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Quantum chemical predictions of the vibrational spectra of polyatomic molecules. The uracil molecule and two derivatives

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Abstract

This work describes the different scaling procedures used to correct the quantum-chemical theoretical predictions of the IR and Raman vibrational wavenumbers. Examples of each case are shown, with special attention to the uracil molecule and some derivatives. The results obtained with different semiempirical and ab initio methods, and basis sets, are compared and discussed. A comprehensive compendium of the main scale factors and scaling equations available to obtain the scaled wavenumbers is also shown. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The theoretical prediction 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. Unfortunately an experimental spectrum can be very difficult to assign, even when the identity of the molecular species is certain, often because of the complexity resulting from many effects, such as Fermi resonance, and solvent effects, etc. Today the theory is sufficiently accurate to complement the experi-

mentation and to predict and identify the vibrational spectra.

The motivation for predicting vibrational spectra is to make vibrational spectroscopy a more practical tool [1,2]. From a practical point of view, the main disadvantage of vibrational spectroscopy is the lack of a direct spectra–structure relation. This makes it impossible or difficult to determine the structure of a molecule only from its vibrational spectrum, except in very small molecules, and mainly restricts the vibrational spectroscopy to the identification of known molecules, and the detection of some characteristic functional groups (carbonyl, amide, etc.). This lack of the vibrational spectroscopy can be removed in principle if it is complemented with theoretical methods. If a method that could pre-

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dict the vibrational spectra reliably is found, it could then be used to calculate the expected spectra of the 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 its conformation also. In addition, if vibrational spectroscopy is complemented with other analytical methods, in particular mass spectrometry, the number of possible structures could be restricted to a reasonably small number, by providing summary formulas and some information about the functional groups, and thus reduce the theoretical task.

However, in general, the computation of the vibrational spectrum of a polyatomic molecule of even modest size is lengthy. In spite of the tremendous advances made in theoretical methods and computer hardware, the more accurate of the quantum chemical methods are still too expensive and cumbersome to apply as a 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 wavenumbers. This overestimation can be remarkably reduced with the use of transferable empirical parameters for the force fields, or for the calculated wavenumbers. Only the most expensive methods available today are accurate enough without empirical corrections to predict spectra to the required accuracy. Further advance in computer hardware and theoretical methods might as well make it possible to predict accurate spectra without empirical corrections.

The scale factor is therefore designed to correct the calculated harmonic wavenumbers to be compared with the anharmonic wavenumbers found by the experiment. The scale factor is a consequence of the deficiency of the theoretical approach and potentially allows vibrational wavenumbers and thermochemical information of useful accuracy to be obtained from procedures of modest computational cost only. Widespread application to molecules of moderate size is then possible. The compilation of scale factors, empirical equations and methods presented here are the ones mainly tested and used in the literature, and obviously is not the complete list of all the reported factors, equations and methods.

Computational methods can also be used to assign the bands of the spectra. Until recently, chemical spectroscopists have attempted to interpret the vibrational spectra of more complex molecules by a transposition of the 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 (IR) and Raman spectra of larger molecules. However, to make such 'assignments' for all the bands in the spectra is risky, owing to the fact that while some of the assignments may be credible, others can be highly speculative. Further, the modes assigned to these vibrations are often grossly oversimplified in an attempt to describe them as group wavenumbers in localized bond systems. The use of adequate quantum-chemical methods and scaling procedures, remarkably reduce the risk in the assignment and can accurately determine the contribution of the different modes in an observed band. Now this procedure appears to be used extensively in the journals of vibrational spectroscopy.

2. Molecules studied

The essential biological importance of uracil and its derivatives has motivated a number of recent studies on the structure and spectroscopy of these molecules [3]. Although free pyrimidine and purine bases do not occur in natural biological systems, the interpretation of certain biological processes (e.g. genetic damage) as monitored by IR and Raman spectroscopy, and the analysis of more complex systems (such as nucleosides and nucleotides), should be based on a sound understanding of the spectra of the free base molecules. Unfortunately, there are serious deficiencies in such understanding in the case of uracil.

Apart from an early work by Nowak et al. [4], who studied the ν_{NH} and ν_{CH} stretching regions, and the work by Bardi et al. [5], the studies by Nunziante and Cesaro [7a,b] are only available reference that undertake the gas-phase vibrational

spectrum of uracil. We selected the study by Colarusso et al. [7b] for comments, as the assignments given there correspond most closely to that of our own. Comparisons were also made from spectra in argon [6,7] and Kr and Ne matrices [8]. Spectra in inert gas matrices are, indeed, better resolved than the gas-phase data as they lack in rotational envelopes owing to low temperature. However, there are wavenumber shifts and intensity variations arising from the interaction with the host matrix. For ground-state organic molecules with strong intermolecular bonds such as uracil, the wavenumber shifts are serious owing to matrix effects. Examination of the available experimental data [6–8] on the spectra of uracil in argon matrix lacks full agreement with the assignment of fundamental modes and also, to some extent, in the direct experimental observations of band wavenumbers and intensities. Because of the small, though not negligible discrepancies in the experimental data, a degree of caution is required when comparing the computed spectra with those available from the experiments.

A clear prediction of the vibrational spectra of uracil 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 monitored frequently by means of vibrational spectroscopy. Thus, our main purpose in this work is to attempt an unambiguous assignment of the matrix isolation spectra of uracil and to derive specific scale factors and scale equations to be used in uracil derivatives. Thus, the accuracy of the semiempirical, *ab initio* and DFT methods, in the prediction of the vibrational spectra of these molecules is improved. This procedure of scaling the wavenumbers was shown to be highly successful for a wide range of other molecules [9]. As examples of the adequacy of this procedure, the present work shows the prediction of the vibrational spectra in the molecules of 2-thiouracil (2-TU) and 5-bromouracil (5-BrU) having great medical importance [10,11]. In general, both the use of an adequate level of computation and the application of a suitable scaling procedure are required to obtain the accuracy desired [12].

3. Computational methods

The semiempirical procedures MNDO (Modified Neglect of Diatomic Overlap) [13], AM1 (Austin Model 1) [14], and PM3 (Parametric Method 3) [15] are implemented in the GAUSSIAN [16], MOPAC [17a] and AMPAC [17b] program packages. The most modern one, the SAM1 (Semi-*Ab-initio* Model 1) [18] is only included in AMPAC 5.0. The keywords OPT and FREQ are used for optimization and wavenumber calculations, respectively, with the GAUSSIAN series, while the PRECISE and FORCE keywords correspond to the AMPAC series.

Semiempirical methods are potentially attractive for the computation of vibrational wavenumbers because of their inherent low computational cost. AM1 is a well-balanced and reliable method for standard organic chemistry of the elements C, H, N, and O. PM3 is a reparametrization of AM1, using rather different techniques and parametrization data sets from those used in AM1. PM3 was designed to perform better for nitro-compounds and hypervalent molecules than AM1, and for systems with lone-pairs on adjacent atoms [19].

In *ab initio* calculations [20], including Hartree–Fock (HF) and MP2 (second-order Møller–Plesset perturbation theory) [21], and in Density Functional methods (DFT) [22], several basis sets are normally used to get accurate wavenumbers, from 6-31G* to 6-311G(df,p). In MP2 two options can be employed: the core electrons of the heavy atoms held frozen (indicated by MP2-fc); and the core electrons explicitly included (indicated by MP2-fu). In DFT methods, the most prominent are B-LYP and B3-LYP. B-LYP uses a combination of the Becke exchange functional [23] (B) coupled with the correlation functional of Lee, Yang and Parr [24] (LYP) while the hybrid B3-LYP procedure uses Becke's three-parameter exchange functional [25] (B3), in combination with the LYP correlation functional. The B and B3 exchange functionals can be used with other correlation functionals [26] such as P86 and PW91 to compute vibrational wavenumbers, although they have received less attention in the recent literature. In all cases, the harmonic

wavenumbers are determined by the analytic evaluation of the second derivative of the energy with respect to the nuclear displacement.

General application of these *ab initio* and DFT methods has been limited to considerably small molecules. For larger molecules, more than 30 heavy atoms, calculations have been prohibitively expensive in computer memory and time-consuming, even with a small basis set, although the fast advance in the computer facilities could soon exceed it.

4. Wavenumber calculations

Owing to the nature of the computations involved, wavenumber calculations are valid only at stationary points on the potential energy surface and thus, must be performed on optimized structures. For this reason, it is necessary to run a geometry optimization prior to making a wavenumber calculation. To ensure that a real minimum is located on the potential energy surface, imaginary values should not appear among the calculated harmonic wavenumbers.

A wavenumber job must use the same theoretical model and basis set as employed in the optimized geometry. Wavenumbers computed with different basis sets or procedures have no validity. A wavenumber job begins by computing the energy of the input structure. It then goes on to minimize this energy and recalculate a new geometry. The process is successively repeated until the change in the forces and in the displacements of the atoms of the molecule, is lower than a certain fixed threshold. When the threshold is reached, the geometry corresponds to an optimum structure and then the wavenumbers can be computed. The wavenumbers, intensities, Raman depolarization ratios and scattering activities for each spectral line are therefore predicted. However, calculated values of the intensities should not be taken literally, owing to a high degree error in their computation, although relative values of the intensities for each wavenumber may be qualitatively compared.

In addition to the wavenumbers and intensities, the output of the programs used [16,17] also displays the atomic displacements for each computed wavenumber. These displacements are presented as *XYZ* coordinates, in the standard orientation, which can be plotted to identify each vibration. An example is shown in Fig. 1, which bring together the characterization of the uracil modes by B3LYP/6-31G**, with their calculated wavenumbers.

