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Approximate First-Principles Anharmonic Calculations of Polyatomic Spectra Using MP2 and B3LYP Potentials: Comparisons with Experiment

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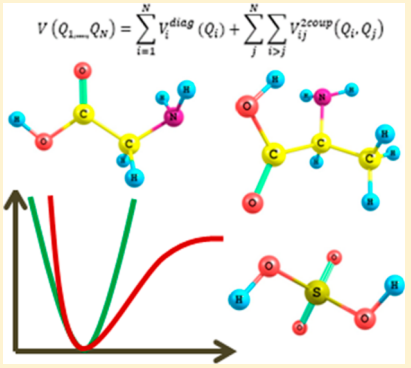
ABSTRACT: Anharmonic vibrational spectroscopy calculations using MP2 and B3LYP computed potential surfaces are carried out for a series of molecules, and frequencies and intensities are compared with those from experiment. The vibrational self-consistent field with second-order perturbation correction (VSCF-PT2) is used in computing the spectra. The test calculations have been performed for the molecules HNO_3, C_2H_4, C_2H_4O, H_2SO_4, CH_3COOH, glycine, and alanine. Both MP2 and B3LYP give results in good accord with experimental frequencies, though, on the whole, MP2 gives very slightly better agreement. A statistical analysis of deviations in frequencies from experiment is carried out that gives interesting insights. The most probable percentage deviation from experimental frequencies is about −2% (to the red of the experiment) for B3LYP and +2% (to the blue of the experiment) for MP2. There is a higher probability for relatively large percentage deviations when B3LYP is used. The calculated intensities are also found to be in good accord with experiment, but the percentage deviations are much larger than those for frequencies. The results show that both MP2 and B3LYP potentials, used in VSCF-PT2 calculations, account well for anharmonic effects in the spectroscopy of molecules of the types considered.



1. INTRODUCTION

Vibrational spectroscopy is a powerful and widely used tool for characterizing the properties of molecular systems. In particular, it is an important tool for probing the quality of potential surfaces.[1−5] Accurate computation of spectra generally requires many accurate ab initio points, an excellent fitting or interpolating function, good basis functions, and a means of calculating eigenvalues of the matrix representing the Hamiltonian in the basis.[6−11] The question of which potential surfaces can be used to satisfactorily interpret experiment is of paramount importance. Our main objective of this paper is to explore how two extensively used quantum chemical methods B3LYP and MP2 describe the vibrational spectra in comparison with experiment and what their relative merits are. Previous comparisons between these methods were not systematic and were either limited to very few small molecules[12] or to some specific vibrational modes.[13] Also, the important observable intensities given by different electronic structure methods were not tested satisfactorily. A few studies compared computed and experimental intensities for a few selected modes.[13,14] Additionally, so far, no systematic analyses have been performed to generalize the error pattern given by these potentials when comparing with experiment. It is desirable to pursue some statistical analysis in order to get more general useful information as it is indeed important to have some prior knowledge about the nature of deviations in calculated frequencies. What was done so far in this direction is not sufficient for those important and practical questions, and that motivates the present paper.

To calculate molecular vibrations, the harmonic oscillator (HO) approximation is often used, especially for large (e.g., biological) molecules.[15−17] However, its accuracy is limited. An alternative for a better match with experiment is to use scaling factors. However, scaling of the HO[18−20] is empirical and hence does not reflect on the quality of the potential. To achieve better accuracy, one needs to consider anharmonic approximations. For example, one can diagonalize a matrix representation of the Hamiltonian in a sufficiently large basis. The cost of such a calculation scales exponentially with the number of atoms in the molecule. We aim at molecules beyond the smallest ones; therefore, such rigorous vibrational methods cannot be used. Less expensive alternatives include perturbation theory[21−25] and classical molecular dynamics (MD) simulation methods.[26] There are other approaches available in the literature.[7,27−32]

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One such inexpensive and useful method is the vibrational self-consistent field (VSCF) approximation, which we have used here as a tool for testing the potentials. It was developed by Bowman,[33] Carney et al.,[34] Cohen et al.,[35] and Gerber and Ratner[36] and has been widely used.[37−39] Initially, it was applied to small systems and later to large molecules such as proteins.[40,41] Gerber and co-workers[42] introduced a method that uses VSCF using the potentials given as points on a grid, obtained from electronic structure calculation. Several methods using ideas related to VSCF but including corrections or providing more accurate treatments were introduced. One such "corrected VSCF" algorithm, referred to as vibrational self-consistent field with second-order perturbation correction (VSCF-PT2[43,44] or CC-VSCF) improved the VSCF algorithm by corrections from second-order perturbation theory. This method seemed to offer a useful balance between computational simplicity and accuracy. Later modifications made this method more suitable for large systems.[45,46] Since then, a large number of applications have been derived by VSCF and VSCF-PT2. Bowman and co-workers have used VSCF + CI to study many molecules.[27,47,48] Several other VSCF codes and various improved approaches also exist in the literature.[49−67]

