational spectra for small molecules (from one to six first- or second-row atoms) in the gas phase.[13,14] In this study it is applied to computation of "gas-phase" IR intensities for a set of 23 test molecules including from 3 to 12 first- or second-row atom systems. Another set of 6 test molecules (5 or 6 first-row atoms; IR spectra registered for CCl_4 solutions) was used to assess the ability of the computations to reproduce the experimental relative intensities in the spectra of condensed-phase systems.

■ COMPUTATIONS

All calculations were carried out using the Gaussian-03 suite of programs.[18] Following full geometry optimizations at each level of theory, harmonic vibrational frequencies and IR intensities were calculated for the widely used DFT methods employed in this study, corresponding to the Becke's three-parameter exchange functional[19] in combination with the Lee–Yang–Parr correlation functional[20] (B3LYP). Calculations were carried out with the following basis sets: 6-31G*,[21,22] 6-31+G*,[21−24] Sadlej's polarized triple-ζ basis sets, optimized for electric properties (pVTZ[25−30] and Z3PolX[31]), and Dunning's "correlation consistent" cc-pVTZ and aug-cc-pVTZ basis sets.[32] The calculated force fields were transformed to a redundant set of individual internal coordinates,[6] and the scaling procedure was applied with the use of the program described in refs 33 and 34. F_{ij}(scaled) $= (s_i s_j)^{1/2} F_{ij}$, where s_i and s_j are scaling factors for internal coordinates i and j, respectively. Transferable scaling factors, employed for this purpose,[6,7,35] are summarized in Table 1S (Supporting Information). Infrared intensities were computed in the double harmonic approximation, ignoring cubic and higher force constants and omitting second and higher order dipole moment and polarizability derivatives. To minimize possible influence of this neglect of the anharmonicity effects on a comparison of the computed and experimental (anharmonic) intensities, the bands of the most anharmonic CH stretching modes were excluded from the comparison. Therefore, we compared the computed IR intensity ratio from a given level of theory I_k/I_{max} (where I_k is the IR intensity of the kth vibration mode, I_{max} is the IR intensity of strongest band in the region of $\nu \leq 2200$ cm^{-1}) with the same IR intensity ratio obtained either by experiment or by means of high-level ab initio methods.

The possible influence of surrounding media on IR spectral parameters was evaluated within the framework of the polarized continuum model (PCM) as it is implemented into Gaussian03[18] (IEF-PCM by default[36,37]). Also PCM calculations using Klamt's form of the conductor reaction field (COSMO)[38] were carried out with the ORCA 2.9 program.[39] The IR spectral calculations were based on the molecular structures preliminary optimized within the corresponding PCM approach.

■ RESULTS AND DISCUSSION

Assessment of "Gas-Phase" Infrared Intensities. In previous studies,[40,41] it was found that high-level correlated ab initio methods, QCISD[42] and CCSD(T),[43] with large basis sets produce IR intensities in good agreement between both theoretical methods, but both showed larger discrepancies with respect to experimental values. Therefore, a large fraction of the difference may be attributed to the experimental uncertainties (usually estimated as ±10%) and the double

harmonic approximation. A comparison of IR intensities computed for small molecules (comprising from one to three first- or second-row atoms) by Hartree–Fock (HF), second-order Moller–Plesset perturbation theory (MP2), and various DFT methods with both the high-level ab initio computations and experiment demonstrated[12,13] that the hybrid DFT approaches with large basis sets produced results much better than HF and of approximately equal or even better quality than MP2. There was a reasonable agreement when the DFT results were compared with experiment or with high-level ab initio computations, though discrepancies with respect to experimental values were systematically larger than with respect to QCISD and CCSD(T) results.