The wavenumbers can be calculated by a generic internal coordinates system created by the computer program, GAUSSIAN, or by specific internal coordinates defined by us in the molecule, and in general standardized [12,28] to permit the

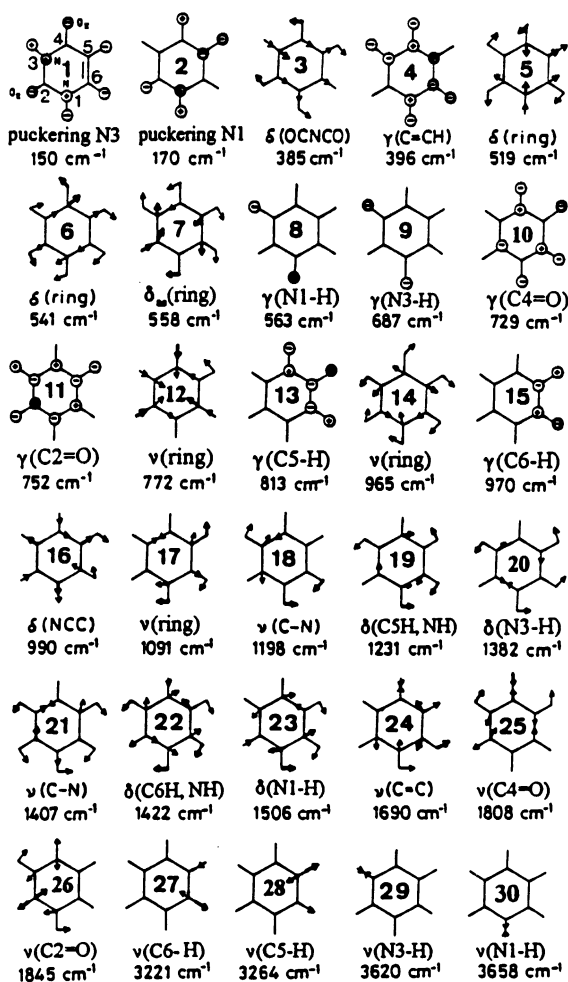


Fig. 1. Characterization of the normal modes in uracil molecule by B3LYP/6-31G** (from Ref. [27]).

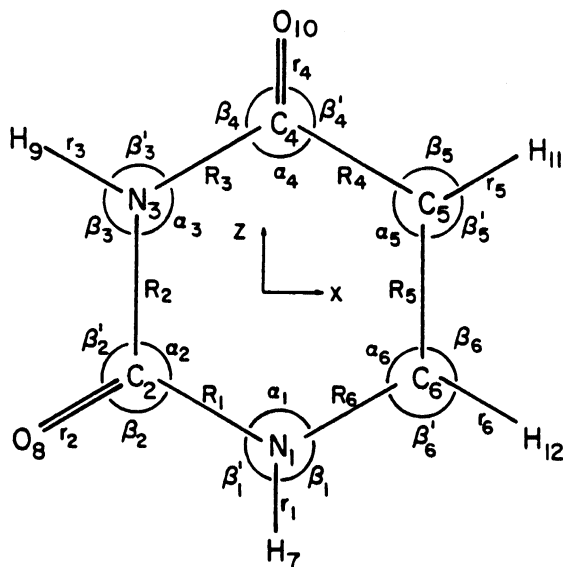


Fig. 2. Definition of the internal coordinates of uracil (reprinted with permission from Ref. [7]).

transferability of the scale factors among the related molecules, e.g. Fig. 2 and Table 1 of uracil. The choice depends on whether the wavenumbers (first case) are scaled, or the force constants are scaled before computing the vibrational wavenumbers (second case).

We believe that our introduction of scaling factors for the wavenumbers themselves is preferable to the more indirect approach of scaling the force constants [29]. Firstly, the wavenumbers are physically observable and the force constants are not. Secondly, the definition of the force constant matrix is not unique because the number of matrix elements is usually much larger than the number of known wavenumbers. The third argument in favor of our procedure is the pragmatic observation that we could be primarily interested in a few major characteristic wavenumbers only and not in the whole spectrum.

Thus following our procedure, the wavenumbers and intensities of uracil, Table 2, were calculated [27] using the GAUSSIAN program. The first column refers to the number of the calculated vibration, given in an increasing order to the increase in the wavenumbers, plotted in the center of the rings of Fig. 1. The relative IR intensities were obtained by

dividing the computed values by the intensity of the strongest line. The last three columns bring together the experimental wavenumbers reported in the gas phase and in the Argon matrix [7,8], and the characterization observed with the theoretical methods used.

Table 3 gives the computed wavenumbers obtained in 2-thiouracil (2-TU) and 5-bromouracil (5-BrU), with their respective relative intensities. The first column refers to the number of the calculated vibrational wavenumber of uracil, Fig. 1, and identified in 2-TU and 5-BrU.

In these compounds and in uracil it is noted that the N–H stretching modes are essentially pure group modes and substitution only induces shifts of about 1% or less. The N–H in-plane bendings are highly coupled to other groups or ring modes and the influence of substitution is not straightforward. The carbonyl stretching couples significantly with the N1–H and N3–H bending motions, and the replacement of a C=O group by the C=S group has the largest effect on the N–H stretching wavenumbers. It also increases strongly the bending of the vicinal N–H, while substitution at C5 has a limited effect. The C=O out-of-plane modes are almost insensitive to substitution, with the exception of the $\gamma(\text{C4=O})$ in 5-substituted uracils.

5. The Error

The relative accuracy of the results obtained, at some chosen computational level, is better than the absolute accuracy [30]. On this basis, Fig. 3 shows the error in one kind of parameter (e.g. a vibrational mode), as computed in a variety of molecular environments, with different methods and sized basis sets. The vertical axis shows the difference between the true value in a given molecule of some particular vibrational mode, and the value computed with different methods and various sizes of SCF basis sets. The errors in computing the chosen vibrational mode in many different molecules are found to fall within the shaded area of the diagram. The HF convergence limit, approached by very large basis sets, still differs from the true value, but this residual error has been empirically found to be remarkably constant for a given parameter, and is

Table 1

Definition of the internal coordinates in uracil (reprinted with permission from Ref. [7])

No.	Description	Symbols	Definition ^a
<i>In-plane</i>			
1	C=C stretching	$\nu_{C=C}$	R_5
2	C–C stretching	ν_{CC}	R_4
3–6	C–N stretching	ν_{CN}	R_1, R_2, R_3, R_6
7,8	C–H stretching	ν_{CH}	r_5, r_6
9,11	C=O stretching	$\nu_{C=O}$	r_4, r_2
10,12	N–H stretching	ν_{NH}	r_1, r_3
13–15	Ring in-plane deformations	$\alpha_{ring,1}$ $\alpha_{ring,2}$ $\alpha_{ring,3}$	$\alpha_6 - \alpha_5 + \alpha_4 - \alpha_3 + \alpha_2 - \alpha_1$ $2\alpha_6 - \alpha_5 - \alpha_4 + 2\alpha_3 - \alpha_2 - \alpha_1$ $\alpha_5 - \alpha_4 + \alpha_2 - \alpha_1$
16,17	C–H bending	β_{CH}	$\beta_6 - \beta'_6; \beta_5 - \beta'_5$
18,20	C=O bending	$\beta_{C=O}$	$\beta_2 - \beta'_2; \beta_4 - \beta'_4$
19,21	N–H bending	β_{NH}	$\beta_3 - \beta'_3; \beta_7 - \beta'_7$
<i>Out-of-plane</i>			
1–3	Ring torsions	$\tau_{ring,1}$ $\tau_{ring,2}$ $\tau_{ring,3}$	$\tau_{6123} - \tau_{5612} + \tau_{4561} - \tau_{3456} + \tau_{2345} - \tau_{1234}$ $\tau_{6123} - \tau_{4561} + \tau_{3456} - \tau_{1234}$ $2\tau_{6123} - \tau_{4561} - \tau_{3456} + 2\tau_{2345} - \tau_{1234} - \tau_{5612}$
4,5	C–H out-of-plane bending	γ_{CH}	$\gamma'_{11}, \gamma'_{12}$
6,8	C=O out-of-plane bending	$\gamma_{C=O}$	γ'_8, γ'_{10}
7,9	N–H out of-plane bending	γ_{NH}	γ'_7, γ'_9

^a The torsional angle τ_{ijkl} is positive if, viewing from the direction of atom k , a counter-clock-wise rotation is needed to bring atoms i and l into eclipsed conformation.

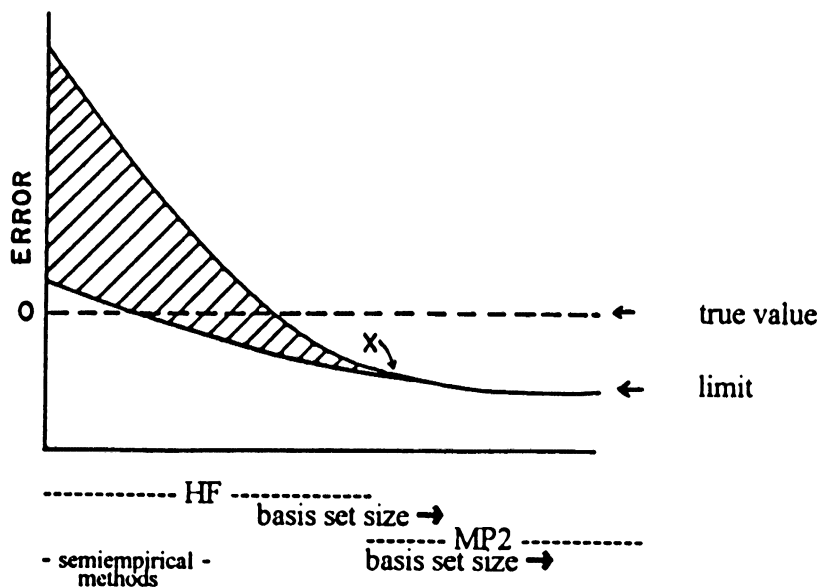


Fig. 3. Schematic representation of the error in calculating some vibrational mode in a variety of molecular environments. For wide families of systems, the error is expected to fall within the shaded area.