In this paper, we have tested two extensively used quantum chemical methods MP2 and B3LYP for the VSCF-PT2 calculations against experiment. To study the quality of these quantum chemical methods, we chose several types of molecules with 5−13 atoms and compared their frequencies with experiment. Also, we compared measured intensities with the computed where they were available. This was an additional demanding test. Next, we also computed and analyzed the distributions of deviations from experiments because this can give insights about the nature and range of errors that can be expected when using such quantum chemical methods. The main reason for choosing MP2 and B3LYP is that they are two high-level methods that can be used beyond the smallest molecules. Higher-level methods such as coupled cluster and MP4 are too costly for such calculations. In the sprit of this consideration, we will apply both methods with the cc-pVTZ basis, which by experience has given satisfactory results for relatively large molecules. In this study, we compute zero-point energies, fundamental frequencies, overtones and combination bands, and also intensities for a set of molecules for which these quantities are known experimentally.

In the next section, we briefly describe the VSCF-PT2 methodology and the approximations used in this work. Section 3 illustrates a few examples with error analysis, and in section 4, we discuss the accuracy of the MP2 and B3LYP potentials. Finally, the conclusions are given in section 5.

2. THEORY

In the VSCF method, coupling between different modes is treated by assuming that the full vibrational wave function can be factorized into single-mode wave functions. The single-mode wave functions are called modals. In practice, the factorization assumption is made for the normal modes. Equations for the wave functions and energy levels of the system are then derived on this basis. For each modal, a mean field potential that represents the average effects of the other modes is employed. All of the corresponding equations are solved numerically. The VSCF method and its extensions are discussed in detail in many previous publications. Details of the VSCF theory can be found in a recent review.[68]

We can write the VSCF potential as a sum of one-mode (diagonal approximation) and pairwise coupling in terms of normal coordinate (Q)

$$V(Q_{1,\ldots,}Q_N) = \sum_{i=1}^{N} V_i^{\mathrm{diag}}(Q_i) + \sum_{j=1}^{N}\sum_{i>j} V_{ij}^{2\mathrm{coup}}(Q_i, Q_j) \tag{1}$$

The potential represented in this form needs multidimensional grid point calculations, and the number of grid points increases rapidly with the dimensionality of the potential. If NG is the number of grid points along a normal mode and NV is the number of vibrational modes, then the number of total grid points (NP) is

$$\mathrm{NP} = [\mathrm{NV} \times \mathrm{NG}] + \frac{[\mathrm{NV}(\mathrm{NV}-1) \times \mathrm{NG}^2]}{2} \tag{2}$$

To improve on VSCF further, vibrational levels are computed using second-order perturbation theory. This method is analogical to the Møller−Plesset method known in the context of electronic structure. The PT2 correction is described by the following equation

$$E_n^{\mathrm{PT2}} = E_n^{\mathrm{VSCF}} + \sum_{m\neq n} \frac{|\langle \prod_{j=1}^{N} \psi_j^{(n)}(Q_j)|\Delta V| \prod_{j=1}^{N} \psi_j^{(m)}(Q_j)\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \tag{3}$$

where E_n^{PT2} is the correlation-corrected energy of the state n. The calculations here are carried out using GAMESS computational code.[69] Note that VSCF-PT2 can suffer from the problem of small denominators in cases of degeneracy, which may lead to the erroneous results. The simpler VSCF method, which is not a perturbative approach, does not suffer from this problem. VSCF-PT2 has been extended for dealing with such vibrational degeneracy and the corresponding resonances. This involves applying degenerate perturbation theory for correction beyond VSCF-PT2 (VSCF-DPT2).[61] The relevant code is also included in recent GAMESS version.

Vibrational band intensities are evaluated (in km/mol) using values of the three components of the dipole moment calculated at the same points as the potential. We use an Eckart frame and compute integrated absorption coefficients for vibrational band intensities

$$I_i = \frac{8\pi^3 N_{\mathrm{A}}}{3hc}\omega_i |\langle \psi_i^{(0)}(Q_i)|\vec{u}(Q_i)|\psi_i^{(m)}(Q_i)\rangle|^2 (n_0 - n_m) \tag{4}$$

This equation is written for the case where all of the initial population is in the vibrational ground state. The thermal effects on population are ignored in this study as $n_0 - n_m$, where n_0 and n_m are fractions of molecules in the initial and final states that are set equal to 1, corresponding to zero temparature.[70] $\psi_i^{(0)}$ and $\psi_i^{(m)}$ are VSCF-PT2 wave functions for the ground and excited vibrational states. The $\vec{u}$, as evaluated from electronic structure theory, is a function of the nuclear coordinates. If we use the equilibrium position as the origin, we can expand $\vec{u}$ in powers of normal coordinates. For fundamental and overtone transitions, it is a good approximation, at least for the low-lying states, to consider only $\vec{u}(0, \ldots, Q_i, \ldots, 0)$, which we denote by $\vec{u}(Q_i)$ for simplicity.[13,71] The computed quantity of eq 4 corresponds to the experimental intensity. For combination

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excitations of modes i and j (ignoring the population effect as stated above), we use

$$I_i = \frac{8\pi^3 N_A}{3hc}\omega_{ij} \times |\langle\psi_i^{(0)}(Q_i)\psi_j^{(0)}(Q_j)|\vec{u}(Q_i, Q_j)|\psi_i^{(m)}(Q_i)\psi_j^{(n)}(Q_j)\rangle|^2 \quad (5)$$

where m and n are the excitation levels for modes i and j and $\vec{u}(Q_i,Q_j)$ is a two-mode coordinate approximation to the dipole.