In our assessment[14] of MP2 and three hybrid density functionals (B3LYP,[19,20] M05,[44] and M05-2X[45]), we compared the relative intensities computed at these levels of theory with the experimental relative intensities measured in the gas-phase IR spectra of the following series of small- and medium-sized molecules with a variety of single and multiple bonds: C_2H_4, C_2D_4, $CH_2=C=CH_2$, $CD_2=C=CD_2$, C_6H_6, H_2CO, CD_2O, C_2H_4O, C_2D_4O, $CH_3CH=O$, $(CH_3)_2C=O$, CH_3CN, CD_3CN, CH_3NC, CS_2, SCO, $COCl_2$, CH_2F_2, CD_2F_2, CH_2Cl_2, further referred to as test set **1**. It was demonstrated that most cost-effective B3LYP computations were in good agreement with the experimental data. More than that, B3LYP calculations of the intensities using highly compact Sadlej's Z3PolX basis set retained the high accuracy of the more CPU expensive Sadlej's pVTZ and much more expensive aug-cc-pVTZ calculations.

It should be noted that the majority of the above test molecules comprised three or four first- or second-row atoms, and benzene was the largest molecule. In addition, thymine and thymine-1,3-d_2 were included, but the IR intensities for these molecules were measured for the species isolated in an Ar matrix instead of the gas phase. Besides, assignments of experimental IR bands were not always straightforward, and a direct comparison of the experimental and computed intensities of all the individual bands was difficult in several cases.

To avoid similar difficulties in the present study, we preferred to include in our test set (**2**) five molecules with IR intensities computed with the use of high-level correlated ab initio method, CCSD(T): pyrrole, thiophene, furan, uracile, and pyrimidine. Relative experimental intensities of IR bands in the gas-phase spectrum of pyrrole and furan are available,[46] though the authors caution that the data are not accurate. Therefore, we compared our results for pyrrole with the CCSD(T)/aug-cc-pVTZ computations,[47] whereas in the case of furan and thiophene CCSD(T)/cc-pVTZ calculated intensities[48] were used for the benchmarking. Vibrational spectra of uracil, also included in set **2**, have been investigated in numerous theoretical and experimental works (the corresponding references can be found in ref 49). However, there are still significant doubts on the interpretation of the IR spectrum of isolated uracil, the main problem being the large number of overtones and combination bands having intensities comparable to those of some fundamentals. Thus, instead of experimental anharmonic data we used for comparison with our computations the harmonic IR intensities computed[49] at the CCSD(T) level and extrapolated to the complete basis set limit. In the case of pyrimidine we preferred to use for the benchmarking the CCSD(T)/aug-cc-pVTZ computed[50] IR intensities, instead of experimental intensities measured for the molecules isolated in an Ar matrix.[51]

Intensities of IR bands in the gas-phase spectra of test molecules from a set (**3**) were taken from available experimental data: ethane,[52] ethane-d_6,[52] propane,[53] propane-d_2,[53] propane-d_6,[53] propene,[54] methylacetylene,[55] methylacetylene-d,[55] methylacetylene-d_3,[55] cyclobutene,[56] dimethylformamide,[57] benzene,[58] cyclohexane,[59] cyclohexane-d_{12},[59] toluene,[60] toluene-d_8,[60] p-xylol,[60] hexafluorobenzene.[61]

Figure 1 shows the basis set dependence of correlation coefficients (R) and standard deviations (SD) of B3LYP
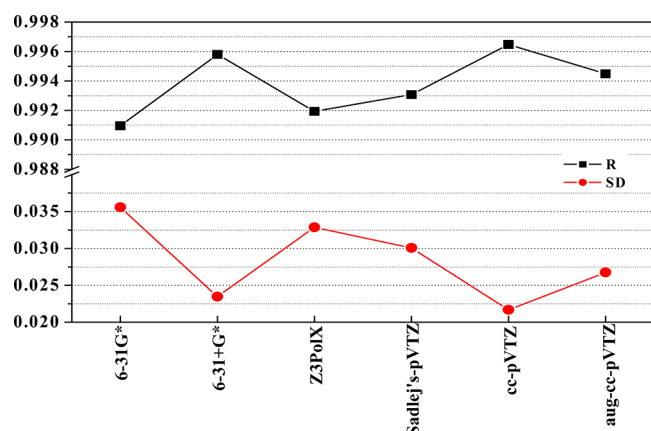
Figure 1. Relative IR intensity basis set dependence for test set **2**; R, correlation coefficient; SD, standard deviation. See Table 2S (Supporting Information) for details (ESI).