Table 2

Calculated wavenumbers and intensities in uracil molecule with some of the methods and levels used

No.	AM1		SAM1		HF/6-31G**		B3P86/6-31G**		B3LYP/6-31G**		Experimental		Characterization
	Wave	Int.	Wave	Int.	Wave	Int.	Wave	Int.	Wave	Int.	Ar matrix ^a	Gas ^b	
1	144	0	145	0	167	0	151	0	150	0	119 ^c		Puckering N3
2	151	0	153	0	179	0	171	0	170	0	185 w	185 w ^c	Puckering N1
3	384	3	409	0	426	3	385	4	385	4	391 m ^c	374 vw	$\delta(\text{OCNCO})$
4	368	8	368	1	429	3	397	4	396	4	411 m	395 w ^c	$\gamma(\text{C}=\text{C}-\text{H}12)$
5	516	1	540	0	561	2	519	3	519	4	516 m	512 w ^c	$\Delta(\text{ring})$
6	553	0	562	0	593	1	543	1	541	1	536 m ^c		$\Delta(\text{ring}) + \delta(\text{C}=\text{O})$
7	603	0	602	0	609	0	560	1	558	1	559 w ^c	588 w	$\Delta_{\text{as}}(\text{ring}) + \delta(\text{C}=\text{O})$
8	465	9	528	1	588	6	571	9	563	8	551 m	545 w ^c	$\gamma(\text{N}1-\text{H})$
9	602	23	679?	3	730	8	693	13	687	14	662 s	660 w ^c	$\gamma(\text{N}3-\text{H})$
10	684	1	655	0	803	0	732	2	729	2	717 w	717 vw ^c	$\gamma(\text{C}4-\text{O}) + \gamma(\text{C}5\text{H})$
11	718	8	691?	0	862	9	760	11	752	10	757 s	757 w ^c	$\gamma(\text{C}2=\text{O})$
12	888	0	891	0	829	0	781	0	772	0	759 sh ^c		$\nu(\text{ring})$
13	878	13	794	0	905	8	814	10	813	10	804 s	802 w ^c	$\gamma(\text{C}5-\text{H}) + \gamma(\text{C}4-\text{O})$
14	1072	0	1060?	1	1053	1	975	0	965	1	958 w	952 w ^c	$\nu(\text{C}-\text{C}) + \delta(\text{N}-\text{H})$
15	954	1	916	0	1110	0	971	1	970	0	963 w	972 w ^c	$\gamma(\text{C}6-\text{H})$
16	1088	0	1095?	1	1076	1	994	1	990	1	982 w	990 w ^c	$\delta(\text{NCC})$
17	1179	0	1146	0	1175	2	1098	1	1091	1	1075 w ^c	1082 m	$\nu(\text{ring}) + \delta(\text{C}5-\text{H})$
18	1283	4	1217	1	1306	9	1210	14	1198	14	1184 vs	1172 s ^c	$\nu(\text{CN}) + \delta(\text{CH}, \text{NH})$
19	1382	1	1275	0	1347	1	1240	0	1231	1	1217 w ^c	1228 m	$\delta(\text{C}5-\text{H}) + \delta(\text{N}-\text{H})$
20	1444	1	1383	2	1530	1	1388	1	1382	3	1359 vw	1356 m ^c	$\delta(\text{N}3-\text{H}) + \delta(\text{C}-\text{H})$
21	1501	0	1471	10	1554	9	1417	8	1407	20	1389 vs	1387 s ^c	$\nu(\text{C}-\text{N}) + \delta(\text{N}3-\text{H})$
22	1531	17	1541	10	1557	6	1428	12	1422	3	1400 vs	1400 s ^c	$\delta(\text{C}6-\text{H}) + \delta(\text{N}-\text{H})$
23	1626	24	1627	17	1647	12	1520	21	1506	18	1472 ms	1461 s ^c	$\delta(\text{N}1-\text{H}) + \nu(\text{N}1-\text{C})$
24	1809	29	1818	57	1847	10	1704	12	1690	12	1644 m	1641 s ^c	$\nu(\text{C}=\text{C})$
25	2039	25	1964	24	1995	100	1830	100	1808	100	1741 vs ^c	1703 vs	$\nu(\text{C}4-\text{O})$
26	1993	100	1902	100	2012	38	1868	94	1845	92	1757 vs	1756 vs ^c	$\nu(\text{C}2=\text{O})$
27	3136	6	2873	1	3394	0	3234	1	3221	1		3076 w ^c	$\nu(\text{C}6-\text{H})$
28	3212	11	2964	1	3429	0	3281	0	3264	0	3084 ^d	3124 m ^c	$\nu(\text{C}5-\text{H})$
29	3447	21	3440	0	3863	8	3643	12	3620	11	3435 s	3436 s ^c	$\nu(\text{N}3-\text{H})$
30	3470	26	3466	0	3902	11	3682	19	3658	17	3484 s	3484 s ^c	$\nu(\text{N}1-\text{H})$

Int.: relative IR intensities, %.

^a From Refs. [6,8].^b From Refs. [7a,b].^c Wavenumbers selected as experimentals in the comparison with the computed values.^d In Raman [7a].

Table 3
Vibrational wavenumbers obtained in 2-TU and 5-BrU with different methods and at the 6-31G** level

No.	2-Thiouracil										5-Bromouracil							
	HF		MP2		BLYP		B3P86		B3LYP		HF		BLYP		B3P86		B3LYP	
	Wave	Int. ^a	Wave	Int. ^a	Wave	Int. ^a	Wave	Int. ^a	Wave	Int. ^a	Wave	Int. ^a	Wave	Int. ^a	Wave	Int. ^a	Wave	Int. ^a
1											168	0	143	0	155	0	153	0
2	178	0	156	0	163	0	168	0	168	0								
3	294	1	276	1	258	2	271	1	270	2	437	3	376	3	397	3	395	3
4											429	3	373	3	393	3	391	3
5	581	1	536	1	517	8	538	1	537	1								
6	540	2	494	1	475	2	493	1	493	2	587	1	513	2	538	1	536	2
7											650	1	574	1	600	0	598	0
8	671	7	614	7	596	5	626	4	620	5	591	9	546	9	574	10	566	9
9	780	7	701	2	692	11	718	10	716	10	726	9	657	14	685	11	680	12
10	828	4	750	11	711	6	750	4	745	5								
12	767	2	730	1	694	1	725	1	719	1	840	14	743	0	784	0		
14	979	1	939	1	868	1	924	0	911	1	1062	1	927	3	981	2	971	2
15	1110	0	940	0	924	0	972	0	972	0	1074	1	878	2	927	2	928	2
16	1088	1	1013	1	967	2	1010	1	1003	1								
17	1162	0	1106	1	1046	2	1093	1	1085	1	1147	6	999	9	1063	7	1047	8
18	1315	13	1244	20	1153	43	1222	18	1212	29	1255	10	1099	0	1187	8	1169	3
19	1349	8	1276	8	1199	2	1249	5	1238	2	1328	6	1144	15	1211	6	1196	12
20	1537	0	1420	6	1335	8	1389	3	1389	4	1482	1	1299	5	1359	1	1353	2
21	1543	12	1440	4	1347	8	1418	6	1407	9	1560	10	1350	4	1400	2	1396	5
22	1596	9	1491	4	1404	3	1474	6	1460	5	1547	9	1333	13	1425	14	1411	13
23	1732	100	1615	100	1511	100	1589	100	1576	100	1641	13	1429	8	1507	16	1493	12
24	1845	10	1706	3	1611	11	1695	12	1681	11	1846	16	1605	10	1695	10	1679	11
25	2009	86	1828	57	1731	87	1836	78	1816	81	2001	100	1722	61	1831	65	1808	65
26											2017	65	1767	100	1870	100	1847	100
27	3399	1	3298	1	3140	1	3238	1	3224	1	3410	0	3154	0	3248	0	3236	0
28	3432	0	3340	0	3183	0	3283	0	3265	0								
29	3853	12	3660	9	3500	10	3629	11	3609	10	3858	12	3507	10	3639	12	3616	11
30	3890	14	3704	13	3532	14	3664	14	3643	14	3896	16	3545	16	3679	19	3654	17

^a Relative IR intensity, %.