3. RESULTS

We have examined the MP2 and B3LYP potentials with available experimental values for a series of various small to medium sized molecules: HNO_3, C_2H_4, C_2H_4O, H_2SO_4, CH_3COOH, glycine, and alanine. The reason to choose such systems is that our interest is largely in the molecules for which very accurate methods such as couple cluster are inapplicable for anharmonic calculations. Consequently, B3LYP and MP2 methods are manifested as the practical choices. It is already known that the final calculated spectra are also dependent on the basis, used and hence, to get better accuracy, we have systematically used correlation-consistent Dunning type triple-ξ (cc-pVTZ) basis sets[72] for all of the systems.

A. HNO_3. Nitric acid is a species of considerable importance in atmospheric chemistry, with nine vibrational modes. A large amount of experimental data is available for this molecule. Table 1 presents all of the fundamentals, selected overtones, and combination bands. It can be seen that the overall agreement between experiment and VSCF-PT2 is good and considerably more accurate than the HO values. However, the MP2 potential largely overestimates the NO_2 asymmetric stretching (ν_2) and underestimates the NO_2 symmetric stretching (ν_3). B3LYP underestimates the NOH bend (ν_4), while the NOH torsional motion (ν_9) is underestimated by both potentials. For other modes, both potentials result in good accuracy. B3LYP and MP2 give overtones and combination bands with acceptable accuracy, though the errors are higher than the fundamental bands.

Table 1. Fundamentals, Overtones, and Combination Bands (cm^{-1}) of HNO_3 Calculated by VSCF-PT2[a] versus Experiment

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1 (OH str.)	3720	3497	3750	3547	3550
ν_2 (NO_2 asy. str.)	1763	1713	1873	1847	1710
ν_3 (NO_2 sym. str.)	1351	1316	1350	1269	1326
ν_4 (NOH bend)	1324	1253	1334	1310	1304
ν_5 (NO_2 deformation)	904	886	909	887	879
ν_6 (ONO_2 out of plane)	786	774	782	772	763
ν_7 (NO stretch)	650	635	672	656	647
ν_8 (ONO bend)	588	568	593	574	580
ν_9 (NOH torsion)	499	402	497	407	458
$2\nu_1$	7441	6857	7501	6946	6944
$3\nu_1$	11161	10096	11251	10225	10173
$4\nu_1$	14881	13323	15002	13482	13250
$3\nu_1 + \nu_9$	11660	10687	11748	10856	10616
$3\nu_1 + \nu_4$	12485	11299	12585	11547	11325

[a]Using 16 grid points per normal mode. [b]Reference 73 and references therein.

B. C_2H_4. Ethylene is an important species in environmental chemistry, with 12 vibrational modes. In Table 2, the calculated frequencies obtained by VSCF-PT2 are given. Here again, MP2 and B3LYP show considerable accuracy. As is true for most of the molecules, the MP2 potential systematically overestimates (except ν_8) the experimental values, whereas B3LYP underestimates (except ν_4) the high-frequency range and overestimates (except ν_8) the mid-IR and low-frequency ranges. For some of the C−H stretches, MP2 is better, and for others, B3LYP is better. Overall, agreement is good for this molecule.

Table 2. Fundamentals and Combination Bands (cm^{-1}) of C_2H_4 Calculated by VSCF-PT2[a] versus Experiment

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1 (CH_2 asy. str.)	3220	3078	3294	3154	3106
ν_2 (CH_2 asy. str.)	3191	3048	3268	3126	3103
ν_3 (CH_2 sym. str.)	3136	2993	3197	3051	3026
ν_4 (CH_2 sym. str.)	3123	2997	3179	3054	2989
ν_5 (CC str.)	1689	1660	1684	1644	1623
ν_6 (CH_2 scis.)	1473	1452	1485	1455	1444
ν_7 (CH_2 scis.)	1380	1358	1384	1358	1342
ν_8 (CH_2 rock)	1245	1231	1247	1232	1236
ν_9 (CH_2 twist)	1067	1049	1076	1058	1023
ν_{10} (CH_2 wag)	982	971	983	971	949
ν_{11} (CH_2 wag)	977	969	960	949	943
ν_{12} (CH_2 rock)	831	844	828	834	826
$\nu_8 + \nu_{12}$	2075	2086	2074	2077	2048
$\nu_{10} + \nu_{11}$	1959	1965	1943	1945	1889

[a]Using 16 grid points per normal mode. [b]Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated Volume I*; National Bureau of Standards: Gaithersburg, MD, 1972, pp 1−160.

