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Ab Initio and DFT Predictions of Infrared Intensities and Raman Activities

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Received: August 25, 2010; Revised Manuscript Received: November 9, 2010

Relative infrared (IR) intensities and relative Raman activities have been computed for vibrations of test molecules, including from two to nine heavy atoms, using second-order Moller–Plesset perturbation theory (MP2), and three hybrid density functionals (B3LYP, M05, and M05-2X). The basis set convergence of vibrational properties is discussed. Our results demonstrate that B3LYP offers the most cost-effective choice for the prediction of molecular vibrational properties, but the predictions of another two tested hybrid functionals are very similar and in very good agreement with experimental data. MP2 shows good performance for the IR intensities, whereas the quality of prediction of the relative Raman activities should be characterized as only moderate. B3LYP calculations of the relative IR intensities using highly compact Sadlej's Z3PolX basis set retain the high accuracy of the more CPU expensive Sadlej's pVTZ and much more expensive aug-cc-pVTZ calculations. Relative Raman activities are more sensitive to basis set effects and require at least Sadlej's pVTZ to obtain quantitative results.

Introduction

Vibrational spectroscopy is one of the most versatile means used in structural studies of organic molecules and, especially, of various materials. Quantum-chemical computations predicting 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. Both ab initio and density functional theory (DFT) methods are used for the spectra simulations. Hartree–Fock (HF) calculations give poor frequencies.^{1,2} Conventional correlated ab initio method, Moller–Plesset theory (MP2), allows much more reliable, though rather time- and resource-demanding simulations.^{1,3,4} Higher levels of theory, like, for example, CCSD(T) or QCISD, simulate spectra in quantitative agreement with the experiment for small molecules (4–5 atoms)^{1,3,5} but are not applicable to the vast majority of practically interesting systems. DFT approximations usually combined with the 6-31G* basis set, being computationally inexpensive, outperform HF and even MP2 for the accuracy of fundamental frequencies. Unfortunately, 6-31G* (in common with all small basis sets) gives unsatisfactory IR and Raman intensities. For large molecules of low symmetry, there may be several bands calculated to lie near the position of a single observed feature. In such a case it is impossible to make an unambiguous assignment if the calculated intensities are so unreliable that they cannot be used as an aid.

It has long been known that the accurate computation of IR and Raman intensities is difficult because of their dependence on dipole moment and polarizability derivatives. These properties sample the tail of the electron density and require the use of large, diffuse basis sets.⁶ Indeed, DFT computations with such basis set as aug-cc-pVTZ produce intensities in quantitative agreement with the gas-phase IR and Raman experiments for small molecules.^{2–4} Sadlej's pVTZ basis sets,⁷ developed for calculating dipole moments and polarizabilities, were also found

to give good intensities for the same molecules.^{2,4} Although Sadlej's pVTZ sets are lower cost than aug-cc-pVTZ they are still much more CPU expensive than 6-31G*, which limits their application to rather moderate-size molecules. In recent years the new Z3PolX⁸ basis set was developed, which leads to the order of magnitude computing time savings for large molecules relative to the Sadlej's pVTZ basis set. B3LYP/Z3PolX simulated Raman spectra of acetone and propionitrile were in a good qualitative agreement with the experimental spectra of these common organic solvents.⁹ These and some other reports for individual compounds suggest that reliable and cost-effective prediction of IR and Raman spectra is possible not only for small and symmetric molecules, but also for larger species of practical interest. Nevertheless, there seem to be no systematic surveys comparing different theoretical methods with different basis sets for a representative collection of medium-sized molecules in the gas phase. In the present work, vibrational spectra are computed by MP2 and three hybrid DFT methods, B3LYP, M05, and M05-2X, with a number of different basis sets, to provide an overview of relative performance. In contrast to B3LYP, the latter two Minnesota functionals provide a correct description of dispersion forces, and it would be interesting to evaluate whether M05-2X or M05 can be safely used for the spectra simulation if B3LYP is to be avoided. Both MP2 and hybrid DFT functionals were estimated as the best approaches to prediction of vibrational spectra for small molecules (from one to three heavy atoms) in the gas phase.^{3,4} In this study they are applied to the computation of IR and Raman intensities for a set of test molecules, including from two to nine heavy atom systems.

Although the calculation of absolute intensities is important, in practice, the major use of the quantum-chemical spectra simulations is in aiding the assignment of the bands in the IR and Raman spectra of medium-sized molecules. If the simulated spectra with accurate intensities were available, it would make assigning IR and Raman bands much more straightforward. In these situations it is invariably the relative, rather than absolute, band intensities that are used because experimental determina-

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tion of absolute band intensities (especially for Raman bands) is difficult, and the effort required to make absolute measurements is not repaid by the extra information obtained. So, in this work we assess the quality of a computational method on how well it reproduces the experimental ratio of the intensities, as our intent is to provide practical information to spectroscopists who wish to use computations to assist in assigning spectra.

