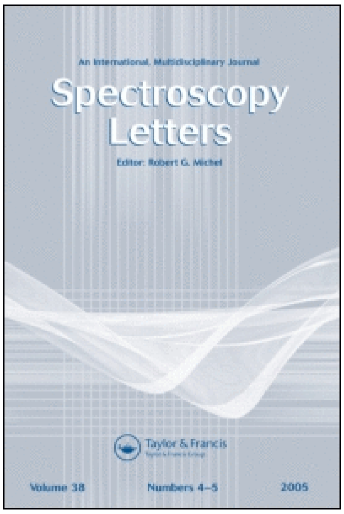

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ABSTRACT This work describes the interest and necessity of scaling to correct the deficiencies in the calculation of the harmonic vibrational wave numbers. The use of adequate quantum-chemical methods and scaling procedures reduces the risk in the assignment and can also accurately determine the contribution of the different modes in an observed band. As an example, the IR and laser-Raman spectra of the 5-bromouracil biomolecule are shown.

KEYWORDS 5-bromouracil, harmonic vibrational wave numbers, quantum chemical methods, scaling

INTRODUCTION

The simulation of vibrational spectra is of practical importance for the identification of known and unknown compounds and has become an important part of spectrochemical and quantum-chemical investigations.[1] Thus the past decades have been highly productive in the interpretation of vibrational experimental spectra by means of quantum-chemical methods. The reliable prediction of the vibrational spectra, particularly in synthetic and natural product chemistry, can be used to calculate the expected spectra of proposed structures, confirming the identity of a product or of a completely new molecule. Other advantages of vibrational spectroscopy are the identification of experimentally observed reactive intermediates for which the theoretically predicted wave numbers can serve as fingerprints and the derivation of thermochemical and kinetic information through statistical thermodynamics.

In general, the motivation for predicting vibrational spectra is to make vibrational spectroscopy a more practical tool. If a method that could predict vibrational spectra reliably is found, it could be used to calculate the expected spectra of proposed structures. Comparison with the observed spectra would then confirm the identity of a product, even that of a completely new molecule, and in some cases also its conformation.[2]

Computational methods can also be used to assign the bands of the spectra. Until recently, the chemical spectroscopists have attempted to interpret the vibrational spectra of more complex molecules by a transposition of the

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results of normal coordinate analysis of simpler molecules, often aided by qualitative comparisons of the spectra of isotopically substituted species, and the polarizations of the Raman bands. Thus it has become an accepted practice to include tables of these vibrational assignments in publications on the infrared and Raman spectra of larger molecules. However, to make such assignments for all the bands in the spectra is risky, due to the fact that while some of the assignments may be credible, others can be highly speculative. Furthermore, the modes assigned to these vibrations are often grossly oversimplified in an attempt to describe them as group wave numbers in localized bond systems.[2]

The problem for small molecules is different from that for large molecules. For small molecules, the experimental vibrational spectra can be assigned without difficulty in comparison with the theoretical wave numbers. Due to the small number of vibrations, the possibility of mistake is very little. Moreover, with small molecules, the calculations can be carried out at high theoretical level, that is, with smaller error in the calculated wave numbers. In this case, the scaling is not necessary. The most expensive methods available today are accurate enough without empirical corrections to predict spectra to the required accuracy. Further advancement in computer hardware and theoretical methods may well make it possible to predict accurate vibrational spectra of larger molecules without empirical corrections.

However, for large polyatomic molecules, the computation of the vibrational spectra is lengthy. The number of vibrations can be huge, and therefore the possibility of mistake in the assignment can be very high in comparison with the experimental spectra, due to the nearness of many vibrations. Thus the larger the molecule is, the more accuracy is required in the prediction of the wave numbers. In spite of the tremendous advances made both in theoretical methods and computer hardware, the more accurate quantum chemical methods are still too expensive and cumbersome to apply as routine research. Thus one may be forced to work at a low level, and consequently one must expect a large overestimation of the calculated vibrational wave numbers.

