Raman and IR spectra of butane: Anharmonic calculations and interpretation of room temperature spectra

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ABSTRACT

First-principles anharmonic calculations are carried out for the IR and Raman spectra of the C—H stretching bands in butane. The calculations use the Vibrational Self-Consistent Field (VSCF) algorithm. The results are compared with gas-state experiments. Very good agreement between the computed and experimental results is found. Theory is successful also in computing a weak peak which is caused by combination transitions. The B3LYP potential surface is found superior to MP2, though both methods give good accord with experiment. The theoretical results provide an understanding of the role of different modes in the spectra of hydrocarbons.

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1. Introduction

n-Butane is of great importance in several disciplines of chemistry, including petroleum chemistry [1,2], environmental chemistry [3,4], geological and planetary chemistry [5,6]. For this reason, the spectroscopy of *n*-butane is of considerable interest. Studies of this kind are obviously useful also for understanding of hydrocarbon spectroscopy in general. Many previous experimental and theoretical studies of vibrational spectra of hydrocarbons, including alkanes and their homologs, date from the 1960's [7–9]. Studies of more recent years brought to bear on this topic high resolution experimental methods, much more accurate *ab initio* calculations, and considerable attention to complexes of hydrocarbons with other molecules [10–12]. Some hydrocarbon molecules related to butane were recently extensively studied by vibrational spectroscopy, e.g. 1-butene [10,13,14] and *n*-dodecane [15].

Investigations of the vibrational spectrum of *n*-butane itself have focused, among other topics, on analysis of the magnitude of torsional barriers and the enthalpy differences between the conformers [16–19]. Experimental and theoretical studies of a wide range (40–3500 cm^{-1}) of the vibrational spectrum of butane and deuterated butane have been carried out by Murphy et al. [20] and Durig et al. [21,22]. In these studies both IR and Raman spectra of *n*-butane and many of its derivatives were computed at the harmonic level with restricted Hartree–Fock (RHF), with 3-21G and 6-31G* basis sets. Empirical scaling factors were applied in order to correct the effects of anharmonicity. Good agreement with experiment was found for the low-frequency region. However, for the high frequencies rather large deviations were found.

The objective of this study is a detailed analysis of the vibrational spectrum of the C–H stretching mode band, i.e. the range of 2700–3100 cm^{-1}. The main question of interest is whether it is possible to calculate the IR and Raman spectra of saturated hydrocarbons with high accuracy. Another important goal of the research is to clarify the roles of various vibrational modes in the spectrum. A third goal is to test and confirm which electronic potentials and vibrational methods are reliable and accurate for this and similar systems and can be reliably applied.

The calculation of the hydrogenic stretches of butane and other hydrocarbons involves a number of challenges: the hydrogenic stretches are known to be particularly anharmonic; therefore anharmonic vibrational methods should be used. An accurate representation of the potential energy surface is obviously important, but must be kept at a level which leaves the calculations feasible. In addition, possible degeneracy effects need to be kept in mind.

For treating the anharmonic effects, the vibrational self-consistent field (VSCF) method is employed [23,24]. The previous record of using the VSCF method for similar or related systems is the key factor for adopting this approach here [25–29].

The experimental conditions and the computational methods used in this study, including the principles of the VSCF method, will be described in Section 2. Results and discussion will be presented in Section 3. The Letter is concluded with final remarks.

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2. Methodology

2.1. Experiment

The gas-phase experimental IR spectrum of butane was taken from data obtained by Chu, Guenther, Rhoderick, and Lafferty [30]. The experiment was carried out at the temperature of 23 °C and at the pressure of 101.3 Pa. Additional experimental details can be found in Ref. [30].

The gas-phase experimental Raman spectrum of butane was taken from Ref. [22], Figure 3. The experiment was carried out using argon ion laser operating on the 514.5 nm line, at seven different temperatures, ranging from 26 to 64 °C.