Computations

All calculations were carried out using the Gaussian03 suite of programs.¹⁰ Following full geometry optimizations at each level of theory, harmonic vibrational frequencies and IR and Raman intensities were calculated for MP2 (second order Moller–Plesset perturbation theory)¹¹ and three DFT methods employed in this study, corresponding to widely used the Becke’s three-parameter exchange functional¹² in combination with the Lee–Yang–Parr’s correlation functional¹³ (B3LYP), and two relatively new hybrid metageneralized gradient approximations M05¹⁴ and M05-2X.¹⁵ Calculations were carried out with the following basis sets: 6-31G*,^{16,17} 6-31+G*,^{16–18} 6-31+G**,^{16–18} 6-311G*,^{17,19} 6-311+G*,^{17–19} Sadlej’s polarized triple- ζ basis sets, optimized for electric properties (pVTZ⁷ and Z3PolX⁸), and Dunning’s “correlation consistent” cc-pVTZ and aug-cc-pVTZ basis sets.²⁰

Infrared and static Raman 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 and NH stretching modes were excluded from the comparison. Therefore, we compared the predicted IR intensity ratio from a given level of theory I_k/I_{\max} (where I_k is the IR intensity of the k th vibration mode, I_{\max} is the IR intensity of strongest band in the region of $\nu \leq 2300 \text{ cm}^{-1}$) with the same experimental IR intensity ratio. Because we did not compute the Raman intensity, rather the Raman activity ($S_k = \{45(\alpha'_k)^2 + 7(\gamma'_k)^2\}/45$) was calculated, the computed S_k/S_{\max} values were compared with the corresponding experimental Raman activities ratios. In a few cases, where computed and experimental spectral curves were compared, the calculated Raman activities were converted, prior to the comparison with the experiment, to the corresponding Raman intensities. In the notation of Long,²¹ the intensity of Raman band for Stokes shift, and power detection (as opposed to photon counting), is proportional to

$$I_k = \frac{N(\nu_0 - \nu_k)^4 S_k Q_k^2 P}{\left[1 - \exp\left(\frac{-h\nu_k}{kT}\right)\right]} \quad (1)$$

where N is a proportionality constant, ν_0 is the exciting laser wavenumber, ν_k is the wavenumber of the vibrational mode, c is the speed of light, h and k are Planck’s and Boltzmann’s constants, T is the temperature, P is the exciting laser irradiance, and Q_k^2 is an amplitude factor. A quantum mechanical treatment of the vibrational amplitude using harmonic oscillator ladder operators leads to the amplitude factor proportional to $1/\nu_k$. Because we have restricted our study to relative intensities, N and P are unimportant, and for comparison with experimental Raman intensities, the computed S_k values are multiplied by a frequency dependent factor

$$\frac{(\nu_0 - \nu_k)^4}{\nu_k \left[1 - \exp\left(\frac{-h\nu_k}{kT}\right)\right]} \quad (2)$$

Results and Discussion

Assessment of Infrared Intensities. In a previous study, Halls and Schlegel³ compared their QCISD/6-311+G(3df,3pd) infrared intensities with the results obtained at the CCSD(T)/TZ(2df,2pd) level⁵ for a small number of molecules. The authors found good agreement between both theoretical methods, but both showed larger discrepancies with respect to experimental values. Very similar results were produced by another high-level ab initio computations CCSD(T)/aug-cc-pVTZ.¹ Therefore, a large fraction of the difference may be attributed to the experimental uncertainties (usually estimated as $\pm 10\%$) and the double harmonic approximation. To avoid these ambiguities in the assessment of MP2 and DFT methods, Halls and Schlegel³ compared the intensities predicted at these levels of theory with their highest level ab initio results. With respect to QCISD hybrid DFT outperformed MP2. Their largest basis set 6-311+G(3df,3pd) produced the best results, though the computations with DZ basis sets comprising diffuse and at least two sets of polarization functions also performed reasonably well.