C. C_2H_4O. Next, we considered the simplest epoxide with seven atoms, ethylene oxide. In Table 3, we present the fundamentals of ethylene oxide. Again, like ethylene, MP2

Table 3. Fundamental Bands (cm^{-1}) of C_2H_4O Calculated by VSCF-PT2[a] versus Experiment

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1 (CH_2 asy. str.)	3173	3023	3261	3113	3065
ν_2 (CH_2 asy. str.)	3157	3005	3246	3097	3065
ν_3 (CH_2 sym. str.)	3086	2947	3156	3057	3024
ν_4 (CH_2 sym. str.)	3079	2947	3150	3018	2978
ν_5 (CH_2 scis.)	1540	1501	1556	1515	1498
ν_6 (CH_2 scis.)	1506	1475	1521	1489	1470
ν_7 (ring str.)	1299	1273	1314	1285	1270
ν_8 (CH_2 rock)	1175	1162	1184	1171	1150
ν_9 (CH_2 twist)	1170	1155	1179	1163	1147
ν_{10} (CH_2 wag)	1154	1145	1159	1149	1159
ν_{11} (CH_2 twist)	1148	1133	1156	1138	1120
ν_{12} (CH_2 twist)	1045	1031	1058	1044	1020
ν_{13} (ring str.)	887	869	909	887	877
ν_{14} (CO str.)	842	818	858	831	822
ν_{15} (CH_2 rock)	818	818	823	822	808

[a]Using 12 grid points per normal mode. [b]Reference 74 and references therein.

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Table 4. Fundamentals and Combination Bands (cm^{-1}) of H_2SO_4 by VSCF-PT2[a] versus Experiment

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1 (OH sym. str.)	3762	3504	3801	3543	3609
ν_2 (OH asy. str.)	3758	3421	3796	3463	
ν_3 (S=O_2 asy. str.)	1474	1448	1518	1493	1465
ν_4 (S=O_2 sym. str.)	1224	1205	1260	1244	1220
ν_5 (SOH asy. bend)	1162	1102	1179	1114	1157
ν_6 (SOH sym. bend)	1145	1068	1161	1083	1138
ν_7 (S$(OH)_2$ asy. str.)	868	852	903	882	891
ν_8 (S$(OH)_2$ sym. str.)	814	799	849	833	834
ν_9 (O−S=O rock)	551	546	563	558	568
ν_{10} (S=O_2 bend)	540	550	552	560	550
ν_{11} (S=O_2 wag)	495	459	504	469	
ν_{12}[c] (O−S=O bend)	431	431	447	447	
ν_{13} (OH asy. torsion)	369	365	383	374	281
ν_{14} (O−S=O twist)	308	293	337	319	
ν_{15}[c] (OH sym. torsion)	223	223	249	249	216
$\nu_1 + \nu_5$	4924	4536	4980	4620	4739
$\nu_2 + \nu_{15}$	3981	3689	4046	3768	3825

[a]Using 12 grid points per normal mode. [b]Reference 75. [c]VSCF-PT2 fails for those transitions, and hence, HO values are kept.

Table 5. Fundamental Bands (cm^{-1}) of CH_3COOH Calculated by VSCF-PT2[a] versus Experiment

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1 (OH str.)	3738	3522	3773	3555	3583
ν_2 (CH_3 d-str.)	3158	2915	3230	2975	3051
ν_3 (CH_3 d-str.)	3107	2848	3187	2920	2996
ν_4 (CH_3 s-str.)	3050	2874	3104	2913	2944
ν_5 (C=O str.)	1825	1775	1833	1785	1788
ν_6 (CH_3 d-deform)	1482	1456	1497	1477	1430
ν_7 (CH_3 d-deform)	1473	1449	1489	1468	1430
ν_8 (CH_3 s-deform)	1410	1358	1423	1373	1382
ν_9 (OH bend)	1342	1298	1350	1309	1264
ν_{10} (CC str.)	1206	1172	1211	1181	1182
ν_{11} (CH_3 rock)	1073	1057	1074	1060	1048
ν_{12} (CH_3 rock)	1005	988	1006	999	989
ν_{13} (CC str.)	859	840	878	858	847
ν_{14} (OCO deform)	672	773	671	772	657
ν_{15} (C=O oop bend)	585	575	585	575	642
ν_{16} (CCO deform)	551	537	553	529	581
ν_{17} (C−O torsion)	426	426	423	431	534
ν_{18} (CH_3 torsion)	72	119	76	125	

[a]Using eight grid points per normal mode. [b]Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated Volume I*; National Bureau of Standards: Gaithersburg, MD, 1972, pp 1−160.

systematically overestimates (except ν_{10}) the experimental values throughout the frequency range, whereas B3LYP systematically underestimates the high-frequency range and overestimates (except ν_{10}, ν_{13}, ν_{14}) the mid-IR and lower-frequency ranges. Here again, for some of the C−H stretching frequencies, MP2 is better, and for some of them, B3LYP is better. However, the magnitude of errors for C−H stretches given by MP2 is less than B3LYP. Overall, for most of the cases, the agreement between the experimental and calculated values is good.