Table 4

Absolute error, $\Delta(\omega^{\text{cal.}} - \nu^{\text{exp.}})$, in cm^{-1} , in the calculated wavenumbers of uracil with some of the theoretical methods used

No.	AM1	SAM1	HF/6-31G**	BLYP/6-31G**	B3P86/6-31G**	B3LYP/6-31G**
1	25	26	48	19	32	31
2	−34	−32	−6	−20	−14	−15
3	−7	18	35	−23	−6	−6
4	−27	−27	34	−15	2	1
5	4	28	49	−11	7	7
6	17	26	57	−17	7	5
7	44	43	50	−23	1	−1
8	−80	−17	43	−2	26	18
9	−58	19	70	6	33	27
10	−33	−62	86	−16	15	12
11	−39	−66	105	−49	3	−5
12	106	109	47	−41	−1	−10
13	76	−8	103	−20	12	11
14	120	108	101	−31	23	13
15	−18	−56	138	−49	−1	−2
16	98	105	86	−35	4	0
17	106	73	102	−24	25	18
18	111	45	134	−41	38	26
19	195	88	160	6	53	44
20	88	27	174	−33	32	26
21	114	84	167	−45	30	20
22	131	141	157	−26	28	22
23	165	166	186	−16	59	45
24	168	177	206	−21	63	49
25	298	223	254	−18	89	67
26	237	146	256	9	112	89
27	60	−203	318	59	158	145
28	88	−160	305	52	157	140
29	11	4	427	73	207	184
30	−14	−18	418	63	198	174
Rms	113	100	184	34	77	66

rms, defined as $[\sum \Delta(\omega^{\text{cal.}} - \nu^{\text{exp.}})^2/n]^{1/2}$. ^a $\nu^{\text{exp.}}$ is from gas phase [4,5]. ^b $\nu^{\text{exp.}}$ is from Raman data.

nearly independent of the molecule studied. The calculations can be carried out efficiently [30] at the point marked ‘X’ in Fig. 3, and therefore this residual error can be removed with the use of scale factors, giving rise to accurate predicted wavenumbers.

For small basis sets (or semiempirical calculations), the error, or range of uncertainty about the ‘true’ value obtained from the experiment, is increased largely. Therefore, instead of a unique scale factor (for a given level of calculation), several scale factors should be used, each one related to a group of similar molecules, to reduce the error and obtain accurate predicted wavenumbers significantly.

A detailed analysis of the error in the calculated wavenumbers is described in the next two sections. The semiempirical methods are studied in Section 5.1 and ab initio methods in Section 5.2.

Table 5

Errors obtained in the calculated wavenumbers with several ab initio and DFT methods

Level	No. molecules	% Error	Reference
HF/6-31G*	36	13	[31]
MP2-fu/6-31G*	36	7	[31,32]
BLYP/6-31G*	20	26 ^a	[33]
B3LYP/6-31G*	20	19 ^a	[33]

^a rms deviation, in cm^{-1} .

Table 6

Absolute error, $\Delta(\omega^{\text{cal.}} - \nu^{\text{exp.}})$, in cm^{-1} obtained in the calculated wavenumbers of 2-TU and 5-BrU

No.	2-Thiouracil				5-Bromouracil			
	HF	BLYP	B3P86	B3LYP	HF	BLYP	B3P86	B3LYP
3	25	−11	2	1	47	−14	7	5
5	51	−13	8	7				
6	49	−16	2	2	55	−19	6	4
7					56	−20	6	4
8	67	−8	22	16	43	−2	26	18
9	86	−2	24	22	70	1	29	24
10	118	1	40	35				
12	40	−33	−2	−8				
14	72	−39	17	4	100	−35	19	9
15					168	−28	21	22
16	102	−19	24	17				
17	102	−14	33	25	99	−49	15	−1
18	124	−38	31	21	101	−55	33	15
19	126	−24	26	15	139	−45	22	7
20	174	−28	26	26	155	−28	32	26
21	167	−29	42	31	183	−27	23	19
22	166	−26	44	30	157	−57	35	21
23	198	−23	55	42	183	−29	49	35
24	211	−23	61	47	211	−30	60	44
25	271	−7	98	78	272	−7	102	79
26					256	6	109	86
27	331	72	170	156	352	96	190	178
29	438	85	214	194	433	82	214	191
30	433	75	207	186	425	74	208	183
rms	163	32	68	59	210	43	90	78

Table 7

Scale factors for the force constants in benzene, toluene and phenylsilane

Description	Mode	No.	Benzene ^a	Toluene ^b	Phenylsilane ^c
C(ring)–C(ring)	Stretching	1–6	0.911	0.911	–
C(ring)–X	Stretching	7		0.873	0.872
C(ring)–H	Stretching	8–12	0.863	0.863	0.863
X–H	Stretching	13–15		0.863	0.863
C(ring)–X	Rocking	16		0.842	0.841
C(ring)–H	Rocking	17–21	0.797	0.797	–
X–H	Deformation	22–26		0.765	0.766
Ring	Deformation	27–29	0.808	0.808	–
C(ring)–X	Wagging	30		0.739	0.739
C(ring)–H	Wagging	31–35	0.739	0.739	0.739
XH ₃ group	Twisting	36		1.000	1.150
Ring	Torsion	37–39	0.768	0.768	–

^a From Ref. [41].^b With X = C, from Ref. [42].^c With X = Si, from Ref. [43].

5.1. Semiempirical methods

In the ring modes of the uracil molecule, the differences between the calculated and experimental wavenumbers are shown in Table 4. The experimental values reported for the Argon matrix

[7,8] are used and tabulated in Table 2. We have used these experimental wavenumbers instead of the gas phase values, because in Ar matrix there are several recent studies that confirm the results, while the gas phase spectrum is quite unknown [4,5]. The first column of Table 4 refers to the

Table 8
SQM force field in other molecules

No.	Molecules	Level of calculation	Reference
1	Uracil	HF/4-21G	[7]
2	Catechol	MNDO	[50]
3	4-Nitropyridine- <i>N</i> -oxide	AM1, MNDO	[51]
4	Thiophene/bithiophene, benzene/biphenyl and oligoenes	SCF/DZP	[52]
5	4-Methylpyridine	HF/4-21G	[53]
6	Formic acid, monomer and cyclic dimer	HF/6-31G* and MP2/6-31G*	[54]
7	Chloramide	HF/6-31G*, 6-31G**, and MP2/6-31G*, 6-311G**	[55]
8	H_2NNO_2	HF/6-31G*	[56]
9	Nucleic acid bases	sto-3G, MINI-1, HF/3-21G, 6-31G*	[57]
10	Dimethyl phosphate anion, and sodium dimethyl phosphate	HF/3-21G*, 6-31G*, MP2/6-31 + G*, B3LYP/6-31G*	[58]

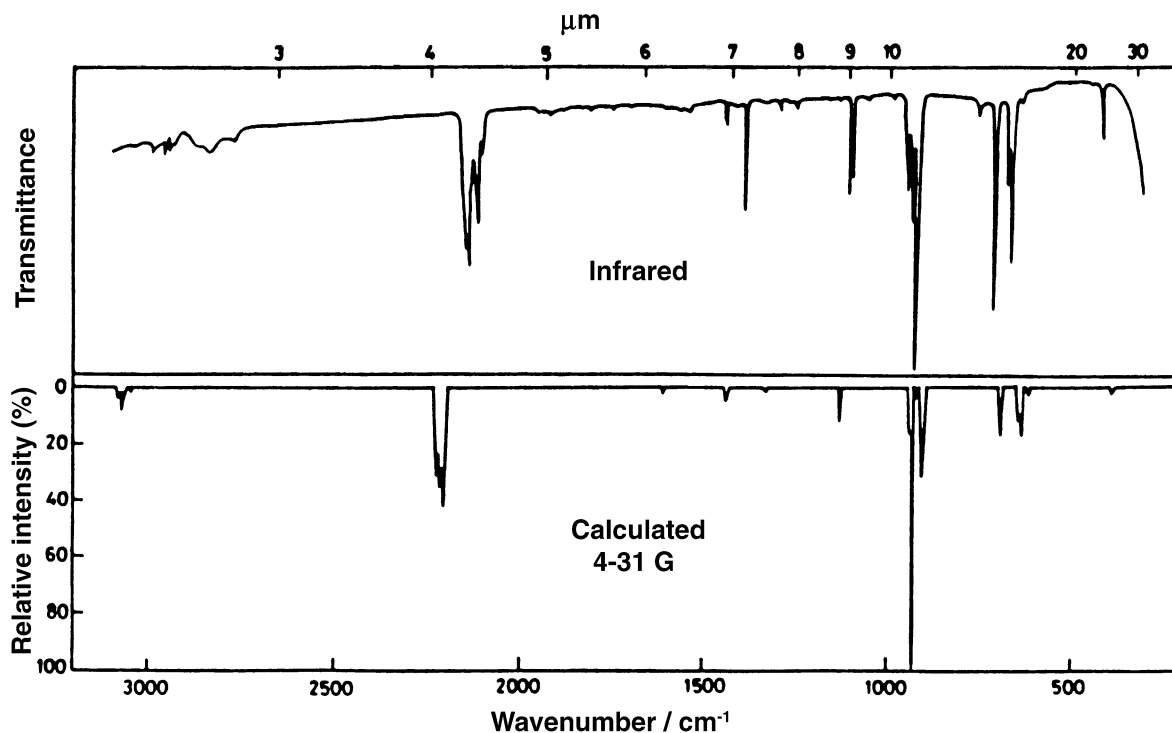


Fig. 4. Calculated theoretical spectrum at 4-31G level and IR spectrum in Ar matrix of phenylsilane.