calculated relative intensities from CCSD(T) computed relative intensities for molecules of test set **2**. The results for test set **3** are given in Table 1. Complete tables of the numeric results for

Table 1. Assessment of Computed Infrared Intensities vs Experimental Results for Test Set 3: Ethane, Ethane-d_6, Propane, Propane-d_2, Propane-d_6, Propene, Methylacetylene, Methylacetylene-d, Methylacetylene-d_3, Cyclobutene, Dimethylformamide, Benzene, Cyclohexane, Cyclohexane-d_{12}, Toluene, Toluene-d_8, p-Xylol, Hexafluorobenzene[a]

basis set	6-31G*	6-31+G*	Z3PolX	Sadlej's pVTZ	cc-pVTZ	aug-cc-pVTZ
R^b	0.9486	0.9807	0.9897	0.9821	0.9881	0.9874
SD^b	0.104	0.065	0.048	0.064	0.051	0.053

[a]Only those modes for which experimental intensities had been available were considered; modes that are inactive were not considered. Total number of data included in the analysis N = 139. For details see Table 3S (Supporting Information) (ESI). [b]R, correlation coefficient; SD, standard deviation.

test sets **2** and **3** are provided as ESI (Tables 2S and 3S, Supporting Information, respectively). As diffuse basis functions are added to the 6-31G* basis, the IR intensities improve essentially, and results obtained with the 6-31+G* and larger basis sets, Z3PolX, Sadlej's pVTZ, cc-pVTZ, and aug-cc-pVTZ, practically coincide with each other. Similar dependencies were found in our previous paper[14] for set **1** of test molecules of comparatively small size. The results obtained then with the Z3PolX basis set were marginally better than with the 6-31+G*, which prompted us to recommend the B3LYP/Z3PolX level of theory as a method of choice. Present data, obtained with more representative sets **2** and **3** of larger molecules, demonstrate that differences in quality of

computations with the 6-31+G*, Sadlej's, and Dunning's basis sets are insignificant. It is especially clearly seen for test set **2**, in which case B3LYP computations with all these basis sets demonstrate the excellent performance. In the case of test set **3** general agreement of our B3LYP computations with the gas-phase experimental data is slightly worse, as should be expected considering the experimental uncertainties (at least ±10%) and the double harmonic approximation. Nevertheless, in all cases B3LYP/6-31+G* simulations produce correct results qualitatively coinciding with the corresponding experiment and much more demanding B3LYP/aug-cc-pVTZ simulations. Similar comparisons for other molecules not included in the test sets (for example, Figure 1S, Supporting Information), also demonstrate practically equal quality of the spectral simulations with 6-31+G* and aug-cc-pVTZ basis sets. Thus, the B3LYP/6-31+G* computations represent an adequate level of theory to calculate IR intensities in the gas-phase spectra of organic molecules. These results are significant in light of substantial savings in CPU time 6-31+G* affords relative to aug-cc-pVTZ and even Sadlej's Z3PolX and pVTZ basis sets.

It should be noted that although we focus on intensities, good prediction of vibrational frequencies is equally necessary to provide secure assignment of experimental IR bands. Numerous examples demonstrate that overall good quality of frequencies computed with the use of the moderate and even large basis sets did not exclude some misassignments in the spectra of medium-size or large molecules of low symmetry. Uniform empirical scaling does not improve the situation, as this sort of scaling just simultaneously shifts all the computed frequencies (see, e.g., ref 13 and references cited therein) and cannot result in, e.g., transposition of two simulated bands. More satisfactory agreement between the computed and experimental vibrational frequencies can be achieved through the scaling of the quantum-chemical harmonic force field (so-called SQM, scaled quantum mechanics[3]). An important advantage of the use of the 6-31+G* basis set is that transferable scaling factors affording high quality of B3LYP/6-31G* SQM computations[4−7] can be applied for B3LYP/6-31+G* SQM simulation as well without loss of accuracy for the calculated frequencies.[7] This is demonstrated in Table 7S (Supporting Information) (ESI). Thus, B3LYP/6-31+G* level of theory offers the most cost-effective choice for the quantitative prediction of both IR intensities and vibrational frequencies.