This overestimation may be due to many different factors that are usually not even considered in the theory, such as anharmonicity, errors in the computed geometry, Fermi resonance, solvent effects, and that can be remarkably reduced with the use of transferable empirical parameters for the force fields or for the calculated wave numbers. These empirical parameters, called the *scaled factors*, are therefore designed to correct the calculated harmonic wave numbers to be compared with the anharmonic wave numbers found by the experiment. The scaled factors are a consequence of the deficiency of theoretical approach and potentially allow vibrational wave numbers (and theoretical information) of useful accuracy to be obtained from procedures of moderate computational cost only.[1,2]

The use of adequate quantum-chemical methods and scaling procedures remarkably reduce the risk in the assignment and can also accurately determine the contribution of the different modes in an observed band. Now, this procedure appears in the journals of vibrational spectroscopy as used extensively.

MOLECULE STUDIED

The theoretical methods predict the vibrational spectra in gas phase. If the vibrational spectra of the molecule selected can be carried out in gas phase, it can be compared directly with the scaled spectra with certain accuracy. However, the differences are higher in the comparison with spectra in the solid state. This fact requires the use of a very accurate procedure of scaling the wave numbers to avoid a mistake in the assignment. This procedure of scaling to predict the accurate vibrational spectra is explained here by considering the example of 5-bromouracil molecule.[3]

The essential biological importance of 5-BrU is that it is one of the well-known uncommon nucleotide bases and has the ability to coordinate with metals or to bind to tissues via metals, which interface with the growth of cancer cells. Molecule 5-BrU is used to treat inflammatory tissues.[4,5] A clear prediction of the vibrational spectra of 5-BrU is essential in the analyses of the spectra of its more complex derivatives, like nucleosides and nucleotides and their polymers, which play an important role in some basic biochemical processes frequently monitored by means of vibrational spectroscopy. From the spectroscopy point of view, the vibrational spectra of 5-BrU have been studied before without any theoretical support: The Raman spectra was studied by Rai,[6] and FT-IR has been studied in an Ar-matrix by Graindourze et al.,[7,8] Gusakova et al.,[9] Srivastava et al.,[10] and Rastogi et al.[11] However, there are doubts in the assignment of several bands.

ERROR IN THE CALCULATED WAVE NUMBERS BY QUANTUM-CHEMICAL METHODS

The vibrational wave numbers are usually calculated using the simple harmonic-oscillator model. Therefore, they are typically larger than the fundamentals observed experimentally.[12] The possible reasons for the deficiency in the calculations are the following:

The Zero Point Vibrational Energy (ZPVE) applies.
Anharmonicity in the vibrational potential energy surface applies.
Basis sets are too small.
Electron correlation is neglected.
The potential energy curve is too steep and therefore wave numbers are too high.

In general, the calculated wave numbers are overestimated. This overestimation using the basis set in the range from 6-31G* to 6-311++G(2d,p) is about 9–12% at the Hartree-Fock level, about 5–8% at the MP2 level, and 3–5% at the B3LYP level.[1,7,8] The overestimation in the wave numbers also depends on the type of vibrational mode and on the wave-number range, varying between 1% and 12%. Thus for modes that appear at high wave number, the difference between the harmonic-oscillator prediction and the exact or Morse-potential–like behavior is about 10%. However, at a very low wave number, below a few hundred wave numbers, this difference can be reduced by a large amount.

SCALING

General

The use of a single overall scale factor[13] is the simplest procedure of scaling, and it is the procedure generally used in the literature.[3,14,15] However, the reduction of the error in the scaled values is in general not enough on some modes and molecules, and it impedes a clear and accurate assignment. Thus, ones observes frequently in the literature some mistakes in the correlation with the experimental wave numbers. To avoid these errors and get a very accurate assignment, one should use some other procedures of scaling that are more accurate, such as the scaling equation, or specific scale factors for each mode.[1,8] In both cases, the scaling is performed in the basic skeleton of molecules from which are extracted scaling equations or specific scale factors to be transferred to related molecules or to their derivatives. In previous articles,[15,16] the accuracy of these procedures has been shown in several molecules.

In this way, the absolute errors obtained in the scaled wave numbers are in general lower than $20\,\mathrm{cm}^{-1}$, reducing the mistakes in the assignments. Moreover, they also lead to a remarkable improvement in the predicted wave numbers in the low–wave-number region, compared with the results when a unique scale factor is used.