Table 9
Scale factors at different levels

Level of theory	Scale factor	
	λ	λ'^a
AM1	0.9532	
PM3	0.9761	
HF/3-21G	0.9085	1.0075
HF/6-31G*	0.8953 ^b	0.9061
HF/6-31 + G*	0.8970	0.9131
HF/6-31G**	0.8992	0.9089
HF/6-311G**	0.9051	0.9110
HF/6-31G(df,p)	0.9054	0.9085
MP2-fu/6-31G*	0.9427	1.0214
MP2-fc/6-31G*	0.9434	1.0485
MP2-fc/6-31G**	0.9370	1.0229
MP2-fc/6-311G**	0.9496	1.0127
QCISD-fc/6-31G*	0.9538	1.0147
SVWN/6-31G*	0.9833	1.0079
B-LYP/6-31G*	0.9945	1.0620
B-LYP/6-311G(df,p)	0.9986	1.0667
B-P86/6-31G*	0.9914	1.0512
B3-LYP/6-31G*	0.9614	1.0013
B3-P86/6-31G*	0.9558	0.9923
B3-PW91/6-31G*	0.9573	0.9930

^a Suitable for the prediction of low-wavenumber vibrations.

^b Recommended value of 0.8929 [61].

number of calculated vibrations in Fig. 1. The bottom of the table shows the root-mean square (rms) error obtained for the calculated wavenumbers with many of the methods used.

It is noted that AM1 overestimates the predicted wavenumbers while SAM1 underestimates the values. Although SAM1 is the newest semiempirical method, it shows errors larger than AM1 and PM3. In general, the errors obtained are in accordance with those reported [41a] for the ring modes: $77 \pm 95 \text{ cm}^{-1}$ with AM1, and $36 \pm 114 \text{ cm}^{-1}$ with PM3.

5.2. Ab initio methods

The vibrational wavenumbers are usually calculated using the simple harmonic oscillator model. Therefore, they are typically larger than the fundamentals observed experimentally [20]. The pos-

sible reasons for the deficiency of simple HF calculations are:

The ZPVE (Zero Point Vibrational Energy).

Anharmonicity in the vibrational potential energy surface.

Basis sets are too small.

Neglect of electron correlation.

The HF potential is too steep and therefore wavenumbers are too high.

In general, the calculated ab initio wavenumbers are overestimated by about 10–20 and 5–10% at the HF and the MP2 level, respectively. This overestimation in the wavenumbers also depends on the type of the vibrational mode and on the wavenumber range, varying between 1 and 12%. Thus for modes that appear at high wavenumber, the difference between the harmonic oscillator prediction and the exact or Morse potential like behavior is about 10%. However, at a very low wavenumber, below a few hundred wavenumbers, this difference can be off by a large amount.

Several detailed studies have been reported with ab initio and DFT methods, and they are tabulated in Table 5. The second column is the number of molecules used in each study, while the third column is the mean percentage deviation of the theoretical harmonic wavenumbers from the experimental fundamentals.

In the uracil molecule, the absolute error with many of the different ab initio levels used are listed in Table 4, while the results in 2-TU and 5-BrU are given in Table 6. As experimental values those reported in Ar matrix in 2-TU [34] and analogously in 5-BrU [35] are used. The rms error shown in the bottom of Table 6 refers to all the absolute errors determined in the molecule [36] with the available experimental data. It is noted in the tables that the calculations at the HF level fail to give the observed experimental pattern. Inclusion of an electron correlation (omitted in Table 4) also fails, although slightly, to improve the computed wavenumbers. Only with DFT methods are the wavenumbers close to the experimental values. However, these results have not reproduced all the experimental patterns of wavenumbers and intensities adequately. Thus, the use of scale factors will solve this problem.

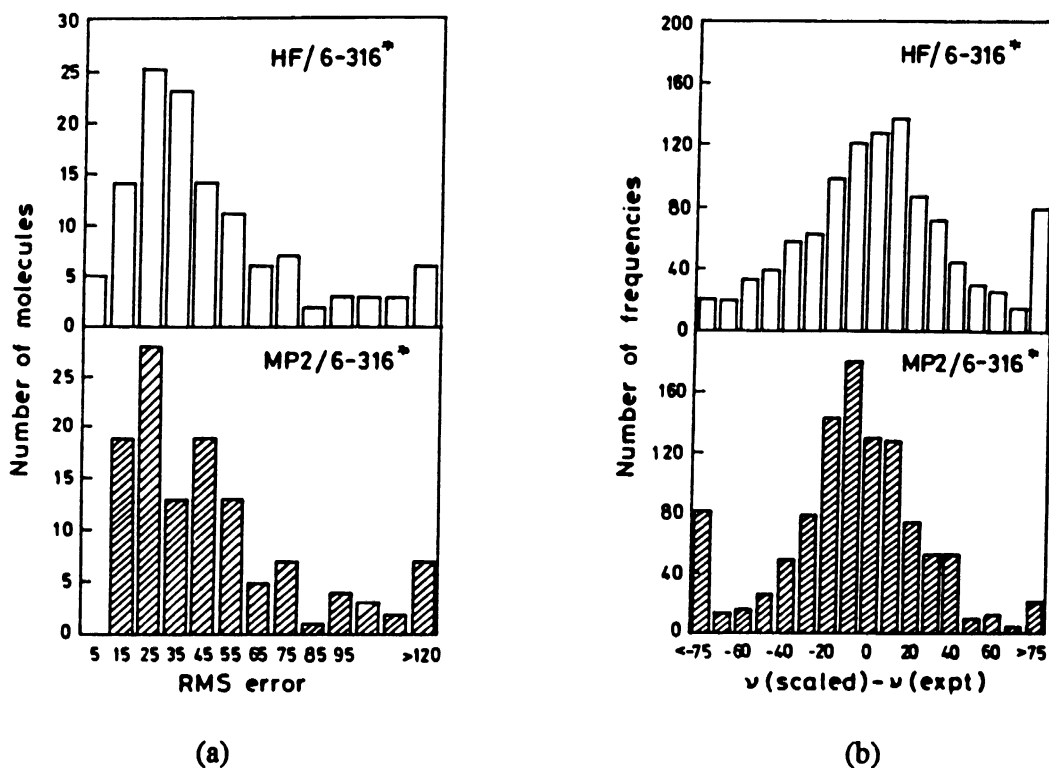


Fig. 5. (a) Histograms of HF/6-31G* and MP2/6-31G* rms errors (cm^{-1}) in theoretical fundamentals after scaling. (b) Histograms of differences $\nu^{\text{scaled}} - \nu^{\text{exp.}}$ (cm^{-1}) at the HF/6-31G* and MP2/6-31G* levels.

Table 10

Percentage of theoretical wavenumbers derived from semiempirical and conventional ab initio procedures that lie (after scaling) within specific error ranges when compared with experimental wavenumbers

% Error	Semiempirical		HF				MP2			
	AM1	PM3	6-31G*	6-31G**	6-311G**	6-311G(df,p)	fu/6-31G*	fc/6-31G*	fc/6-31G**	fc/6-311G**
0–2	19.1	18.9	51.7	50.4	51.1	49.2	56.0	54.7	49.0	50.9
2–4	16.9	13.8	21.6	22.2	21.4	21.2	17.4	17.2	21.0	23.7
4–6	13.0	11.0	9.9	10.7	10.3	10.4	9.9	10.4	9.7	9.9
6–8	8.6	10.9	6.1	5.6	5.5	6.3	5.3	5.5	6.6	4.7
8–10	8.9	8.3	2.8	3.2	3.5	3.5	3.1	2.8	3.6	2.9
10–14	10.6	12.3	3.3	3.1	2.7	3.9	3.7	4.2	5.4	4.8
14–18	4.6	6.2	1.5	1.4	1.7	1.5	1.1	1.0	1.5	0.5
18–24	6.6	5.2	1.6	1.6	2.2	2.3	1.3	1.8	1.4	0.9
24–30	4.4	5	1.1	1.3	1.0	1.1	0.6	0.4	0.4	0.4
>30	7.2	8.4	0.6	0.6	0.7	0.6	1.7	2.1	1.5	1.4

Table 11
Percentage from DFT procedures

% Error	BLYP		BP86	B3LYP	B3P86	B3PW91
	6-31G*	6-311G(df,p)	6-31G*	6-31G*	6-31G*	6-31G*
0–2	61.8	50.1	62.7	57.5	67.3	69.6
2–4	20.1	18.8	19.9	18.1	19.3	16.8
4–6	6.3	11.7	5.9	10.2	3.8	4.0
6–8	3.1	6.1	2.9	5.3	3.6	4.2
8–10	1.5	4.7	2.1	3.2	1.5	1.7
10–14	3.4	4.7	3.3	3.4	2.5	1.6
14–18	1.8	2.0	1.2	1.3	0.2	0.2
18–24	0.4	1.1	0.4	0.2	0.8	0.8
24–30	0.4	0.3	0.8	0.2	0.4	0.2
>30	1.0	0.7	0.6	0.6	0.6	0.8

Table 12
Scaled wavenumbers using an overall scale factor in uracil

No.	AM1	HF/6-31G**	BLYP/6-31G**	B3P86/6-31G**	B3LYP/6-31G**
1 ^a	137	152	147	150	150
2 ^a	144	163	175	170	170
3 ^a	366	387	391	382	385
4 ^a	351	390	404	394	397
5 ^a	492	510	532	515	520
6 ^a	527	539	551	539	542
7 ^a	575	554	569	556	559
8 ^a	443	534	577	567	563
9 ^a	574	663	707	688	688
10 ^a	652	730	744	726	730
11 ^a	684	783	752	754	753
12 ^a	846	753	787	775	773
13 ^a	837	823	830	808	814
14	1022	947	916	932	928
15	909	998	918	928	932
16	1037	968	950	950	952
17	1124	1057	1043	1049	1049
18	1223	1174	1125	1157	1152
19	1317	1211	1186	1185	1183
20	1376	1376	1316	1327	1329
21	1431	1397	1335	1354	1353
22	1459	1400	1366	1365	1367
23	1550	1481	1437	1453	1448
24	1724	1661	1611	1629	1625
25	1944	1794	1714	1749	1738
26	1990	1809	1755	1785	1774
27	2989	3052	3118	3091	3097
28	3062	3083	3159	3136	3138
29	3286	3474	3490	3482	3480
30	3308	3509	3527	3519	3517

^a With the scale factor recommended for low wavenumbers.