Scuseria et al.² compared IR intensities predicted by HF and various DFT methods against both experiment and high-level ab initio results.^{1,3} Their test set of molecules was a combination of the sets used by Halls and Schlegel³ and Galabov et al.:¹ HF, CO, H₂O, HCN, C₂H₂, H₂CO, NH₃, C₂H₄, CH₂F₂, CH₄, and SiH₄. In general, all DFT functionals showed similar behavior and the results were much better than the predictions of HF. There was a reasonable agreement when comparing results against experiment or against high-level ab initio computations,^{1,3} though discrepancies with respect to experimental values were systematically larger than with respect to QCISD/6-311+G(3df,3pd)³ and CCSD(T)/aug-cc-pVTZ¹ results. Three basis sets were considered: 6-31G*, Sadlej’s pVTZ,⁷ and Dunning’s aug-cc-pVTZ,²⁰ the latter two producing practically equally good results, and the former giving much larger errors. Taking Sadlej’s pVTZ as a basis, B3LYP was the best performer when comparing against both experiment and ab initio results.

We computed IR spectra of two sets of test molecules. Test set (a) is a subset of small molecules used by Halls and Schlegel³ and Scuseria et al.:² C₂H₄, H₂CO, and CH₂F₂. Set (b) is a series of small and medium-sized molecules with a variety of single and multiple bonds: C₂D₄, CH₂=C=CH₂, CD₂=C=CD₂, C₆H₆, C₂H₄O, C₂D₄O, CD₂O, CH₃CH=O, (CH₃)₂C=O, CH₃CN, CD₃CN, CH₃NC, CS₂, SCO, COCl₂, CD₂F₂, and CH₂Cl₂. Scuseria et al.² excluded the latter molecule from consideration because of absence of high-level ab initio results for IR intensities of the molecule. In our case it was unimportant, as the assessment of IR intensities was based on comparison against the corresponding experimental values. In addition, thymine and thymine-1,3-*d*₂ were included, which were the largest molecules with available IR intensities measured for isolated molecules (though in Ar matrix instead of the gas phase).^{22,23}

It was already mentioned above that the Sadlej’s pVTZ basis set produced results very similar to the larger aug-cc-pVTZ when comparing computations against experimental absolute intensities.² In Figure 1, the relative intensities calculated in the present work at the B3LYP/pVTZ and B3LYP/Z3PolX levels are compared with experimental relative intensities for the test

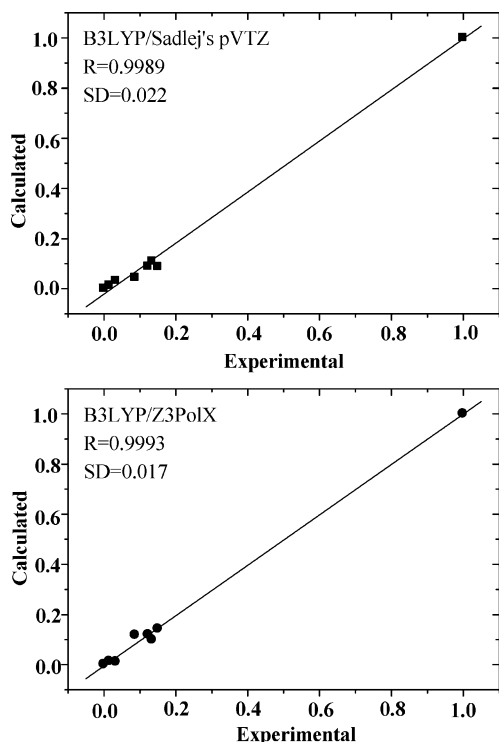


Figure 1. Calculated relative IR intensities for the test set (a) (C_2H_4 , H_2CO , CH_2F_2) vs the corresponding experimental relative intensities from refs 24–26; R , correlation coefficient; SD , standard deviation. See Table 1S for details (ESI).

set (a): C_2H_4 ,²⁴ H_2CO ,²⁵ CH_2F_2 .²⁶ The new highly compact Z3PolX basis set performs even marginally better than Sadlej's pVTZ. Very similar results are obtained for another two DFT functionals (M05 and M05-2X), while the quality of MP2/Z3PolX simulations is still slightly worse than MP2/pVTZ (Table 1). Complete table of the numeric results for the test set (a), including a comparison with MP2/6-311+G(3df,3pd) and B3LYP/6-311+G(3df,3pd) results from ref 3 is provided as ESI (Table 1S). Figure 2 shows the basis set dependence for B3LYP of correlation coefficients (R) and standard deviations (SD) from experimental relative intensities for several molecules of the test sets (a) and (b), taken as typical examples. As additional basis functions are added to the 6-31G* basis, the IR intensities converge to Z3PolX and aug-cc-pVTZ. Similar dependencies are found for all the methods used. These results are significant in light of substantial savings in CPU time Z3PolX affords relative to aug-cc-pVTZ and even Sadlej's pVTZ basis sets. Taking Z3PolX as a basis, all the DFT methods used almost equally outperform MP2 for the test set (a) (Table 1), but for more representative set (b) B3LYP is the best performer (Table 2, experimental intensities were taken from the following refs.: C_2D_4 ,²⁴ CD_2O ,²⁵ CD_2F_2 ,²⁶ CH_3CN and CD_3CN ,²⁷ C_6H_6 , CS_2 ,