Determination of the Scaling Equations from Uracil Molecule

We studied the uracil molecule previously, by extracting scaling parameters to be used in their derivatives, for example, 5-BrU. A list of the calculated and experimental wave numbers in uracil and 5-BrU is collected in Table 1. The labeling of the atoms is plotted in Fig. 1. The errors obtained in the calculated wave numbers of uracil are shown in the 2nd–4th columns of Table 2. As can be observed, they are too large.

The scaling equations are of this general form:

$$\nu^{\mathrm{experimental}} = \mathrm{a} + \mathrm{m} \cdot \omega^{\mathrm{calculated}}$$

By using the calculated and experimental wave numbers of the uracil molecule, one obtains the scaling equations of Table 3 at the different levels. In general a good relationship is observed with correlation coefficients (r) close to unity, especially with DFT methods. To check the accuracy that these equations raise, we introduce the calculated wave numbers of the uracil molecule in them. In this case they appear as follows:

$$\nu^{\mathrm{scaled}} = \mathrm{a} + \mathrm{m} \cdot \omega^{\mathrm{calculated}}$$

For each wave number, the errors ($\nu^{\mathrm{experimental}} - \omega^{\mathrm{calculated}}$) obtained are analyzed. The largest values

TABLE 1 **Calculated Vibrational Wave Numbers With the B3LYP Method and Experimental Ones (cm^{-1})**

Characterization	Ring mode no.[e]	Uracil exp[a]	5-bromouracil[b]		
			6-31G**	6-311 + G (2d,p)	exp.[c]
puckering N3	1		153	148.7	
puckering N1	2	185 w	395	397.0	390
δ(OCNCO)	3	374 vw	392	388.1	532
γ(C=C–H12)	4	395 w	536	539.5	594
δ(ring)	5	512 w	598	597.6	548?
δ(ring) + δ(C=O)	6	588 w	567	551.3	656
δ_{as}(ring) + δ(C=O)	7	545 w	681	667.5	760
γ(N1–H)	8	659.5 w	776	773.5	753
γ(N3–H)	9	717.4 vw	748	757.8	785[f]
γ(C4=O) + γ(C5–X)	10	756.5 w	777	778.5	962?
γ(C2=O)	11	802 w	971	970.8	906?
ν(ring)	12	952 w	928	926.0	1048[d]
γ(C5–X) + γ(C4=O)	13[f]	972 sh	1053	1055.2	1154[d]
ν(C–C) + δ(N–H)	14	990 sh	1170	1156.1	1189[d]
γ(C6–H)	15	1082 m	1196	1191.6	1327
δ(NCC) + δ(C5–X)	16[g]	1172 s	1353	1346.6	1377[d]
ν(ring) + δ(C5–X)	17	1228 m	1396	1399.8	1390[d]
ν(C–N) + δ(C6H,N1H)	18	1356 sh	1411	1408.8	1458[d]
δ(C5–X) + δ(N–H)	19	1387 s	1493	1486.1	1635
δ(N3–H) + δ(C–H)	20	1400 s	1679	1662.0	1729
ν(C–N) + δ(N3–H)	21	1461 s	1808	1759.1	1761
δ(C6–H) + δ(N–H)	22	1641 s	1847	1793.3	3058
δ(N1–H) + ν(N1–C)	23	1688 vs	3237	3213.7	626
ν(C=C)	24	1756 vs	626	629.2	3425[d]
ν(C4=O)	25	3076 w	3616	3589.5	3471[d]
ν(C2=O)	26	3124 m	3653	3632.7	
ν(C6–H)	27	3436 s			
ν(C5–X)	28	3484 s			
ν(N3–H)	29				
ν(N1–H)	30				

[a] [18].

[b] [3].

[c] In Ar matrix,[19].

[d] [11].

[e] [18e].

[f] γ(C5–X) mode.