6. Scaling procedures for the wavenumbers

The values of the force constants and the wavenumbers are close among similar molecules and characteristic groups. Based on this assumption, two kinds of procedures are used for an accurate scaling of the calculated wavenumbers.

6.1. Scaling the force constant matrix, before calculating the wavenumbers

This procedure is based on the transferability of the force constants and dipole moment derivatives among similar molecules. The procedure does not assume that the force constants are similar in related molecules, but makes the weaker assumption

that the error in calculating the force field is similar for related types of vibrational motions in related molecules as determined by the identical computational procedure.

Owing to the complementarity between ab initio and empirical sources of information [1], this empirical scaling technique was introduced [37] in 1972. However, the first systematic application of mixed ab initio–empirical techniques was made in the pioneering work of Blom and Altona [38].

A set of force constants represents a quantitative expression of the forces binding the atoms in a molecule. The valence force field is generally accepted as the most plausible representation of the intramolecular forces from a physical point of view. Unfortunately, the complete force field can-

Table 13

Scaled wavenumbers in 2-thiouracil and 5-bromouracil using an overall scale factor

No.	2-TU					5-BrU			
	HF	MP2	BLYP	B3P86	B3LYP	HF	BLYP	B3P86	B3LYP
1 ^a						153	152	154	153
2 ^a	162	160	173	168	167				
3 ^a	267	282	274	271	268	397	399	394	396
4 ^a						390	396	390	392
5 ^a	528	548	549	539	533				
6 ^a	491	505	504	494	489	534	545	534	537
7 ^a						591	610	595	599
8 ^a	610	628	633	627	615	537	580	570	567
9 ^a	709	717	735	719	710	660	698	680	681
10	744	767 ^a	707	721	712				
12	690	747 ^a	690	697	687	755	739	749	
14	880	961 ^a	863	888	871	955	922	938	934
15	998	881	919	934	929	966	873	886	892
16	978	949	962	971	959				
17	1045	1036	1040	1051	1037	1031	994	1016	1007
18	1182	1166	1147	1175	1158	1128	1093	1135	1124
19	1213	1196	1192	1201	1183	1194	1138	1157	1150
20	1382	1331	1328	1335	1328	1333	1292	1299	1301
21	1387	1349	1340	1363	1345	1403	1343	1338	1342
22	1435	1397	1396	1417	1395	1391	1326	1362	1357
23	1557	1513	1503	1528	1506	1476	1421	1440	1435
24	1659	1599	1602	1630	1607	1660	1596	1620	1614
25	1806	1713	1721	1765	1736	1799	1713	1750	1738
26						1814	1757	1787	1776
27	3056	3090	3123	3113	3081	3066	3137	3104	3111
28	3086	3130	3165	3156	3121				
29	3465	3429	3481	3489	3449	3469	3488	3478	3476
30	3498	3471	3513	3523	3482	3503	3526	3516	3513

^a With the scale factor recommended for low wavenumbers.

Table 14

Absolute error, $\Delta(\nu^{\text{scaled}} - \nu^{\text{exp}})$, in cm^{-1} , in the scaled wavenumbers of uracil using an overall scale factor, with some of the theoretical methods used

No.	AM1	HF/6-31G**	BLYP/6-31G**	B3P86/6-31G**	B3LYP/6-31G**
1	18	33	28	31	31
2	−41	−24	−21	−22	−22
3	−25	−7	−25	−23	−21
4	−44	−9	−17	−16	−14
5	−20	−7	−14	−16	−13
6	−9	−3	−20	−17	−16
7	16	−11	−26	−24	−23
8	−102	−16	−5	1	−4
9	−86	−4	2	2	0
10	−65	5	−20	−17	−16
11	−72	18	−53	−31	−34
12	87	−16	−22	−12	−17
13	35	12	−24	−24	−20
14	70	−5	−36	−20	−24
15	−63	26	−54	−44	−39
16	47	−22	−40	−40	−38
17	51	−16	−30	−24	−24
18	51	2	−47	−15	−20
19	130	−6	−31	−32	−34
20	20	20	−40	−29	−27
21	44	10	−52	−33	−34
22	59	0	−34	−35	−33
23	89	20	−24	−8	−13
24	83	20	−30	−12	−16
25	203	53	−27	8	−3
26	144	53	−1	29	18
27	−87	−24	42	15	21
28	−62	−41	35	12	14
29	−150	38	54	46	44
30	−176	25	43	35	33
rms	87	23	34	24	21

not be obtained from experiment alone, even within the harmonic oscillator approximation, except for the simplest molecules. Thus the force constants for different types of vibrations need to be computed, expressed in internal coordinates, and corrected with a small set of scaling factors. These empirically corrected ab initio force constants and dipole moment derivatives for a variety of basic organic compounds have been assembled in a database [1], from which it is possible to predict the spectra of unknown substances with a modest effort, utilizing the transferability of these quantities.

In the SQM (Scaled Quantum Mechanical) technique [39], for determining ab initio–empirical force fields, a small number of scale factors are used to correct the deficiencies of the ab initio force fields, and the effects of anharmonicity in the observed wavenumbers. The off-diagonal force constants (F_{ij}) are scaled by $(C_i C_j)^{1/2}$, $F_{ij} = (C_i C_j)^{1/2} F_{ij}^{\text{th}}$, where C_i and C_j are the scale factors for F_{ii} and F_{jj} . The scale factors are in general much more transferable than the force constants themselves.

Sometimes the calculations are performed by its simplified version which uses only a single overall

scale factor [20], ca. 0.9, or multiplying [40] all the diagonal stretching force constants by 0.9 and all the diagonal bending force constants by 0.8. The advantage of these methods is their extreme simplicity. In particular, scaling with several scale factors requires the transformation of the force field to a chemically reasonable local internal coordinate system, called *natural internal coordinates*. This is not necessary if only a single scale factor (or two scale factors) is used. However, the accuracy of these simple procedures is lower than the SQM method.

The SQM method can be used with all kinds of quantum mechanical force fields: semi-empirical, density functional, SCF level and high-level correlated wave functions. At a high level of calculations, the empirical corrections required are smaller. However, the compu-

tational costs ultimately limit the level of calculations, which can be performed for large molecules.

A pioneering study on benzene [41] produced a small set of scaling factors (Table 7) which have been transferred with minor modifications to scale the computed force fields of several derivatives, e.g. toluene [42], phenylsilane [43] (Table 7), fluorobenzene [44], aniline [45], benzonitrile [46], phenylacetylene [47], etc. Similar SQM force fields have been derived for other ring systems [48], and acyclic compounds [12,28]. Table 8 gives some of the references for these systems. These calculations although in general have been carried out at the very modest HF/4-21G level, reproduce the experimental vibrational spectra, e.g. Fig. 4 for the phenylsilane molecule accurately. Other examples are outlined in Ref. [49].

Table 15

Absolute error in the scaled wavenumbers of 2-thiouracil and 5-bromouracil molecules

No.	2-TU					5-BrU			
	HF	MP2	BLYP	B3P86	B3LYP	HF	BLYP	B3P86	B3LYP
3	−2	13	5	2	−1	7	9	4	6
5	−2	18	19	9	3				
6	0	14	13	3	−2	2	13	2	5
7						−3	16	1	5
8	6	24	29	23	11	−11	32	22	19
9	15	23	41	25	16	4	42	24	25
10	35	40	−3	11	2				
12	−37	37	−37	−30	−40				
14	−27	54	−44	−19	−36	−7	−40	−24	−28
15						60	−33	−20	−14
16	−8	−37	−24	−15	−27				
17	−15	−24	−20	−9	−23	−17	−54	−32	−41
18	−9	−25	−44	−16	−33	−26	−61	−19	−30
19	−10	−27	−31	−22	−40	5	−51	−32	−39
20	19	−32	−35	−28	−35	6	−35	−28	−26
21	11	−27	−36	−13	−31	26	−34	−39	−35
22	5	−33	−34	−13	−34	1	−64	−28	−33
23	23	−21	−31	−6	−28	18	−37	−18	−23
24	25	−35	−32	−4	−27	25	−39	−15	−21
25	68	−25	−17	27	−2	70	−16	21	9
26						53	−4	26	15
27	−12		55	45	13	8	79	46	53
29	50	14	66	74	34	44	63	53	51
30	41	14	56	66	25	32	55	45	42
rms	26	26	37	30	25	29	44	28	30

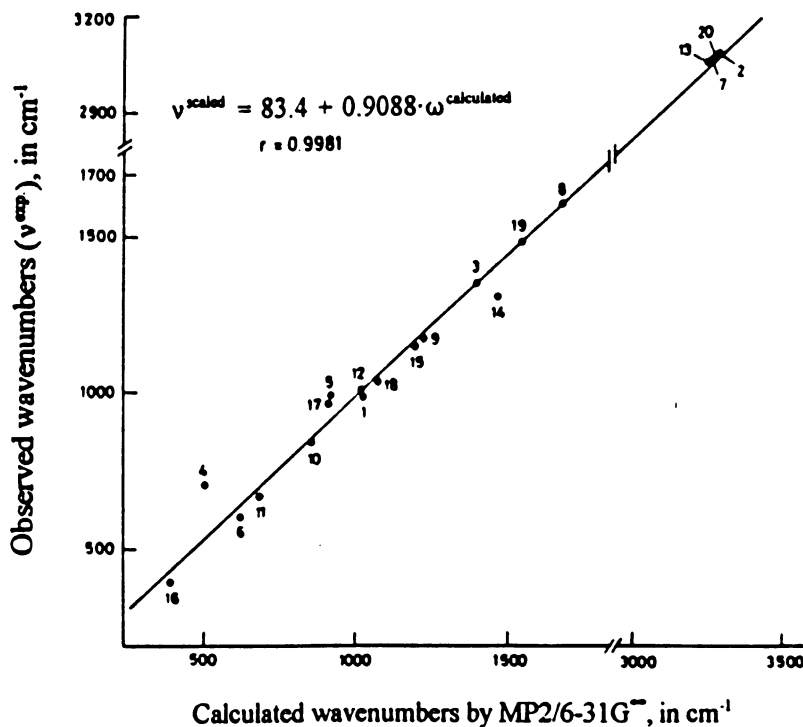


Fig. 6. Calculated wavenumbers by MP2 vs. experimental ones in benzene molecule.