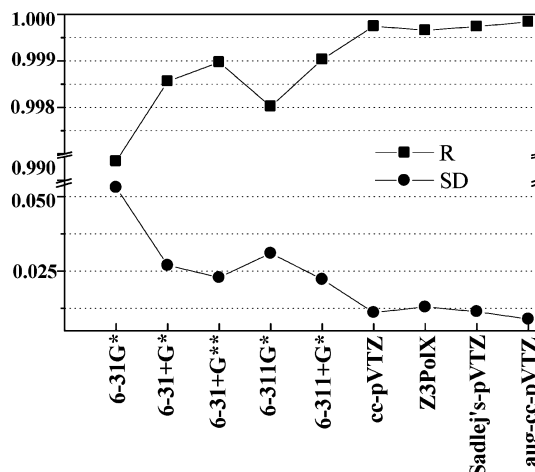


Figure 2. Relative IR intensity basis set dependence for B3LYP computations for C_2H_4 , CH_2F_2 , and COCl_2 molecules; R , correlation coefficient; SD , standard deviation.

SCO , COCl_2 , and CH_2Cl_2 ,²⁸ $\text{CH}_2=\text{C}=\text{CH}_2$ and $\text{CD}_2=\text{C}=\text{CD}_2$,²⁹ $\text{C}_2\text{H}_4\text{O}$ and $\text{C}_2\text{D}_4\text{O}$,³⁰ $\text{CH}_3\text{CH}=\text{O}$,³¹ $(\text{CH}_3)_2\text{C}=\text{O}$,³² and CH_3NC .³³ Complete table of the numeric results for the test set (b) is provided as ESI (Table 2S).

In case of the largest test molecules of thymine and thymine-1,3- d_2 ,^{22,23} (Table 3) M05-2X marginally outperforms B3LYP, though these results must be regarded with care: (i) the compounds were experimentally studied not in the gas state, but in Ar matrix; (ii) because of low symmetry and rather strong coupling of some modes, assignments of experimental IR bands were not always straightforward. For the reason (ii), a direct comparison of the experimental and computed intensities of all the individual bands was difficult in several cases, and we preferred to compare IR intensities integrated over each 100 cm^{-1} spectral interval (Table 3).

Assessment of Raman Activities. Halls and Schlegel⁴ have shown that hybrid DFT functionals MPW1-PW91 and B3LYP are almost as good as MP2 for the prediction of Raman activities of a set of small test molecules (N_2 , H_2S , H_2O , H_2CO , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , SiO_2 , NH_3 , and CH_2F_2). Their largest basis set aug-cc-pVTZ produced the best results, though the computations with Sadlej's pVTZ basis set performed almost equally well. Scuseria et al.² obtained very similar results for the same test set of molecules; the best performer among DFT hybrids was highly parametrized M06-HF, but B3LYP also gave Raman activities close to both the experiment and MP2 predictions.

We computed Raman spectra of two sets of test molecules. Test set (c) is a subset of the largest two species among the above-mentioned set of small molecules used by Halls and Schlegel⁴ and Scuseria et al.:² H_2CO , CH_2F_2 . We excluded larger molecules C_2H_4 and C_2H_6 , as for them at least two sets of experimental Raman intensities, which differ significantly

TABLE 1: Assessment of Computed Infrared Intensities vs Experimental Results for Test Set (a): C_2H_4 ,²⁴ H_2CO ,²⁵ and CH_2F_2 .²⁶

basis set	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ
method	MP2	B3LYP	M05	M05-2X
R^b (SD)	0.9885 (0.069)/0.9992 (0.019)/0.9997 (0.011)	0.9993 (0.017)/0.9989 (0.022)/0.9992 (0.019)	0.9982 (0.028)/0.9974 (0.035)/0.9977 (0.032)	0.9997 (0.011)/0.9991 (0.020)/0.9996 (0.013)

^a Only those modes for which experimental intensities were available were considered; modes that are inactive were not considered, and degenerate modes were considered only once. Total number of data included in the analysis $N = 10$. For details see Table 1S (ESI). ^b R , correlation coefficient; SD , standard deviation.