2.2. Computational methods

2.2.1. Ab initio calculations

The *ab initio* calculations were performed by the GAMESS suit of programs [31]. The electronic energies, serving as potentials in the calculation of vibrational frequencies, were calculated with MP2 [32] and B3LYP [33] methods. We generally used the correlation consistent polarized valence double-zeta basis set (CC-PVDZ) proposed by Dunning [34,35] in both cases. The intramolecular basis set superposition error and the effect of dispersion was studied earlier in the context of enthalpy difference between conformations [36,37]. These effects, in the context of frequency calculations, are minor as they have similar effects on the ground state and on the vibrational exited states. The effect of dispersion was tested by calculating the harmonic frequencies of B3LYP with and without Grimme's empirical dispersion correction (B3LYP-D). For all of the modes, the deviation was less then 2 cm^{-1}.

2.2.2. Vibrational self-consistent field (VSCF) methods

The anharmonic effects, including coupling between different modes, were treated by the vibrational self-consistent field (VSCF) method. The VSCF approximation is based on the assumption that the full vibrational wavefunction is factorizable into single-mode wavefunctions for the different normal modes [38]. For each single-mode wavefunction, a mean field potential that represents the average effects of the other modes is employed. All the equations are solved numerically until convergence is reached. Computationally, VSCF is more demanding than the harmonic calculations by an order of magnitude because it is also necessary to calculate the potential of the normal mode couplings. The VSCF method and its extensions are discussed in detail in many previous publications, see, e.g. Refs. [23,24,39–41].

By the test of experiment, this approach describes well the anharmonic effects in similar systems [25–29]. In particular, good agreement with experiment was obtained for dodecane, a homolog of butane [15].

The VSCF results can be improved using second order perturbation theory (VSCF-PT2), also known as CC-VSCF and as vibrational MP2 (VMP2) [42,43]. This method is analogical to the Møller–Plesset method known in the context of electronic structure [32]. The PT2 correction is described by the following equation:

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

where $\Psi_j^{(n)}(Q_j)$ is the anharmonic vibrational wavefunction corresponding to the normal modes Q_j of the state (n). E_n^{PT2} is the VSCF-PT2 energy of state n, and $E_n^{(0)}$ is the VSCF energy for the same state. The summation is over all the other states. A detailed description of this method and its uses can be found in literature [44,45].

2.2.3. Degeneracy effects

The C—H band in butane is a quasi-degenerate manifold of anharmonic vibrations. Therefore the issue of suitable treatment of degeneracies must be taken into account. There are several possibilities how to address this matter: the lowest level of VSCF theory does not specifically treat degeneracies, but has no problems of singularities due to degeneracy effects. The VSCF-PT2 method is based on a non-degenerate perturbation theory, degeneracies can thus cause singularities, i.e. one may get a near zero denominator. In a simple VSCF-PT2 variant implemented e.g. in GAMESS, all terms with denominators smaller than a critical value are excluded from the calculation, in order to avoid the problems of singularities. A different treatment is based on replacing the denominators with square roots, according to the Taylor series. This approach was introduced by Daněček and Bouř [46] and used, e.g. by Respondek and Benoit [47]. The resulting method will be referred to as VSCF-DCPT2 (VSCF – Degeneracy Corrected Perturbation Theory of the second order).

Finally, methods that are in principle more systematic in treating degeneracies and can elucidate also the role of various degeneracy effects, possibly observable in experimental spectra, are the VSCF-VCI and VSCF-DPT2 [48]. The latter method attempts to correct VSCF by the degenerate perturbation theory, however, it is not clear if the present variant of VSCF-DPT2 is adequate for treating a system of a relatively dense manifold of a quasi-degenerate vibrations.

Here, the resolution of the experimental spectra is not high enough to observe the degeneracy effects. When broadening of the lines is treated, their effects probably disappear due to a high value of the full width at the half-height (FWHH).

2.2.4. Combination transitions

Combination transitions involve changes of vibrational quantum numbers of more than one mode. Within the harmonic approximation, and using only the linear term of the dipole moment operator, such transitions are forbidden. However, in some systems they can play a significant role [49]. The VSCF code implemented in GAMESS [31] enables us to calculate the frequencies and the IR intensities of these transitions *ab initio*, using anharmonic (VSCF) wavefunctions and transition dipole moments.