6.2. Scaling the wavenumbers

This section describes how the calculated wavenumbers can be directly scaled with three procedures: using an overall scale factor, using a scaling equation, or using specific scale factors for each mode.

6.2.1. With a single overall scale factor for the calculated level

Through this procedure, the calculated wavenumbers of a molecule at a specific level of theory are scaled with a unique scale factor (or correction factor) which is common for all the molecules with the same level of calculation. Therefore, different scale factors are used for the distinct levels of theory, Table 9.

The procedure to determine this scale factor is reported to be delicate [59], because the scale factor depends not only on the basis set or theoretical method used but also on the group of molecules used for comparison irrespective of

whether the comparisons are made with only harmonic wavenumbers or with all fundamentals. Thus by comparing the measured wavenumbers of polyatomic molecules, it is found that the computed wavenumbers from 6-31G* calculations have an average percent deviation of 13.9%. However, if the comparison is limited to harmonic wavenumbers, then the average deviation is 12.8%, or if one limits the comparison further to polyatomic hydrides, then the percent deviation is 10% on the measured wavenumbers and 7.8% on the harmonic wavenumbers [59].

The procedure for calculating the scale factor [59] is as follows: with a full set of theoretical wavenumbers, ω_i^{cal} , for different molecules, and with their corresponding experimental fundamental wavenumbers, ν_i^{exp} , the scaling factors λ are those, which minimize the residuals.

$$\Delta = \sum (\lambda \omega_i^{\text{cal}} - \nu_i^{\text{exp}})^2$$

and thus,

$$\lambda = \frac{\sum \omega_i^{\text{cal.}} v_i^{\text{exp.}}}{\sum (\omega_i^{\text{cal.}})^2}$$

Therefore, for the different levels of theory and from a dataset containing 122 molecules and 1066 wavenumbers, the scale factors of the second column of Table 9 have been obtained [59,60].

To minimize the large errors in wavenumbers at the lower end of the wavenumber range, an inverse wavenumber scaling factor, λ' , is used [59] which minimizes the residual

$$\Delta = \sum_i^{\text{all}} \left(\frac{1}{\lambda \omega_i^{\text{th.}}} - \frac{1}{v_i^{\text{exp.}}} \right)^2 \quad \text{giving} \quad \lambda' = \frac{\sum_i^{\text{all}} \left(\frac{1}{\omega_i^{\text{th.}}} \right)^2}{\sum_i^{\text{all}} \frac{1}{\omega_i^{\text{th.}} v_i^{\text{exp.}}}}$$

The final scaling factors are listed in the third and sixth columns of Table 9.

With the optimum scale factors of the second column of Table 9, rms errors for the wavenumbers of a dataset of 122 molecules have been evaluated [61]. The result is plotted in Fig. 5a, while Fig. 5b shows the distribution of $v^{\text{scaled}} - v^{\text{exp.}}$. It is noted that the remaining rms errors

Table 16

Scaling equations obtained in benzene and uracil molecules

Methods	Benzene			Uracil		
	<i>a</i>	<i>m</i>	<i>r</i>	<i>a</i>	<i>m</i>	<i>r</i>
<i>Semiempirical</i>						
MNDO	89.4	0.8729	0.9977			
AM1	−1.6	0.9529	0.9977	−21.5	0.9620	0.9956
PM3	−0.7	0.9898	0.9960	−260.8	96.1458	0.8928
SAM1	−71.5	1.0692	0.9920	−46.5	1.0040	0.9947
<i>SCF</i>						
HF/4-21G*	−3.8	0.9128	0.9993			
HF/6-31G*	−4.0	0.9103	0.9994	4.6	0.8924	0.9998
HF/6-31G**	−8.6	0.9162	0.9994	5.7	0.8867	0.9992
HF/6-31++G**	−6.2	0.9153	0.9994	10.5	0.8938	0.9998
<i>Post-SCF</i>						
MP2/6-31G*				34.5	0.9372	0.9996
MP2/6-31G**	83.4	0.9088	0.9981			
MP2/6-311G**	97.3	0.9156	0.9972			
MP2/TZ2P+f	41.4	0.9360	0.9995			
<i>Density functional</i>						
SVWN/6-31G**	30.3	0.9692	0.9994			
SLYP/6-31G**	27.8	0.9811	0.9991			
BP86/6-31G*				40.7	0.9713	0.9998
BP86/6-31G**	32.7	0.9752	0.9998	46.0	0.9678	0.9998
BP86/6-311G(2d,1p)	28.8	0.9819	0.9999			
BLYP/6-31G*				42.7	0.9742	0.9998
BLYP/6-31G**	27.2	0.9791	0.9999	46.4	0.9718	0.9998
Becke3P86/6-31G*	25.0	0.9473	0.9999	29.9	0.9412	0.9999
Becke3P86/6-31G**	27.2	0.9476	0.9999	34.1	0.9389	0.9999
Becke3LYP/6-31G*	23.3	0.9519	0.9999	30.8	0.9468	0.9999
Becke3LYP/6-31G**	22.1	0.9543	0.9999	34.6	0.9447	0.9999
Becke3LYP/6-311G**	17.8	0.9614	0.9999			
Becke3LYP/6-311G(2d,1p)	18.6	0.9616	0.9999			
Becke3LYP/6-311+G(2d,1p)	21.2	0.9597	1.0000			
Becke3PW91/6-31G*				30.1	0.9421	0.9999
Becke3PW91/6-31G**	24.8	0.9501	0.9999	34.9	0.9393	0.9999

Table 17
Scaled wavenumbers of uracil using the scale equations

No.	AM1	SAM1	HF	BLYP	B3P86	B3LYP
1	118	101	155	178	174	174
2	124	108	165	207	195	195
3	350	366	386	404	396	398
4	334	325	389	416	407	409
5	477	499	507	533	521	525
6	513	521	535	551	544	546
7	561	561	549	567	560	562
8	428	487	531	574	570	566
9	560	639	657	694	685	684
10	640	615	723	728	721	723
11	672	651	775	734	748	745
12	837	853	746	766	767	764
13	827	755	814	806	798	803
14	1015	1024	946	941	949	946
15	901	878	997	943	946	951
16	1030	1059	966	974	967	970
17	1118	1111	1055	1066	1065	1065
18	1219	1182	1172	1145	1170	1166
19	1314	1241	1208	1206	1198	1198
20	1374	1350	1372	1332	1337	1340
21	1429	1439	1393	1351	1364	1364
22	1458	1509	1396	1382	1375	1378
23	1550	1596	1476	1451	1461	1457
24	1727	1789	1655	1621	1634	1631
25	1949	1937	1787	1721	1752	1743
26	1905	1874	1802	1762	1788	1778
27	3010	2854	3036	3093	3070	3078
28	3083	2946	3067	3133	3115	3118
29	3310	3427	3455	3456	3454	3454
30	3333	3453	3489	3493	3491	3490

(after scaling) appear to be around 50 cm^{-1} , for both HF/6-31G* and MP2/6-31G* fundamentals, although the MP2 errors can be much larger for particular cases.

Tables 10 and 11 show the proportion of wavenumbers calculated by the various methods that lie with different percent error from the experimental values.

In the uracil molecule the scaled wavenumbers using this procedure are listed in Table 12, while the results in 2-TU and 5-BrU are tabulated in Table 13.

The absolute error obtained between the scaled wavenumbers and the corresponding experimental ones, is shown in Table 14 for the uracil molecule, while Table 15 refers to the 2-TU and 5-BrU molecules.

With the AM1 semiempirical method, the errors are very large, by the overestimation or underestimation of the computed wavenumbers, especially in the stretch region. A similar result is obtained with 2-TU and 5-BrU molecules. Thus, with AM1 it is not recommended to use a single overall scale factor for the computed wavenumbers. Instead, another procedure of scaling should be used, as is described in the following sections.

With ab initio methods the error is remarkably reduced, especially in HF with more than four times in the uracil molecule and about seven times in 2-TU and 5-BrU. However, in several modes the error is still very large and far from the desired accuracy, e.g. in uracil the number of vibrations is 25 and 26 at the HF level.

With the DFT procedures, although the errors are reduced, they are in general slightly greater than HF, and especially larger in several modes, and therefore it is recommended to use another procedure of scaling.

Logically, having one scaling factor for all wavenumbers at one level of theory is a simplification. Procedures that are more accurate are described in the following sections.