D. H_2SO_4. H_2SO_4 is a common acid that is important in atmospheric chemistry. Its vibrational spectra have been studied experimentally.[76,77] As can be seen in Table 4, both the MP2 and B3LYP have generally reasonable agreement with experiment, with a few exceptions. For combination bands, MP2 has smaller errors than B3LYP. However, the overall error in this system is higher than that in the other systems that we have studied. That may be due to the inadequacy in the basis for heavy atoms like sulfur.

E. CH_3COOH. Next, we calculated an 18 vibrational mode molecule, acetic acid. In Table 5, we show the comparison of the calculated and experimental results for the fundamentals. It can be seen that both methods underestimate the experimental values in the high-frequency range. Overall, the MP2 potential is again superior to the B3LYP. In the mid-IR and lower-frequency range, both methods result in errors on both sides of the experimental values, however, with reasonable accuracy.

F. Glycine. Finally, we have tested the B3LYP and MP2 potentials for two amino acids, glycine and alanine. Glycine, the smallest amino acid, has been the topic of several theoretical

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and experimental spectroscopic studies.[66,78−81] This flexible 24 vibrational mode system has three low-energy conformers. In Table 6, we show the comparison among calculated and

Table 6. Fundamental Bands (cm^{-1}) of Glycine Calculated by VSCF-PT2[a] versus Experiment

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1 (OH str.)	3735	3501	3770	3542	3560
ν_2 (NH_2 asy. str.)	3562	3255	3623	3321	3410
ν_3 (NH_2 sym. str.)	3495	3192	3538	3299	
ν_4 (CH_2 asy. str.)	3064	2856	3148	2925	
ν_5 (CH_2 sym. str.)	3037	2864	3100	2938	2958
ν_6 (C═O str.)	1819	1767	1827	1776	1779
ν_7 (NHN bend)	1675	1620	1677	1623	1630
ν_8 (HCH bend)	1463	1418	1473	1431	1429
ν_9 (C−O(H) str.)	1399	1348	1421	1373	1373
ν_{10} (CCN bend)	1385	1340	1399	1349	
ν_{11} (NCH2 bend)	1311	1259	1317	1270	
ν_{12} (CCN oop bend)	1188	1157	1195	1161	
ν_{13} (CN str.)	1159	1135	1181	1152	1136
ν_{14} (CO_2 bend)	1122	1079	1142	1100	1101
ν_{15} (CNH_2 bend)	925	925	956	951	907
ν_{16} (CCO oop bend)	911	912	925	919	883
ν_{17} (CO_2−C str.)	821	800	843	827	801
ν_{18} (CO_2 oopb)	654	741	656	743	619
ν_{19} (NCCO(H) shear)	638	632	639	634	
ν_{20} (OCOH tors)	504	492	515	483	500
ν_{21} (NCCOH shear)	463	457	468	463	463
ν_{22} (NCCO shear)	262	268	260	272	
ν_{23}[c] (NH_2 group tors)	219	219	218	218	
ν_{24}[c] (NCCOH tors)	56	56	65	65	

[a]Using eight grid points per normal mode. [b]Reference 66 and references therein. [c]VSF-PT2 fails for this transition, and hence, HO values are kept.

experimental results for the fundamentals of the lowest-energy conformer of glycine.[66] It is found that the ν_5 in B3LYP and ν_2 and ν_{18} in both methods have large errors. Other modes are quite satisfactory compared to the experiment. In this case, the high-frequency modes are underestimated by both methods, and the mid-IR and low-frequency ranges are overestimated, for most cases with reasonable accuracy.

G. Alanine. The largest system that we studied is alanine, with 33 vibrational modes. Alanine also has three low-energy conformers, and we chose the second lowest structure as it has the largest number of available experimental frequencies.[82] As can be seen from Table 7, except ν_5 (asym. CH stretching) and ν_9 (HNH bend), all other vibrational modes show impressive accuracy for the MP2 potential. The errors are distributed on both sides of the experimental values. The B3LYP potential shows higher errors than MP2 in particular for ν_4, ν_5, ν_{15}, and ν_{20}, and most of the vibrational modes are underestimated.