2.2.5. IR and Raman spectra modeling

The spectra curves were constructed by our software, while the transitions were assumed to be Lorentzian bands with the full widths at the half-height (FWHH) of 10 cm^{-1} (this value was estimated according to the profile of the experimental spectrum). A similar approach was used for other systems, e.g. for some saccharides [50]. For the IR calculated spectra, no thermal correction was used; both frequencies and intensities were obtained anharmonically. The backscattering nonresonance Raman intensities were calculated by a standard formula implemented in GAMESS. For the Raman calculated spectra, the temperature was set to 295 K and the intensity expression used is harmonically-derived, the only anharmonic part of the calculation are thus the frequencies. Both the experimental and calculated spectra were normalized respectively to the highest peak.

3. Results and discussion

3.1. Conformer analysis

There are three conformers of butane, differing in the CCCC torsion angle. For the lowest energy minimum conformer, referred to as the *anti* conformation, the torsion angle value is 180°. This conformer structure corresponds to that of fatty acids in lipids and also to that of the dodecane energetically preferred conformer – a molecule that we recently studied spectroscopically [15]. The torsion angle values

of the other two conformers are about $-60°$ and $+60°$, while the absolute value is the same for both of them. Note that they differ just in the direction of the rotation around the central C—C bond and are mutual mirror images. These conformers are referred to as the *gauche* conformers and their IR and Raman spectra should be identical. This assumption was verified at the harmonic level. This means that for a good estimate of the butane spectrum, including conformer contributions, it is sufficient to calculate the spectra of the optimal structure and of one of the *gauche* conformers. Then it is possible to calculate the average spectra, weighted according to the population of each conformer. The population was determined for the temperature of 295 K, supposing the Boltzmann distribution, while the MP2 energies (including the harmonic ZPE correction) were used. The resulting ratio of the conformers (*anti*:*gauche* 1:*gauche* 2) was about 63.2:13.4:13.4. All of the conformers are depicted in Figure 1. However, because of computational time demands, the anharmonic VSCF calculations were carried out only for the *anti* conformer.

Unlike for dodecane [15], the main origin of the spectral band broadening is not the presence of many different conformers. However, in the available experimental spectra of gaseous butane the transitions are not highly resolved and we can thus observe wide absorption bands. In this case, the main origin of the broadening are probably rotational transitions. The other sources of broadening that must be taken into account are van der Waals interactions, Doppler and collision broadening, and others. We used the
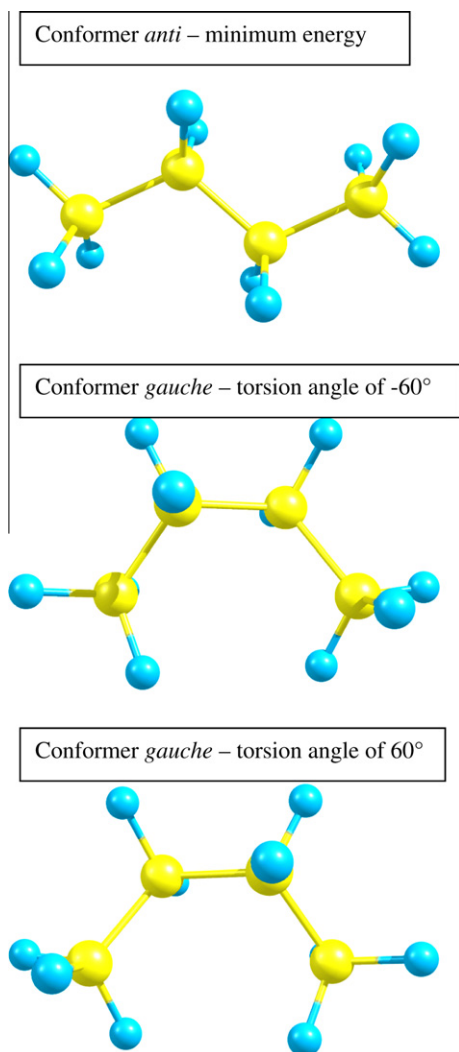
Lorentzian function, with the full width at the half-height (FWHH) of 10 cm^{-1}, as for dodecane. Note that the real FWHH values are always dependent on experimental conditions and there is no way to calculate them *ab initio*. Our choice of this value can be justified by a good agreement of the computed spectra with the experiment.