Assessment of Infrared Intensities for Molecules in Aprotic Solvents. Surprisingly, there seem to be no systematic surveys comparing different theoretical methods for a representative collection of medium-size molecules in the aprotic solvents. In the present work we compare B3LYP computations of IR intensities for various basis sets with the corresponding experimental values measured for CCl_4 solutions of the following test molecules: dimethylformamide,[62] trioxane,[63] methylethanoate,[64] pyridine,[65] cyclohexane,[59] cyclohexane-d_{12}[59] (set **4**).

Table 2 shows the basis set dependence for correlation coefficients (R) and standard deviations (SD) from experimental relative intensities for test set **4**. Similar to the case of the gas phase, 6-31G* gives unsatisfactory intensities, but the results for all other basis sets are only marginally better.

The results of a similar comparison for a smaller subset (**5**) of test molecules are presented in Table 3. Set **5** comprises the molecules with available relative intensities of IR bands

Table 2. Assessment of Computed "Gas-Phase" Infrared Intensities vs Experimental Results for Test Set 4 Measured for CCl$_4$ Solutions of the Following Molecules: Dimethylformamide, Trioxane, Methylethanoate, Pyridine, Cyclohexane, Cyclohexane-d_{12}[a]

basis set	6-31G*	6-31+G*	Z3PolX	Sadlej's pVTZ	cc-pVTZ	aug-cc-pVTZ
R[b]	0.9017	0.9447	0.9421	0.9565	0.9645	0.9626
SD[b]	0.132	0.102	0.112	0.094	0.085	0.088

[a]Only those modes for which experimental intensities had been available were considered; modes that are inactive were not considered. Total number of data included in the analysis N = 60. For details see Table 4S (Supporting Information) (ESI). [b]R, correlation coefficient; SD, standard deviation.

Table 4. Assessment of IEF-PCM Computed Infrared Intensities vs Experimental Results for Test Set 4 Measured for CCl$_4$ Solutions of the Following Molecules: Dimethylformamide, Trioxane, Methylethanoate, Pyridine, Cyclohexane, Cyclohexane-d_{12}[a]

basis set	6-31G*	6-31+G*	Z3PolX	Sadlej's pVTZ	cc-pVTZ	aug-cc-pVTZ
R[b]	0.8880	0.9405	0.9392	0.9536	0.9608	0.9598
SD[b]	0.143	0.107	0.116	0.098	0.090	0.092

[a]Only those modes for which experimental intensities had been available were considered; modes that are inactive were not considered. Total number of data included in the analysis N = 60. For details see Table 4S (Supporting Information) (ESI). [b]R, correlation coefficient; SD, standard deviation.

measured both in the gas phase and in CCl$_4$ solutions: dimethylformamide, cyclohexane, cyclohexane-d_{12}. Table 3 clearly demonstrates that the simulations offering reasonably good agreement for the gas-phase spectra produce unsatisfactory results for the solutions of the same molecules.

To improve the quality of the harmonic frequencies and IR intensities, the solvent effects should be taken into account. In explicit solvent models both solute and solvent molecules are treated quantum-chemically at equal levels, e.g., within the framework of CPMD[66] and the DFT-based molecular dynamics,[67,68] or at different levels as in QM/MM[69] or ONIOM[70] approaches. Among the implicit solvent models, the polarizable continuum model (PCM) is widely used.[71−75] When solvents are capable of hydrogen-bonding interactions with solutes, explicit consideration of several solvent molecules has significant impacts on the harmonic frequencies and IR intensities.[76−79] A serious drawback of this discrete-continuum model[80,81] is the uncertainty in the minimal number of solvent molecules required to simulate the diluted aqueous solutions.[82]

Clearly, implicit solvent models are affordable, whereas more rigorous approaches are too time- and resource-demanding to be used in everyday spectrochemical practice. As our intent is to provide practical information to spectroscopists who wish to use computations to assist in assigning spectra, we focus on assessment of the various PCM models. The results presented in Table 4 and Table 5S (Supporting Information) clearly demonstrate that implicit treatment of the solvent effects on the solutes' spectra does not improve the quality of the calculated IR intensities, irrespective of the PCM model used.