TABLE 2: Assessment of Computed Infrared Intensities vs Experimental Results for Test Set (b): C₂D₄,²⁴ CD₂O,²⁵ CD₂F₂,²⁶ CH₃CN, CD₃CN,²⁷ C₆H₆, CS₂, SCO, COCl₂, CH₂Cl₂,²⁸ CH₂=C=CH₂, CD₂=C=CD₂,²⁹ C₂H₄O, C₂D₄O,³⁰ CH₃CH=O,³¹ (CH₃)₂C=O,³² and CH₃NC^{33 a}

basis set method	Z3PolX/Sadlej's pVTZ MP2	Z3PolX/Sadlej's pVTZ B3LYP	Z3PolX/Sadlej's pVTZ M05	Z3PolX/Sadlej's pVTZ M05-2X
<i>R^b</i> (SD)	0.9766 (0.085)/0.9908 (0.053)	0.9849 (0.069)/0.9821 (0.076)	0.9779 (0.084)/0.9561 (0.112)	0.9832 (0.073)/0.9741 (0.091)

^a Only those modes for which experimental intensities were available were considered; modes that are inactive were not considered, and degenerate modes were considered only once. Total number of data included in the analysis *N* = 71. For details see Table 2S (ESI). ^b *R*, correlation coefficient; SD, standard deviation.

TABLE 3: Assessment of Computed Infrared Intensities vs Experimental Results for Thymine²² and Thymine-1,3-*d*₂^{23 a}

method	MP2	B3LYP	M05	M05-2X
basis set	Z3PolX/Sadlej's pVTZ	Z3PolX/Sadlej's pVTZ	Z3PolX/Sadlej's pVTZ	Z3PolX/Sadlej's pVTZ
Thymine				
<i>R^b</i> (SD)	0.9958 (0.025)/0.9959 (0.025)	0.9981 (0.017)/0.9984 (0.016)	0.9976 (0.019)/0.9973 (0.021)	0.9985 (0.015)/0.9979 (0.018)
Thymine-1,3- <i>d</i> ₂				
<i>R^b</i> (SD)	0.9990 (0.013)/0.9994 (0.010)	0.9985 (0.016)/0.9996 (0.008)	0.9989 (0.014)/0.9995 (0.009)	0.9987 (0.015)/0.9996 (0.008)

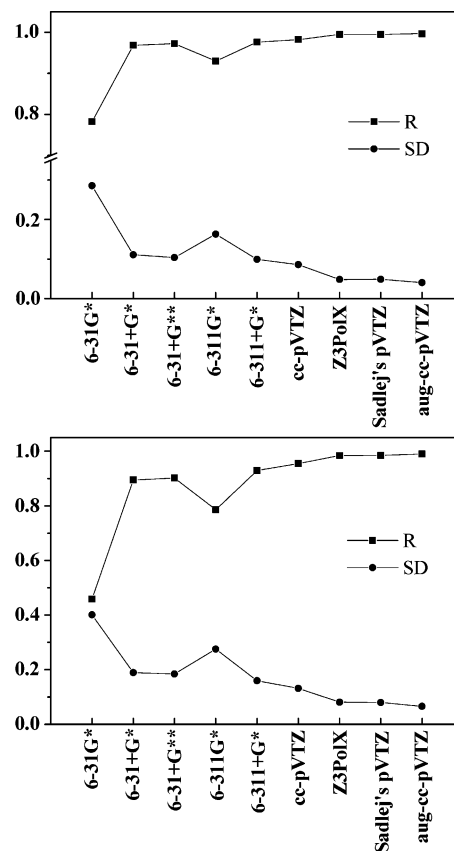
^a Infrared intensities of bands integrated over each 100 cm⁻¹ spectral interval were compared. Total number of data included in the analysis *N* = 13 for thymine and *N* = 12 for thymine-1,3-*d*₂. ^b *R*, correlation coefficient; SD, standard deviation.

(refs 28, 34 and 35, 36, respectively), can be found. Set (d) is a series of small- and medium-sized molecules comprising test set (c) as a subset: H₂CO, CH₂F₂, CH₂Cl₂, CH₃Cl, CH₃Br, C₂D₄, CH₃CN, and C₆H₆. In addition, cyclohexane C₆H₁₂ and perdeuterated cyclohexane C₆D₁₂ were included, which were the largest molecules with available Raman intensities measured for the gas phase. Raman spectra of thymine and anisole C₆H₅OCH₃ were also simulated and compared with the experimental spectra of thymine in Ar matrix²² and of liquid anisole,³⁷ respectively.