[g] δ(C5–X) mode.

are listed in Table 2. A summary of the calculated rms errors in the wave numbers from these scale equations and the two procedures of scaling is also collected in Table 2. These values indicate (1) the maximum accuracy that can be raised with these equations when they are used in uracil derivatives and (2) the best procedure of scaling and the best theoretical level used.

A detailed analysis of Table 2 gives rise to the following conclusions.

The most cost-effective procedures for predicting vibrational wave numbers are HF and the B3-based DFT procedures. MP2 does not appear to offer a significant improvement in performance over HF and occasionally shows a high degree of error. For this reason and because of the excessive time and computer-memory consumption, it is preferable to use another method instead of MP2.

In DFT methods, the use of the scaling equations reduces the errors to about 30% of those found with an overall scale factor, showing that the errors in the calculated wave numbers with DFT methods are systematic and partially associated with the kind of molecules studied; and therefore they can be

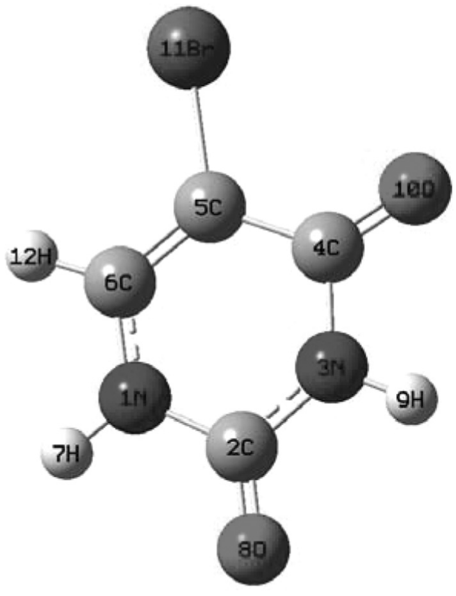

FIGURE 1 Labeling of the atoms in 5-BrU.

TABLE 3 Scaling Equations $\nu^{\text{experimental}} = a + b \cdot \omega^{\text{calculated}}$ From the Uracil Molecule

Methods	a	b
HF/6-31G*	4.6	0.8924
HF/6-31G**	5.7	0.8867
HF/6-31++G**	10.5	0.8938
MP2/6-31G*	34.5	0.9372
BP86/6-31G**	46.0	0.9678
BLYP/6-31G**	46.4	0.9718
B3P86/6-31G*	29.9	0.9412
B3P86/6-31G**	34.1	0.9389
B3LYP/6-31G**	30.8	0.9468
B3LYP/6-31G**	34.6	0.9447
B3LYP/6-311+G(2d,p)	30.8	0.9538
B3LYP/6-311++G(3df,pd)	31.9	0.9512
B3LYP/aug-cc-pVDZ	28.6	0.9543
B3LYP/CEP	33.1	0.9589
B3LYP/SDAll	16.3	0.9535
B3LYP/DGDZVP	39.2	0.9472
B3PW91/6-31G**	34.9	0.9393
MPW1PW91/6-31G**	32.7	0.9334

reduced employing scaling equations determined in related molecules. The B-based DFT procedures, while not performing quite as well as the corresponding B3-based procedures, have the attraction of standard wave-number scale factors close to unity, meaning that they can often be used without scaling. The LYP functional method is superior in precision to the P86 and PW91 functional methods. Thus combining the most accurate exchange with the correlation functional method leads to B3-LYP, which gives the lowest errors in uracil molecule (and derivatives), and therefore it is the recommended method.

The accuracy of the results obtained with the scaling is similar to that in using the much more expensive anharmonic computations, although in several specific bands these computations improve the results.[17]

Regarding these features, the 5-BrU molecule is studied.