3.2. Butane VSCF spectra

The harmonic vibrational spectra of butane were carried out first at the MP2/CC-PVDZ and B3LYP/CC-PVDZ level (data not shown). The spectral profiles obtained by both methods were reasonable. The frequency shift predicted by MP2 was about 200 cm^{-1}, which is almost the same value as was obtained for dodecane by the same method [15]. However, the B3LYP harmonic shift is significantly lower (about 120 cm^{-1}) and, as will be shown later, also the B3LYP anharmonic frequencies match the experiment much better than the MP2 anharmonic ones. Therefore we decided to present and discuss mainly the B3LYP results.

The VSCF IR and Raman spectra are shown in Figure 2. The IR spectrum includes also combination modes that significantly influence
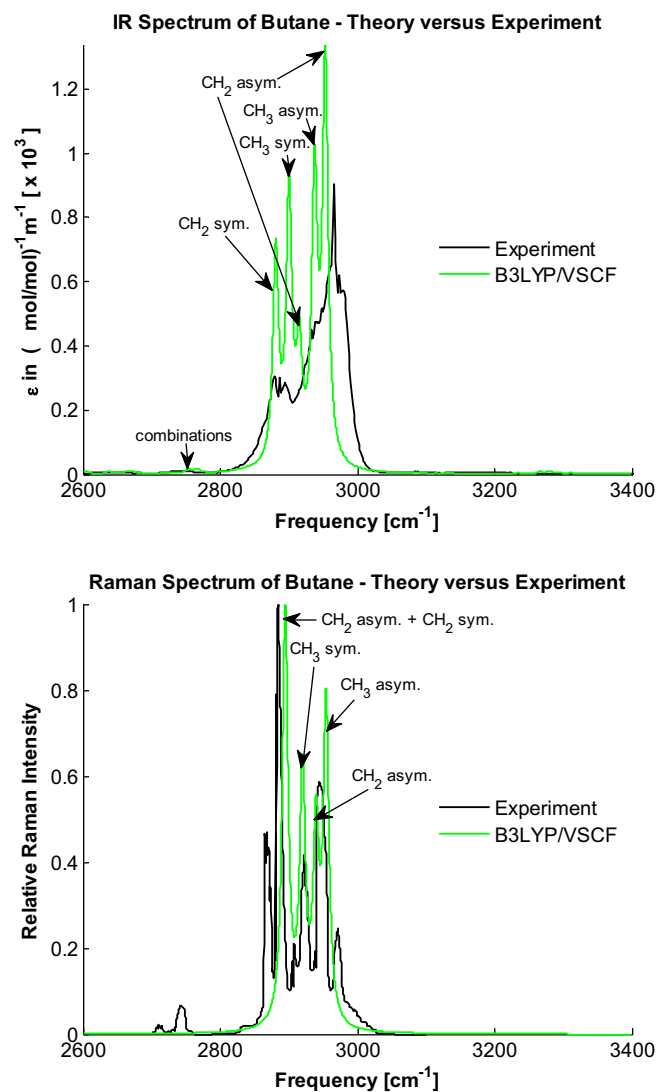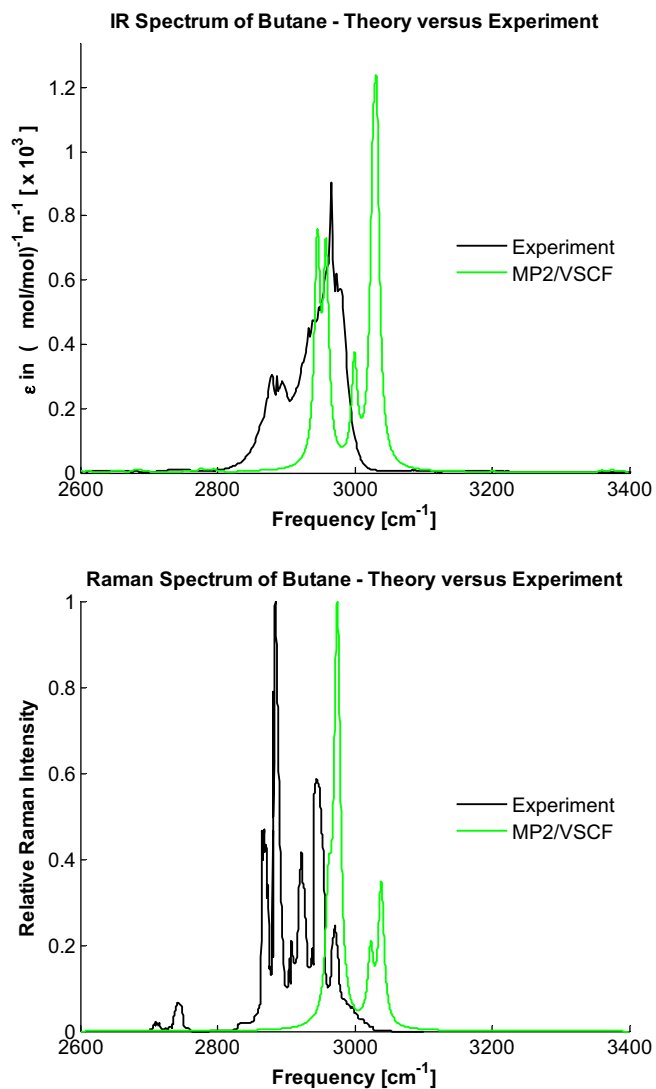