As was already demonstrated by Halls and Schlegel⁴ and Scuseria et al.,² the convergence with basis set is slower for Raman activities than for infrared intensities, in agreement with the observation that Raman activities require a better description of the tail of the electron density. The density near the nuclei is held tightly by the nuclear charges, whereas the tail of the density is more polarizable and thus becomes important in the prediction of the Raman response, which depends on the derivative of the polarizability. Figure 3 shows the basis set dependence for MP2 and B3LYP of correlation coefficients (*R*) and standard deviations (SD) from experimental relative activities for CH₃CN molecule, taken as a typical example (for details, see also Tables 3S and 4S, ESI). Relative Raman activities do not quite converge to Z3PolX, though the convergence is faster for B3LYP than for MP2. Figure 3 also demonstrates importance of diffuse orbitals on heavy atoms: 6-31G* is unsuitable for reliable prediction of relative Raman activities, while 6-31+G* basis set produces results of reasonable quality and better than 6-311G*. This effect was already mentioned in our previous work.³⁸

The data presented in Tables 4 and 5 show that, in contrast to absolute Raman activities for the whole spectral range,^{2,4} relative Raman activities for $\nu \leq 2300$ cm⁻¹ are better predicted by hybrid DFT functionals than by MP2 for the both test sets of molecules (c and d), B3LYP being the best performer in all cases.

The predicting power of B3LYP computations of relative Raman activities is clearly seen in Figure 4, where "experimental" Raman spectrum of thymine in Ar matrix²² is compared with the theoretical spectra calculated with different basis sets. The smallest Z3PolX basis set still does not provide reliable intensities in the whole spectral range, while Sadlej's pVTZ and aug-cc-pVTZ basis sets produce the spectra, which practically coincide with the experiment.²² Since the Sadlej's pVTZ

**Figure 3.** Relative Raman activity basis set dependence for B3LYP (top) and MP2 (bottom) computations (CH₃CN molecule). *R*, correlation coefficient; SD, standard deviation. See Table 3S for details (ESI).

basis is about the same size as the 6-31+G(2d,2p) basis set, but performs almost as well as the aug-cc-pVTZ basis, it is clearly the best choice of the basis sets considered in the present work for the prediction of relative Raman activities.

Similar comparison of the computed and experimental spectra of anisole (Figure 5) demonstrates that B3LYP/Sadlej's pVTZ computations are able to reproduce all the qualitative features of the Raman spectrum of this liquid compound.

Relative performance of B3LYP and MP2 methods for thymine and anisole can be seen from Tables 6 and 7,

TABLE 4: Assessment of Computed Raman Relative Activities vs Experimental Results (Refs 41 and 42) for Test Set (c): H₂CO, CH₂F₂

method	MP2	B3LYP	M05	M05-2X
basis set	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ
R^a (SD)	0.9415 (0.160)/0.9436 (0.151)/0.9348 (0.163)	0.9924 (0.063)/0.9922 (0.060)/0.9973 (0.036)	0.9691 (0.120)/0.9779 (0.099)/0.9705 (0.114)	0.9572 (0.142)/0.9620 (0.131)/0.9925 (0.061)

^a R , correlation coefficient; SD, standard deviation.

TABLE 5: Assessment of Computed Raman Relative Activities vs Experimental Results for Test Set (d)^a

method	MP2	B3LYP	M05	M05-2X
basis set	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ	Z3PolX/Sadlej's pVTZ/aug-cc-pVTZ
R^b (SD)	0.9536 (0.119)/0.9764 (0.085)/0.9676 (0.099)	0.9763 (0.088)/0.9880 (0.062)/0.9925 (0.050)	0.9678 (0.100)/0.9739 (0.091)/0.9802 (0.080)	0.9653 (0.104)/0.9764 (0.085)/0.9907 (0.055)

^a The experimental data are taken from refs 41 (H₂CO), 42 (CH₂F₂), 28 (CH₂Cl₂, CH₃Cl, CH₃Br, CH₃CN), 34 (C₂D₄), 43 (C₆H₆), 44 (C₆H₁₂, C₆D₁₂). Only those modes for which experimental intensities were available were considered; modes that are inactive were not considered, and degenerate modes were considered only once. ^b R , correlation coefficient; SD, standard deviation.