Scaling of the 5-bromouracil Molecule

The results for the 5-BrU molecule are shown in Table 4. In the 5-BrU molecule, the use of a scaling equation or the specific scaling equation procedure remarkably reduces the error to a value similar to that of uracil. This low error facilitates the

TABLE 2 Errors Obtained in the Calculated and Scaled Wave Numbers of the Uracil Modes by the Different Procedures and Methods

	Calculated wave numbers			Scaled wave numbers with an overall factor			Scaled wave numbers with the scaling equations		
		Largest error			Largest error			Largest error	
Method	rms	Positive	Negative	rms	Positive	Negative	rms	Positive	Negative
HF/6-31G**	184	427 (29)	6 (2)	23	53 (25,26)	37 (12)	22.6	46 (26)	57 (28)
HF/6-31++G**	177	418 (29)	11 (2)	37	53 (9)	95 (15)	16.7	27 (19)	50 (28)
MP2/6-31G*	82	187 (27)	44 (12)	33	56 (29)	50 (11)	25.4	50 (10)	66 (15)
BP86/6-31G**	35	86 (29)	44 (11)	34	54 (29)	54 (15)	18.1	34 (9)	32 (21)
BLYP/6-31G**	34	73 (29)	49 (11,15)	24	46 (29)	44 (15)	19.6	34 (9)	36 (21)
B3P86/6-31G**	77	207 (29)	14 (2)	21	44 (29)	40 (12)	15.0	32 (26)	26 (15)
B3LYP/6-31G**	66	184 (29)	15 (2)	25	50 (29)	41 (15)	13.8	24 (9)	23 (21)
B3LYP/6-311+G(2d,p)	54	156 (29)	20 (2)				13.7	21 (29)	34 (25)
B3PW91/6-31G**	75	206 (29)	14 (2)				14.9	30 (26)	26 (22)

TABLE 4 **Rms Errors[a] Obtained in the Calculated and Scaled Wave Numbers of 5-BrU by the Different Procedures, Methods, and Levels**

Method	a	b	c	d	e
HF/6-31G**	181	26.6	23.5	21.9	17.0
HF/6-31++G**	179	—	28.6	27.9	26.9
BLYP/6-31G**	40	38.5	27.0	19.6	19.5
B3P86/6-31G**	76	25.4	19.5	18.3	14.2
B3LYP/6-31G**	67	25.9	18.7	16.6	15.2
B3LYP/6-311+G(2d,p)	55	—	18.6	15.0	15.6
B3LYP/aug-cc-pVDZ	75	—	19.6	14.4	14.2
B3PW91/6-31G**	86	26.2	19.0	18.4	14.2
MPW1PW91/6-31G**		—		18.3	13.9

Note. a, calculated wave numbers; b, scaled wave numbers with an overall factor; c, scaled with one scaling equation; d, scaled with two scaling equations; and e, scaled wave numbers with specific scale factors for each mode.

[a] Rms, $(\Sigma(\omega^{\text{cal.}} - \nu^{\text{exp.}})^2/n)^{1/2}$, where the sum is over all the modes *n* and where $\nu^{\text{exp.}}$ is from the experimental wave numbers.[3]

one-by-one correspondence between the experimental wave numbers and the calculated values, and therefore an accurate assignment can be reached.

The experimental Raman and IR spectra of 5-BrU in the solid state are plotted in Figs. 2 and 3, respectively. The assignment and the wave numbers of the main vibrational bands of the spectra are also included in these figures. Below the experimental spectra the simulated scaled and calculated IR and Raman theoretical spectra are also plotted. The values of the scaled and calculated wave numbers of the main modes are also included in these figures.

Comparing the theoretical and experimental spectra, one notes remarkable differences in the intensity of the bands, but they are not of interest in the present article. By observing the values of the experimental wave numbers, nearness of several bands can be noted. In this case, a good scaling is very important to matching experimental wave numbers to well-scaled values. Thus only with well-scaled spectra can the experimental spectra be assigned satisfactorily.

Thus for example, the experimental Raman band observed at 3052 cm^{-1}, as in Fig. 2, can be well matched with the scaled vibration at 3093 cm^{-1} and assigned as ν(C6-H), but the relation is not clear with the calculated vibration at 3213.7 cm^{-1}.