Figure 1. Conformers of butane.

Figure 2. The VSCF IR (top) and Raman (bottom) spectra of the energetically preferred butane conformer calculated with the MP2 potentials (green curves) compared to experiment (black curves). The IR calculated spectra include also combination modes. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Figure 3. The VSCF IR (top) and Raman (bottom) spectra of the energetically preferred butane conformer calculated with the MP2 potentials (green curves) compared to experiment (black curves). The IR calculated spectra include also combination modes. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)
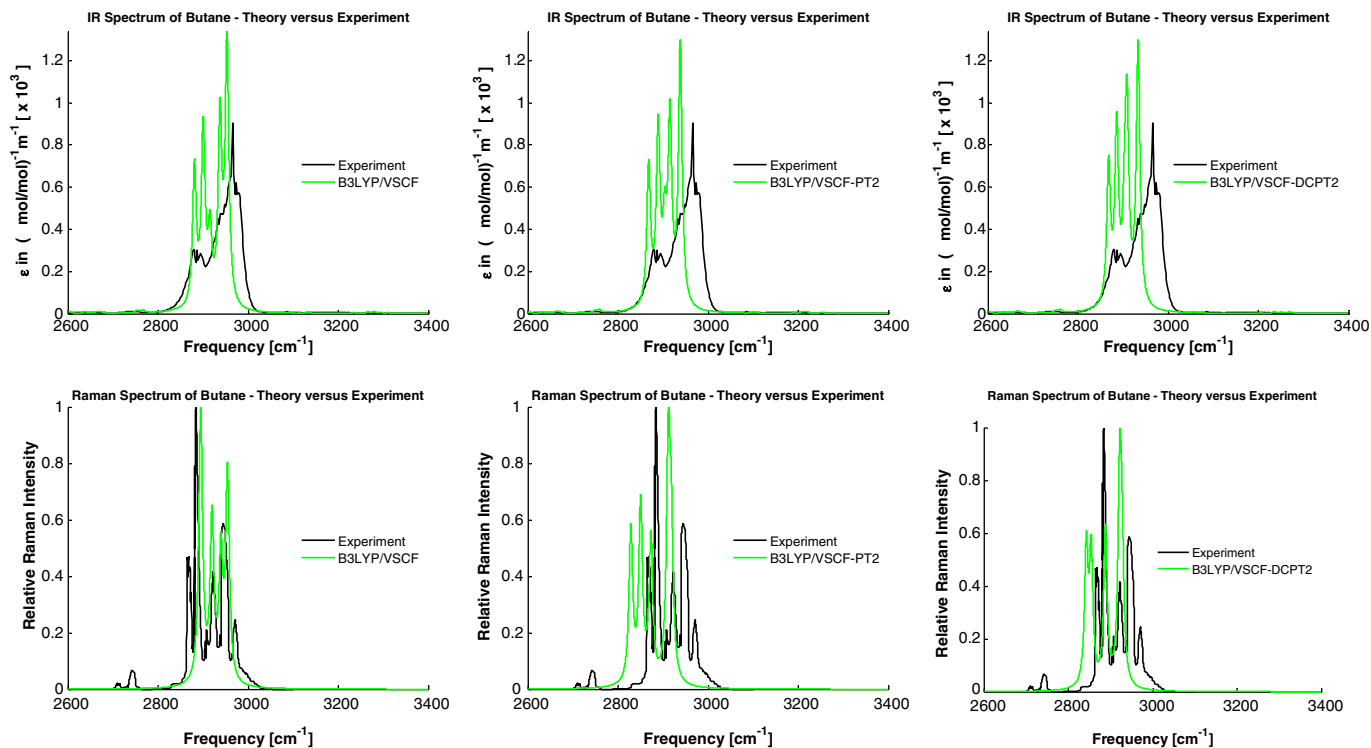
3.3. Comparison of MP2 and B3LYP results