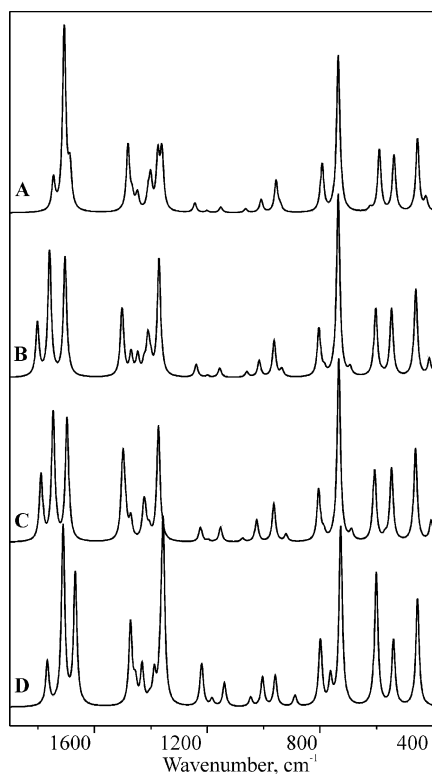


Figure 4. Raman spectra of thymine: (A) B3LYP/Z3PolX, (B) B3LYP/pVTZ, (C) B3LYP/aug-cc-pVTZ, (D) “experimental” spectrum, which represents tabulated frequencies and activities from ref 22, measured from thymine in Ar matrix at $T = 12$ K and $\nu_0 = 9398.5$ cm⁻¹, plotted with a Lorentzian broadening (fwhm = 15 cm⁻¹). The Raman activities are transformed to the Raman intensities according to the formulas (1, 2). Then the relative intensities are plotted against nonscaled computed frequencies.

respectively. The values of correlation coefficient R (and standard deviation SD) for B3LYP/Sadlej's pVTZ for thymine and anisole are 0.9930 (0.047) and 0.9253 (0.111), respectively, and for MP2/Sadlej's pVTZ, the values of R (SD) are equal to 0.9212 (0.132) and 0.9573 (0.081), respectively. Better quality of B3LYP in comparison with MP2 simulation of the spectrum of thymine is reflected in the above statistical analysis, though the spectrum of anisole is better reproduced by MP2 computations. The latter result seems contrary to the results of comparative analysis of computations made for test sets (c) and (d), but

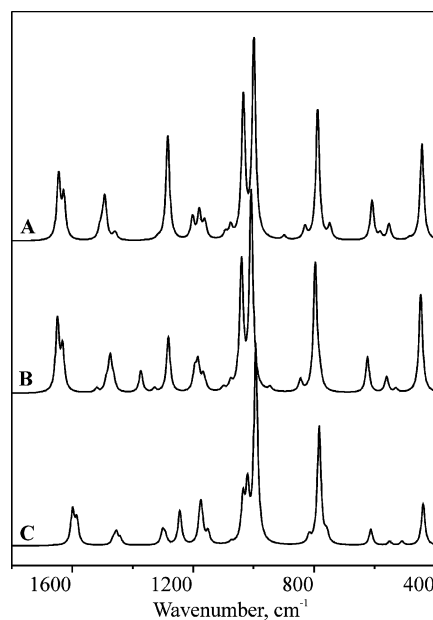


Figure 5. Raman spectra of anisole: (A) MP2/pVTZ, (B) B3LYP/pVTZ, (C) “experimental” spectrum, which represents tabulated frequencies and relative intensities from ref 37, measured from liquid anisole at room temperature and $\nu_0 = 632.8$ nm, plotted with a Lorentzian broadening (fwhm = 15 cm⁻¹). The calculated Raman activities are transformed to the Raman intensities according to the formulas (1, 2). Then the calculated relative intensities are plotted against nonscaled computed frequencies.

most probably this could be explained by the influence of intermolecular interactions on the spectrum of liquid anisole. In any case, both the ab initio and DFT methods almost equally reproduce the main features of the Raman spectra of these compounds, and because MP2 computations are much more time and resource demanding, B3LYP is clearly the method of choice for the prediction of relative Raman activities.

Conclusions

In summary, the results presented here demonstrate that the hybrid DFT methods offer excellent quantitative performance in the prediction of *relative* infrared intensities and *relative* Raman activities for the bands of vibrations ($\nu \leq 2300$ cm⁻¹) of not only small but also medium-size molecules. MP2 shows

TABLE 6: Experimental and Calculated Values for the Relative Raman Activities (S_{rel}) of Thymine

experimental ²²		calculated S_{rel} , Sadlej's pVTZ	
ν , cm^{-1}	S_{rel}	B3LYP	MP2
1800–1700 ^a	0.87	0.92	1
1668	0.48	0.58	0.18
1490–1340 ^a	1	1	0.65
1240–1120 ^a	0.15	0.06	0.09
1070–870 ^a	0.12	0.13	0.06
820–700 ^a	0.28	0.32	0.19
680–580 ^a	0.10	0.08	0.05
540	0.04	0.06	0.04
455	0.06	0.06	0.04
330–260 ^a	0.02	0.01	0.00
170–120 ^a	0.00	0.00	0.00

^a As assignments of experimental bands in this spectral region were not always straightforward and direct comparison of the experimental and computed activities of all the individual bands was difficult, Raman activities were integrated over the corresponding spectral interval given in the table.