Another example appears in the experimental Raman band observed at 1618.1 cm^{-1}, which can be well matched with the scaled vibration at

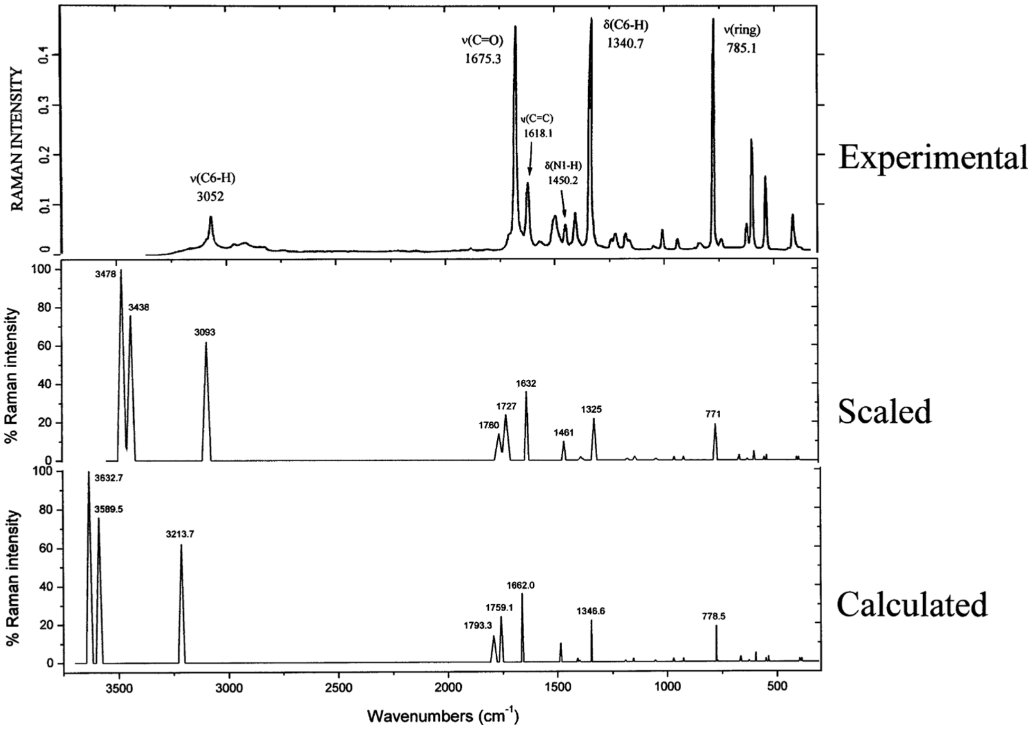

FIGURE 2 **Comparison of the experimental Raman spectrum of 5-BrU in the solid state with those spectra simulated (calculated and scaled) theoretically at the B3LYP/6-311+G(2d,p) level. The scaled spectrum was carried out with the two–scaling-equations procedure.[3]**