H. IR Absorption Intensity. IR absorption intensities are important observables in vibrational spectroscopy. Their computed values are often in much less satisfactorily accord with experiment than frequencies. Intensities depend directly on the vibrational wave functions of the initial and final states of the transition. Therefore, the intensity provides additional information for the accuracy of a given PES. In Table 8, we show the relative intensities of ethylene oxide obtained from

Table 7. Fundamental Bands (cm^{-1}) of Alanine Calculated by VSCF-PT2[a] versus Experiment

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1 (NH_2 asy. str.)	3589	3240	3635	3308	
ν_2 (NH_2 sym. str.)	3510	3411	3541	3353	
ν_3 (OH str.)	3467	3172	3495	3201	3193
ν_4 (CH_3 asy. str.)	3126	2893	3191	2971	2982
ν_5 (CH_3 asy. str.)	3089	2798	3163	2885	2943
ν_6 (CH str.)	3033	2873	3103	2940	2914
ν_7 (CH_3 sym. str.)	3028	2887	3076	2900	2885
ν_8 (C═O str.)	1844	1788	1847	1793	1792
ν_9 (HNH bend)	1664	1591	1655	1597	1642
ν_{10} (HCH bend (Me))	1504	1459	1516	1476	1460
ν_{11} (HCH bend (Me))	1499	1456	1512	1473	1457
ν_{12} (C−Me str., CH_3 bend)	1419	1356	1433	1373	1368
ν_{13} (C−O(H) str.)	1408	1370	1408	1370	1376
ν_{14} (CN str.)	1360	1312	1367	1319	
ν_{15} (MeCN bend)	1328	1285	1348	1303	1336
ν_{16} (MeCN oop bend)	1275	1226	1284	1242	
ν_{17} (CO_2 sym. str.)	1205	1163	1225	1187	1211
ν_{18} (CN str.)	1125	1094	1151	1111	
ν_{19} (CCC bend)	1058	1038	1067	1048	
ν_{20} (C−Me str.)	1019	983	1031	1010	1037
ν_{21} (MeCN bend)	941	939	963	958	
ν_{22} (CN str.)	871	778	895	809	
ν_{23} (OCOH tors)	849	807	865	828	812
ν_{24} (HO_2C−CH str.)	799	799	816	813	786
ν_{25} (CO_2 oop bend)	744	734	749	738	
ν_{26} (CCC oop bend)	635	624	646	638	625
ν_{27} (CO_2 bend)	530	521	535	529	493
ν_{28} (NCCO tor)	393	386	391	376	
ν_{29} (NCCO(H) shear)	343	340	346	349	
ν_{30} (NH_2 group tors)	279	365	297	410	
ν_{31} (CH_3 group tors)	266	381	260	339	
ν_{32} ($MeCCO_2$ tors)	245	216	242	221	
ν_{33} (CO_2 group tors)	73	89	79	93	

[a]Using eight grid points per normal mode. [b]Reference 66 and references therein.

the HO and VSCF-PT2 algorithm for both the MP2 and B3LYP potentials and compare them with experimental values. For fundamentals and overtones, we include only a single-coordinate term in the dipole operator. For combination bands, we use a two-mode coordinate approximation for the dipole operator. It is found that VSCF-PT2 intensities using both the potentials result in better agreement with experiment than the HO values. For most of the cases, the VSCF-PT2 correction over HO shifts toward the experimental values. Once again, as we have seen in frequency tables that the MP2 potential gives better intensities than the B3LYP potential.

I. Error Analysis. To assess the errors in the calculated frequencies given by the MP2 and B3LYP potentials, we evaluated the mean absolute percentage error (MAPE) for the fundamentals of the molecules stated above. We use the equation

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Table 8. Comparison of the Relative Intensities of C_2H_4O Calculated by VSCF-PT2 versus Experiment (km/mol)[a]

	B3LYP		MP2		exp[b]
mode	HO	VSCF-PT2	HO	VSCF-PT2	
ν_1	0.716	0.774	0.464	0.507	0.567
ν_2	0.002	0.000	0.003	0.000	0.000
ν_3	0.264	0.248	0.227	0.206	0.094
ν_4	0.631	0.656	0.447	0.460	0.693
ν_5	0.049	0.038	0.037	0.026	0.016
ν_6	0.002	0.000	0.002	0.000	0.005
ν_7	0.201	0.218	0.162	0.176	0.206
ν_8	0.003	0.000	0.003	0.000	0.000
ν_9	0.043	0.052	0.047	0.056	
ν_{10}	0.025	0.053	0.029	0.023	
ν_{11}	0.002	0.000	0.013	0.007	
ν_{12}	0.001	0.000	0.001	0.000	0.000
ν_{13}	1.000	1.000	1.000	1.000	1.000
ν_{14}	0.172	0.018	0.136	0.145	0.134
ν_{15}	0.0032	0.000	0.004	0.0002	0.003

[a]Normalized with respect to the maximum intensity (ν_{13}). [b]Reference 83 and references therein.