TABLE 7: Experimental and Calculated Values for the Relative Raman Intensities (I_{rel}) of Anisole

experimental ³⁷		calculated I_{rel} , Sadlej's pVTZ	
ν , cm^{-1}	I_{rel}	B3LYP	MP2
1560–1620 ^a	0.20	0.34	0.30
1420–1520 ^a	0.09	0.09	0.13
1220–1320 ^a	0.19	0.24	0.31
1130–1200 ^a	0.20	0.15	0.18
950–1100 ^a	1	1	1
800–910 ^a	0.02	0.05	0.04
740–810 ^a	0.43	0.42	0.40
590–710 ^a	0.06	0.11	0.13
490–570 ^a	0.02	0.06	0.05
390–460 ^a	0.15	0.29	0.27
180–330 ^a	0.15	0.48	0.40

^a As assignments of experimental bands in this spectral region were not always straightforward and direct comparison of the experimental and computed intensities of all the individual bands was difficult, Raman intensities were integrated over the corresponding spectral intervals given in the table.

good performance for the IR intensities, whereas the quality of prediction of the relative Raman activities should be characterized as only moderate. Taking into consideration the results of this study as well as those assessing DFT vibrational frequencies,^{2,4} B3LYP offers the most cost-effective choice for the prediction of molecular vibrational properties, but the predictions of another two tested hybrid functionals are very similar and in very good agreement with experimental data. In particular, this means that M05-2X or M05 can be safely used if B3LYP is to be avoided (e.g., because a correct description of dispersion forces is also desired).

It is shown in the present paper that B3LYP calculations of the relative IR intensities using highly compact Z3PolX basis set retain the high accuracy of the more CPU expensive Sadlej's pVTZ and much more expensive aug-cc-pVTZ calculations. Relative Raman activities are more sensitive to basis set effects and require larger basis sets than infrared intensities to obtain quantitative results. Nevertheless, the medium-sized Sadlej's pVTZ basis set predicts relative Raman activities similar in accuracy to those obtained with much larger aug-cc-pVTZ basis set. Earlier Halls and Schlegel⁴ came to the same conclusion on the grounds of comparison of *absolute* Raman activities of several small molecules. Inclusion of larger molecules in our case and comparison of *relative* Raman activities have not

influenced the results, except that, in contrast to Halls and Schlegel's⁴ results, the relative Raman activities for $\nu \leq 2300 \text{ cm}^{-1}$ were better predicted by hybrid DFT functionals than by MP2.

Both intensity and frequency data are important for simulation of vibrational spectra. Although we have concentrated on intensities, because these are the more challenging property, it is necessary to have good prediction of vibrational frequencies to provide secure assignment of experimental IR and Raman bands. In our attempt to simulate the spectra of thymine and anisole, we have found some evidence that overall good quality of frequencies computed with the use of the moderate and large basis sets did not exclude some misassignments in the spectra of these species. Uniform empirical scaling does not improve the situation as this sort of scaling just simultaneously shifts all the computed frequencies (see, e.g., ref 2 and refs cited therein), and cannot result in, for example, transposition of two simulated bands. More satisfactory agreement between the computed and experimental spectra of such comparatively large molecules of low symmetry could be achieved through the scaling of the quantum-chemical harmonic force field (so-called SQM: scaled quantum mechanics³⁹), which was recently demonstrated for thymine.⁴⁰ Earlier, using a set of 13 transferable scaling factors, we were able to improve essentially the quality of vibrational frequencies computed with the use of B3LYP and double- ζ basis sets.³⁸ The next obvious step for this work will be to develop a similar set of transferable factors, suitable for the SQM scaling of the force constants computed with the triple- ζ basis sets tested in the present study.

Acknowledgment. The authors are indebted to all staff members of the Supercomputer centre of the Kazan Scientific Centre of the Russian Academy of Sciences and especially to Dr. D. Chachkov for technical assistance in the computations and valuable advice.

Supporting Information Available: Table 1S, computed relative IR intensities vs experimental results for test set (a); Table 2S, computed relative IR intensities vs experimental results for test set (b); Table 3S, computed relative IR intensities vs experimental results for thymine; Table 4S, computed relative IR intensities vs experimental results for thymine-1,3- d_2 ; Table 5S, experimental and calculated values for the relative Raman activities (S_{rel}) of CH_3CN ; Table 6S, assessment of computed Raman relative activities vs experimental results for CH_3CN . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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