It is worth noting that if published results of application of implicit solvent models are analyzed, in no case is there an obvious improvement of the IR spectral simulations for the spectral range of $\nu \leq 2200$ cm^{-1}. This comes true even for systems like cyclohexane in CCl$_4$ from test sets **4** and **5**, which are seemingly not prone to pronounced intermolecular interactions. Thus, both the present assessment and literature data suggest that solvent effects on IR intensities cannot be

properly accounted for within the framework of PCM approach.

CONCLUSIONS

In summary, the results presented here demonstrate that there are two answers to the question put in the title of present paper. First, the hybrid DFT functional B3LYP, combined with the highly compact double-ζ basis set 6-31+G* and SQM techniques, offers excellent quantitative performance in the calculations of relative infrared intensities and frequencies for the bands of vibrations ($\nu \leq 2200$ cm^{-1}). Computations at this level of theory are so economical that allow using a PC or even laptop for sufficient simulation of IR spectra of medium-size *isolated* molecules. Second, there is no simple way to equally good simulations for the condensed-phase systems, in which case intermolecular interactions can strongly deteriorate the agreement of the IR intensities computed for the isolated species with the experimental intensities. Neither larger basis sets nor implicit treatment of the media effects seem to improve the agreement.

At the same time, there are grounds to believe that explicit modeling of media effects could result in better quality of the IR spectral simulations for the condensed-phase systems.[79] We hope that the quantitative analysis described herein should facilitate further studies on the media effects in computational IR spectroscopy and ultimately it could aid the design of practical approaches to reliable IR spectral simulations for both gas- and condensed-phase systems.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Table 1S, transferrable scaling factors used in the work. Table 2S, computed relative IR intensities vs high-level ab initio results for test set (**2**). Table 3S, computed relative IR intensities vs experimental results for test set (**3**). Table 4S, computed relative IR intensities vs experimental results for test set (**4**). Table 5S, assessment of COSMO computed infrared

Table 3. Assessment of Computed Infrared Intensities vs Experimental Results for Test Set 5 Measured for Gas/CCl$_4$ Solutions of the Following Molecules: Dimethylformamide, Cyclohexane, Cyclohexane-d_{12}[a]

basis set	6-31G*	6-31+G*	Z3PolX	Sadlej's pVTZ	cc-pVTZ	aug-cc-pVTZ
R[b]	0.8948/0.8025	0.9721/0.8970	0.9971/0.9634	0.9932/0.9308	0.9954/0.9384	0.9964/0.9398
SD[b]	0.157/0.200	0.086/0.154	0.030/0.102	0.045/0.135	0.101/0.126	0.107/0.128

[a]Only those modes for which experimental intensities had been available were considered; modes that are inactive were not considered. Total numbers of data included in the analysis N = 20/22 for gas/CCl$_4$ solutions. For details see Tables 3S/4S (Supporting Information) (ESI). [b]R, correlation coefficient; SD, standard deviation.

intensities vs experimental results for test set (**5**). Table 6S, computed absolute and relative IR intensities and vibrational frequencies vs high-level ab initio results for test set (**2**). Table 7S, computed absolute and relative IR intensities and vibrational frequencies vs experimental results for test set (**3**). Table 8S, computed absolute and relative IR intensities and vibrational frequencies vs experimental results for test set (**4**). Figure 1S, IR spectra of isopropylbenzene-d_{12}: simulations vs experiment. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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