$$\text{MAPE} = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{\nu_{\text{ref}}^{i} - \nu_{\text{calc}}^{i}}{\nu_{\text{ref}}^{i}}\right| \quad (16)$$

where n is the number of vibrational modes. Here, ν_{ref} are the experimental values, and ν_{calc} are the calculated values. The ν_{calc} are values from either HO or VSCF-PT2, for both quantum chemistry methods. The MAPEs for all of the cases are shown in Table 9. It is clearly seen that MP2 consistently improves MAPEs for VSCF-PT2 better than those for HO. On the contrary, B3LYP does not improve MAPEs for many cases. We note that the VSCF-PT2 corrections by B3LYP over HO are relatively more erroneous for some of the transition. Those large deviations lead to MAPEs that are larger than their HO counterparts. Additionally, B3LYP gives more such large deviations than MP2, which makes it somewhat less accurate than MP2. As a further analysis of errors in the calculated frequencies, we plot two histograms to assess the statistical distribution of the percentage error by B3LYP and MP2 with experiment. We have included the fundamental frequencies of all of the molecules tested here with an error range of −5 to 10%. As can be seen from Figure 1, the accuracy of both methods is roughly the same with an error range of ±2%. A sharp peak for the MP2 potential at −2 to −1% shows that the majority of the errors are localized in this range. On the other hand, the B3LYP errors are more distributed on both sides of the experimental values, and the majority of the errors are located between 0 and 2%. Overall, the most probable transition by MP2 is blue-shifted with respect to experiment, and for B3LYP, it is red-shifted. It shows that the MP2 potential is stiffer and binds stronger, whereas B3LYP leads to a softer potential. It is also found that for the high-frequency range, the MP2 potential overestimates most of the experimental values, and B3LYP underestimates them. In the low-frequency range, both potentials generally overestimate the frequencies, where MP2 overestimates more frequencies than B3LYP. That finally makes MP2 blue-shifted, while B3LYP is red-shifted. Such different natures of the error pattern given by the two potentials should provide ideas about the expected accuracy of calculations with these methods.

Table 9. Comparison of the MAPE in Frequencies with Experiment (eq 16)

	B3LYP		MP2	
molecule	HO versus exp	VSCF-PT2 versus exp	HO versus exp	VSCF-PT2 versus exp
HNO_3	3.11	2.75	4.42	3.17
C_2H_4	3.10	1.52	3.73	1.35
C_2H_4O	2.26	1.03	3.72	1.38
H_2SO_4	4.60	5.62	6.56	6.12
CH_3COOH	4.47	4.72	5.35	4.52
Glycine	2.62	2.89	4.15	2.76
Alanine	3.43	2.00	4.47	1.76

4. DISCUSSION

From the series of molecules we have studied to test the accuracy and performance of the MP2 and B3LYP potentials against experiment, it was found that MP2, in general, gives somewhat better accuracy than B3LYP throughout the frequency range. B3LYP has comparable accuracy to MP2 for the lower-frequency range but underestimates the higher-frequency range more in particular for hydrogenic stretches. For example, B3LYP underestimates all of the C−H stretching frequencies of ethylene (except ν_4), ethylene oxide, and acetic acid. In particular for acetic acid, the errors are substantial. On the other hand, MP2 systematically overestimates these frequencies for ethylene and ethylene oxide but underestimates them for acetic acid. For most of the cases, the magnitude of errors for the stretching frequencies in MP2 is less than that in B3LYP. Similarly, we found that one of the C−H stretches (ν_5) in alanine shows a larger deviation in B3LYP than in MP2. It seems that the vibrations of the $-CH_3$ group are not well described by these two potentials, B3LYP in particular. Roie et al.[13] found that for some small organic molecules, B3LYP

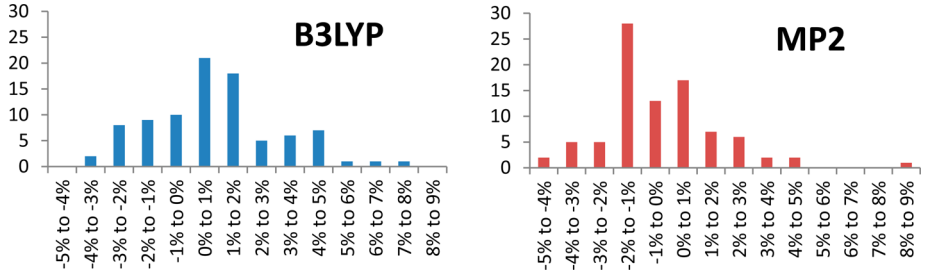

Figure 1. Histograms of the % error distributions by B3LYP (blue) and MP2 (red) against experiment for all of the vibrational modes. The y axis corresponds to the number of vibrations that belong to the error range given in the x axis.

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shows somewhat better accuracy than MP2 for C−H stretching using the cc-pVDZ basis. Our systematic study using larger bases shows that this is not the case, in general. The calculated intensities by both potentials are comparable with experiment and generally better than HO, though the correction is not dramatic. Here again, MP2 results in slightly better agreement than B3LYP.