For comparison, also the VSCF results obtained with MP2 potentials are shown in Figure 3. In this case, the calculated spectral bands match the experimental ones much worse. The frequency shift of the MP2 frequencies is about 90 cm^{-1}, which roughly corresponds to the difference between the MP2 and B3LYP harmonic frequencies. In this case the B3LYP potential showed to be more accurate than the MP2 potential. This finding is quite surprising, especially if we take into account that the semiempirical scaled PM3 potential, which uses the MP2 harmonic frequencies to correct the simple PM3 method (data not shown), gives very good results, comparable to B3LYP. Also some previous studies, e.g. on allene, propyne, glycine and imidazole, found MP2 method superior over B3LYP [27]. At the VSCF-PT2 level, as well as with VSCF, better results are obtained for B3LYP (see Supplementary Material for this Letter).

3.4. Assignment of vibrational modes to spectral bands

Unlike for dodecane, the vibrational modes of butane are not so clearly distinguished. Even though it was possible to distinguish in principle the same four basic types (CH$_3$ symmetric, CH$_3$ asymmetric, CH$_2$ symmetric, and CH$_2$ asymmetric), in reality the modes are almost always mixed (e.g. CH$_2$ and CH$_3$ asymmetric). One cause is probably the equal number of CH$_2$ and CH$_3$ groups. Because of the strong interaction between CH$_2$ and CH$_3$ groups, the frequencies corresponding to the mode types cannot be resolved as they were in the case of dodecane. As can be seen from Figure 2, the order of the normal modes in the IR spectra is different from that of the Raman spectra. The reason is that the transitions visible in IR spectra are always invisible in the Raman ones and vice versa (each of the spectra is formed by five intensive fundamental transitions), while the difference between the frequencies of nearly degenerate modes of the same type is sometimes bigger than the difference between some frequencies corresponding to different mode types. It can be also seen, for example, that the CH$_2$ asymmetric vibrational transitions are visible in a different part of the IR and Raman spectra. Moreover, in the case of Raman one of the CH$_2$ asymmetric transitions has almost the same frequency as an intensive CH$_2$ symmetric one, which gives rise to a very intensive absorption band, caused by two different types of transition [15]. The conclusion is that the assignment of modes to the experimental spectrum is very problematic for molecules like butane. Note also that the assignment is different for different potentials and vibrational methods, as was pointed out in the study of dodecane.