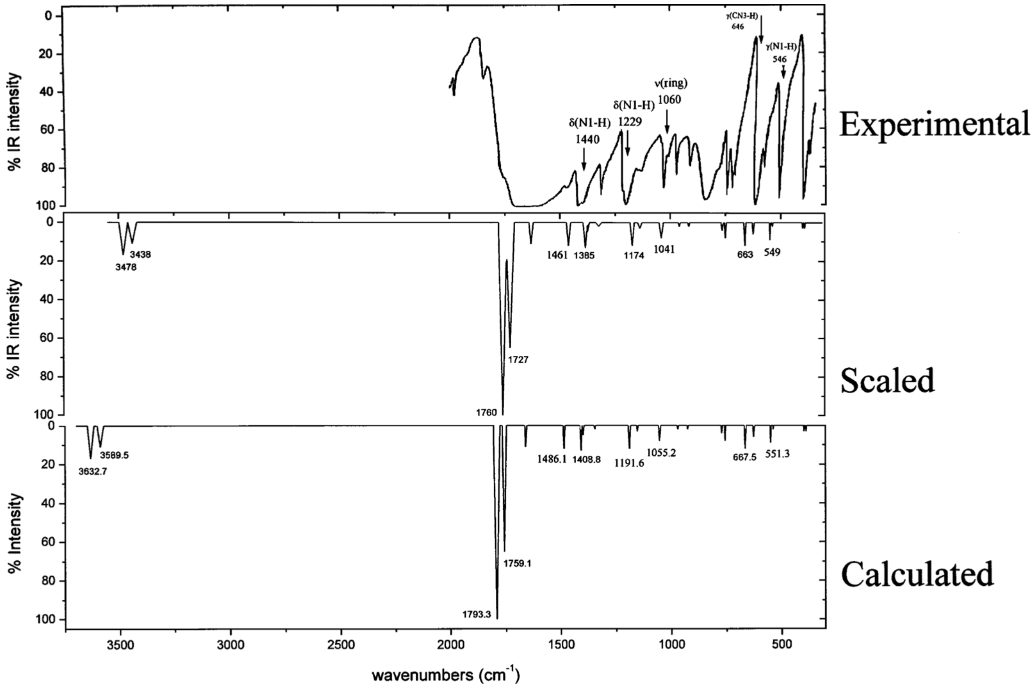

FIGURE 3 **Comparison of the experimental IR spectrum of 5-BrU in the solid state with those spectra simulated (calculated and scaled) theoretically at the B3LYP/6-311+G(2d,p) level. The scaled spectrum was carried out with the two-scaling-equations procedure.[3]**

1632 cm^{-1} and assigned as ν(C=C). However, the relation is not clear with the calculated strong-intensity vibration at 1662.0 cm^{-1}, because it could be poorly matched with the very strong Raman band at 1675.3 cm^{-1} and assigned as ν(C=O).

Finally, in Table 5 are collected the rms errors obtained for other uracil derivatives. It can be noted that always the scaling equation procedure and the specific scale factor procedure lead to the lowest errors, and therefore they are the procedures recommended for scaling.

TABLE 5 **Rms Errors Obtained in the Calculated and Scaled Wave Numbers of Several Uracil Derivatives at the B3LYP/6–31G** Level**

Molecules	a	b	c	d
Uracil	66.4	21.4	13.8	–
5-fluorouracil	70.3	29.8	23.5	14.7
5-bromouracil	76.2	29.2	18.5	13.7
5-methyluracil	59.8	21.5	18.4	13.1
5-nitrouracil	71.7	26.1	16.5	13.0
1-methyluracil	69.2	27.0	17.9	15.8
2-thiouracil	79.0	26.5	15.5	11.5
3-methyluracil	63.2	22.8	15.6	11.0
1,3-dimethyluracil	49.4	23.1	16.5	12.1

Note. a, Calculated wave numbers; b, scaled wave numbers with an overall factor; c, scaled wave numbers with the scaling equations; d, scaled wave numbers with specific scale factors.

SUMMARY AND CONCLUSIONS

The accuracy of several of the quantum chemical methods is determined in the wave numbers of the uracil normal modes. To improve the calculated wave numbers, two accurate procedures can be used. The scaling equations procedure gives rise to improvement in the predicted wave numbers that is slightly greater than when a single overall scale factor is used. Although the specific scale factor procedure gives the lowest error, we recommend using the scaling equation procedure, mainly because of its simplicity. A list of scaling equations that we used for uracil derivatives is shown in Table 3.

The procedure selected for scaling depends on the size of the organic molecule and the accuracy required for the predicted wave numbers. With larger organic molecules, but less than 20 heavy atoms, HF, MP2, and DFT methods and large basis sets can be used for calculating wave numbers. If the accuracy required is not very high (the errors in the predicted wave numbers could be 0–4%), then the use of one or two scale factors with the calculated wave numbers is the simplest and easiest procedure. In this case, among the HF, MP2 and DFT methods, the most cost-effective are the HF- and B3-based. If the accuracy required is high, then at the same level, scale factors for each mode should have been calculated previously from related and simpler molecules.

For uracil molecule the best predicted wave numbers for the ring modes were obtained using HF- and B3-based methods. Thus in this molecule and in related derivatives, these methods should be used.

With molecules larger than 20 atoms, semiempirical methods and HF and DFT methods with small basis sets can be used for calculating wave numbers. However, the cost-effective ratio with HF and DFT methods is very high relative to those of semiempirical methods, and therefore their use is not recommended. In contrast the AM1 and SAM1 semiempirical methods, when a specific scale factor for each mode is used, give good predicted wave numbers, with error lower than 5%. We found no advantage in the newer SAM1 method relative to that of AM1.

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