The error analyses show that in MP2, the probability of getting a large error (magnitude > 2%) is less than that in B3LYP, that is, the errors are more localized. In general, MP2 overestimates a larger number of frequencies, while B3LYP underestimates, and that finally results in MP2 being blue-shifted and B3LYP being red-shifted with respect to experiment.

It is noted that the MP2 and B3LYP methods produce very similar anharmonic corrections ($\nu_{HO} - \nu_{Anharm}$), which shows that both methods estimate the anharmonicity to the same level of accuracy. For example, the anharmonic corrections for the first four high-frequency modes of ethylene are 142, 143, 143, and 126 cm^{-1} and 140, 142, 146, and 125 cm^{-1} using B3LYP and MP2 potentials, respectively. The same trend is also observed for the mid-IR and low-frequency ranges and also for other systems. That implies that the final accuracy also depends on the quality of the HO values given by a particular method. To check the anharmonic correction in a more systematic way for some physical insight extracted from numerical calculation, we have examined the stepwise corrections due to VSCF-PT2 algorithm in each step for the C−H stretching frequencies of ethylene. We have found that for most of the cases, the intrinsic anharmonicity (diagonal approximation) increases the frequency values by a few tens of wavenumbers on top of the HO values. Next, the VSCF approximation brings down the values extensively toward the experimental values, and finally VSCF-PT2 generally further reduces the frequencies by a few tens of wavenumbers on top of the VSCF values for final results that are then close to the experimental values.

Within this direct VSCF-PT2 approximation, the number of grid points is another source of error. We have tested a few molecules with variable grid points and found that for rigid and semirigid molecules, 8−10 grid points per normal mode are sufficient, and for soft systems 12−16 grid points are necessary. For example, C_2H_4O gives converged results for 12 grid points but not for 8 grid points. Note that the CPU time largely depends on the number of multidimensional grid points, and hence, one should choose it depending on the size and nature of the molecule of interest.

To this end, it is also important to comment on the VCSF-PT2 approximation with another common approach, the second-order perturbative correction on the harmonic vibrational levels (VPT2). We have performed VPT2 calculation for a subset of molecules that we have studied here using Barone's algorithm given in the Gaussian package.[84] We found that both approximations work equally well for most of the cases. The mean deviations for VPT2 from experiment are essentially of the same magnitude as those for VSCF-PT2. We found that when using B3LYP, both approximations work well, and the differences are small for most of the cases. For example, the mean % deviations due to B3LYP using VPT2 and VSCF-PT2 are the same (1.03%) for ethylene oxide, while for ethylene, these are 1.52 and 1.20%, respectively. However, for the H_2SO_4 molecule, VPT2 has a larger error (13.17%) in comparison to VSCF-PT2 (5.62%) due to the poor description of the lower vibrational modes. On the other hand, it seems that VPT2 using MP2 does slightly better on the average frequencies than VSCF-PT2. Overall, MP2 works marginally more consistently than B3LYP for VPT2 with fewer fluctuations in error, which is also the case of VSCF-PT2 calculations. Finally, it is found that for most of the cases both with B3LYP and with MP2, VPT2 gives comparable results to the VSCF-PT2 method. Further systematic study is needed in this direction.

We should also note that the potential in our VSCF-PT2 approximation is based on normal coordinates. It is found that for various cases, the normal coordinate representation is not sufficient to represent some soft vibrations such as torsional motion of $-CH_3$, where the couplings between the torsional modes and other normal modes are large. Several other coordinate systems have been explored and used successfully with higher accuracy.[65,85−93] However, due to large cross terms in the kinetic energy operator, those methods have been applied only on some limited small systems. More studies are needed in this direction for other coordinate systems.

Finally, we show how two reliable first-principle-based methods can predict the anharmonic vibrational frequencies and intensities. The accuracy and error distribution given by these two potentials in comparison to the experimental data offer a choice for future calculations. Overall, this study offers the efficacy of computed spectra for a choice of potentials, which can help future analyses while comparing extensive computed data with experiment.

5. CONCLUDING REMARKS

In this contribution, we have assessed the performance, accuracy, and applicability of MP2 and B3LYP potentials for the VSCF-PT2 algorithm with applications for a set of molecules. It is found that both methods are satisfactory tools for computing the vibrational spectra in the present state-of-the-art methods, while MP2 seems on the whole somewhat more accurate. The intensities calculated with these two potentials are comparable and better than HO, and MP2 again comes out as a marginally better method than B3LYP. Statistical analysis revealed that the distribution pattern of errors of these two methods is different, and most of the errors are in the range of ±2%. Overall, MP2 results in blue-shifted frequencies and B3LYP in red-shifted. Finally, the statistical analysis in order to characterize the deviation from experiment suggests that it can be useful in extracting conclusions from extensive test calculations. Finally, these two widely used standard algorithms B3LYP and MP2, which are viewed generally as approximately of the same level of accuracy, give a reasonable level of agreement with experiment, which would be useful in the future for the interpretation of vibrational spectroscopic data.

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Notes

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