3.5. The effect of PT2 corrections

The spectra obtained at advanced anharmonic levels, that include the second level PT2 correction, are shown in Figure 4. No significant improvement of the VSCF spectra is observed. Both perturbation theory methods shift the VSCF spectrum to the left, this effect is evident especially in the Raman spectra. The VSCF frequencies and also spectral profile correspond to the experiment better than the spectra obtained by the other two methods, in spite of the fact that their accuracy is supposed to be better. For quasi-degenerate bands where degeneracy effects can be strong, both PT2 and DCPT2 corrections may have problems, since they are not theoretically suitable for degenerate bands. However, as for dodecane, degeneracy effects do not seem to play a significant role. The spectra obtained by perturbation theory methods are similar to each other. The different approaches for dealing with the denominator problem for degenerate systems do not seem to change the spectral profile significantly. The accuracy of both VSCF-PT2 and VSCF-DCPT2 is acceptable, but slightly better results are obtained with the basic VSCF method that does not involve the denominator issue.

the low-frequency region. In this region (2600–2800 cm^{-1}), the calculated spectrum based solely on fundamental transitions does not include any absorption bands. However, some low-intensity peaks can be found in the IR experiment, while their position agrees with the peaks received by the calculation of some combination modes. Most absorption bands in this region are caused by absorption of some CH$_3$ umbrella and CH$_2$ wagging modes combined with some modes of the same kind or with CH$_3$ and CH$_2$ scissoring modes. The presence of several peaks in the same region in the Raman experimental spectra is even more striking. Our VSCF code does not include as yet overtones and combination modes, and so the present calculated spectrum is based solely on the fundamentals. Similar Raman experimental bands, which were not reproduced by the calculations, were present also in the dodecane spectra. Our findings for butane thus strongly support the hypothesis that this non-reproduced peak is caused by the combination modes [15]. The agreement of the calculated VSCF spectra with experiment in the other regions is very good. Also the absolute value of the molar absorption coefficient was predicted with a good accuracy (note that the absolute scale of the calculated IR spectra is identical to that of the experimental ones).

Figure 4. The anharmonic IR (top) and Raman (bottom) spectra of the energetically preferred butane conformer calculated with the B3LYP potentials (green curves) compared to experiment (black curves). There are included the basic VSCF spectra (left), the VSCF-PT2 spectra (middle), and the VSCF-DCPT2 spectra (right). All the IR calculated spectra include also combination modes. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

4. Concluding remarks

The main message of this Letter is that the IR and Raman spectra of C—H stretches can be reproduced to a high accuracy by anharmonic calculations using *ab initio* potentials. The results confirm that the vibrational methods and potential energy surfaces used here are suitable for hydrocarbons and provide a powerful tool for quantitative interpretation of experiments of such systems. Both the B3LYP and MP2 potential surfaces tested in this study yield good results, B3LYP being somewhat superior to MP2. The basic VSCF method is completely sufficient to describe the spectral features and the resulting spectra are in a good agreement with the experiment. Second order perturbation theory corrections to VSCF do not change the spectra significantly. To our knowledge, this is the first time that the combination vibrations were computed in the IR spectra of hydrocarbons. These contribute to the spectra and satisfactorily explain the origin of the weak absorption bands in the low-frequency region. The assignment of the vibrations to the spectral bands may be sensitive to vibrational method and potential, but the detailed analysis provides a clearer picture about the role of the different functional groups in the molecule and their vibrations. Vibrational degeneracy effects seem to be rather modest at the resolution of the experiments, as the applied value of the full width at the half-height (FWHH), fitting well the profile of the experimental spectra, is quite large. The degeneracy effects may have more pronounced manifestatitons in higher-resolution experiments. In view of the quality of the results, a wide range of applications to other hydrocarbons systems seems attractive.

Acknowledgments

Appendix A. Supplementary data

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