6.2.2. With a scaling equation

The use of a single overall scale factor is the simplest procedure of scaling, but leads to a high degree of error in the scaled values of some modes and molecules, and impede a clear and accurate assignment. Thus, in the literature some mislays in the correlation with the experimental wavenumbers is observed frequently. To avoid these errors and to obtain an actually accurate assignment, new procedures of scaling should be used. Based on this suggestion, two new procedures of scaling are shown in the present manuscript: the scaling equation and the use of specific scale factors for each mode. In both cases, the scaling is carried out in the basic skeleton molecules from which the scaling equations or specific scale factors to be transferable to related molecules or to their derivatives are extracted. In earlier papers [2,64], we studied several benzene derivatives through the scale factors obtained in the benzene molecule. Now the present article studies the uracil molecule, extracting scaling

parameters to be used in their derivatives, e.g. 2-TU and 5-BrU.

Therefore, the scale factors or scaling equations extracted are not of widespread application, and can be used only in related molecules. By contrast, the absolute errors obtained in the scaled wavenumbers are in general lower than 20 cm^{-1} , which reduces mislay in the assignments. These new scaling procedures also lead to remarkable improvement in the predicted wavenumbers of the low-wavenumber region, compared with the results when an unique scale factor is used.

In general, the idea of using a scaling equation is to find an empirical relation between all the computed and experimental wavenumbers of a molecule. It has two advantages: (1) high differences (i.e. $> 20\text{ cm}^{-1}$) can be detected between

the scaled wavenumbers obtained with the scaling equation, and the corresponding experimental wavenumbers; and therefore the error in the assignment of a mode can be corrected with a new correspondence of our scaled wavenumbers with another experimental value. It is necessary to note that the difference ($\omega^{\text{scaled eqn.}} - \nu^{\text{exp.}}$) is remarkably lower (ca. 30%) than ($\omega^{\text{scaled overall factor}} - \nu^{\text{exp.}}$), which reduce the number of experimental bands to be checked and the risk to an error. (2) The excellent transferability of the scaling equation to other related molecules or more complex derivatives, which permits a better scaling of their spectra than the standard procedure with a single overall factor.

For these reasons, in the present section we show the description of the scaling procedure and

Table 18

Scaled wavenumbers with the scaling equations in 2-thiouracil and 5-bromouracil molecules

No.	2-TU				5-BrU			
	HF	BLYP	B3P86	B3LYP	HF	BLYP	B3P86	B3LYP
1					156	185	180	179
2	164	205	193	191				
3	268	297	291	288	396	412	407	408
4					389	409	403	404
5	524	549	543	538				
6	488	508	500	497	530	545	539	541
7					586	604	597	600
8	605	626	626	616	533	577	573	569
9	702	719	713	706	654	685	677	677
10	745	737	743	734				
12	690	721	720	709	756	768	770	
14	880	890	907	889	954	947	955	952
15	997	944	953	947	965	900	904	911
16	977	986	989	976				
17	1043	1063	1067	1053	1030	1017	1032	1024
18	1180	1167	1189	1172	1126	1114	1149	1139
19	1210	1212	1215	1196	1191	1158	1171	1164
20	1378	1344	1347	1338	1329	1309	1310	1313
21	1383	1355	1374	1355	1398	1358	1349	1353
22	1431	1411	1427	1405	1387	1342	1372	1368
23	1552	1515	1536	1514	1471	1435	1449	1445
24	1653	1612	1636	1612	1654	1606	1626	1621
25	1799	1729	1769	1739	1792	1720	1753	1743
26					1806	1764	1790	1779
27	3040	3098	3094	3061	3050	3111	3084	3092
28	3070	3140	3136	3100				
29	3446	3448	3463	3423	3450	3454	3451	3451
30	3479	3479	3496	3455	3484	3491	3488	3487

Table 19

Absolute error, $\Delta(\nu^{\text{scaled}} - \nu^{\text{exp}})$, in cm^{-1} , in uracil and using the scaling equations

No.	AM1	SAM1	HF	BLYP	B3P86	B3LYP
1	−8	8	−36	−59	−55	−55
2	−61	−77	−19	22	10	10
3	−41	−25	−5	13	5	7
4	−61	−70	−6	21	12	14
5	−35	−13	−5	21	9	13
6	−23	−15	−1	15	8	10
7	2	2	−10	8	1	3
8	−117	−58	−14	29	25	21
9	−100	−21	−3	34	25	24
10	−77	−102	6	11	4	6
11	−84	−106	18	−23	−9	−12
12	78	94	−13	7	8	5
13	25	−47	12	4	−4	1
14	63	72	−6	−11	−2	−6
15	−71	−94	25	−29	−26	−21
16	40	69	−24	−16	−23	−20
17	45	38	−18	−7	−8	−8
18	47	10	0	−27	−2	−6
19	97	24	−9	−11	−19	−19
20	18	−6	16	−24	−19	−16
21	42	52	6	−36	−22	−23
22	58	109	−4	−18	−25	−22
23	89	135	15	−10	0	−4
24	86	148	14	−20	−7	−10
25	208	196	46	−20	11	2
26	149	118	46	6	32	22
27	−66	−222	−40	17	−6	2
28	41	−178	−57	9	−9	−6
29	−126	−9	19	20	18	18
30	−151	−31	5	9	7	6
rms	85	93	23	29	24	24

the results obtained with its use. The scaling equations are of the general form:

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

Fig. 6 is an example with the benzene ring modes. The numbering corresponds to Wilson's notation [62,63]. By fitting, the scaling equation: $\nu^{\text{scaled}} = 83.4 + 0.9088 \cdot \omega^{\text{calculated}}$ with the correlation coefficient (r) of 0.9981 is obtained.

Table 16 tabulates the equations at other levels of theory, for the simple molecules of benzene [64] and uracil [23]. In general, a good relationship is observed with correlation coefficient (r) close to unity, especially with the DFT methods.

Using these scale equations, the values obtained for the uracil molecule are given in Table 17, while the scaled wavenumbers in 2-TU and 5-BrU are given in Table 18. For uracil, the absolute errors obtained with this procedure are listed in Table 19. A resume of the calculated rms errors in the wavenumbers and in the two procedures of scaling used, is listed in Table 20. The results for the 2-TU and 5-BrU molecules are given in Table 21.

An analysis of these tables gives rise to the following conclusions: by using an overall scale factor or a scaling equation for scaling, the semiempirical methods offer a poor prediction of the experimental wavenumbers, with rms errors

ca. 90 cm^{-1} . The SAM1 method, although it is the newest semiempirical method, has no significant improvement over AM1, with particularly large errors in vibrations numbers 27 and 25.

With the scaling, a slight reduction in the error is observed in AM1, but it is insignificant or worse with PM3 and SAM1. The error in the calculated wavenumbers by AM1 is partially systematic, and therefore can be eliminated by using a scaling procedure. However, the error in PM3 and SAM1 is largely inherent to the method, and it is not appreciably reduced by the simple use of an overall scale factor or a scaling equation. Although with AM1 the error is reduced slightly with the scaling, it is still large, by the overestimation or underestimation of the computed wavenumbers, especially in the C=O stretching modes (vibrations numbers 25 and 26). This is because the other part of the error is associated

with the mode itself, with its calculated wavenumber (e.g. the semiempirical methods fail in the description of groups with high-electronic density as the C=O). This error is systematic for the same mode in related molecules, and can be eliminated by using only the specific scale factors for each vibration, as described in the next section.

Although in the calculated wavenumbers, the semiempirical methods have better rms errors than the HF-based methods, indicating that their parametrizations have accounted for some of the effects of electron correlation, their errors are less systematic than the HF, and thus they are less reduced with the use of a single overall scale factor or a scaling equation. In HF, the reduction is drastic and the used basis has little effect. However, in several modes the error is again very large; e.g. modes 26–28, and thus to reduce the error, specific scale factors should be used.

The most cost-effective procedures found for predicting vibrational wavenumbers 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 for the excessive time and memory consumed by the computer, it is preferable to use other methods instead of MP2.

In HF, for the uracil molecule, the use of a scaling equation leads to the same error as with an overall scale factor. However, in 2-TU and 5-BrU molecules, the use of a scaling equation reduces the error remarkably to a value similar to that in uracil.

In DFT methods, the use of the scaling equations reduces the errors by ca. 30% of those found with an overall scale factor (Tables 14 and 15), showing that the errors in the calculated wavenumbers with DFT methods are systematic and partially associated with the kind of molecules studied; and therefore they can be reduced by employing the scaling equations determined in the related molecules. The B-based DFT procedures, while not performing quite as well as the corresponding B3-based procedures, have the attraction of standard wavenumber scale factors close to unity, meaning that they can be used often without scaling. The LYP functional is su-

Table 20

Resume with the rms errors in the calculated and scaled wavenumbers of the uracil modes by the different procedures, methods and levels

Method	(1)	(2)	(3)
<i>Semiempirical</i>			
AM1	113	87	86
PM3	81	101	
SAM1	100		94
<i>SCF</i>			
HF/6-31G*	185		19
HF/6-31G**	184	23	23
HF/6-31++G**	177		17
<i>Post-SCF</i>			
MP2/6-31G*	82	37	25
<i>Density functional</i>			
BP86/6-31G*	31		16
BP86/6-31G**	35	33	18
BLYP/6-31G*	31		18
BLYP/6-31G**	34	34	20
B3P86/6-31G*	75		13
B3P86/6-31G**	77	24	15
B3LYP/6-31G*	65	21	12
B3LYP/6-31G**	66	21	14
B3PW91/6-31G*	73		13
B3PW91/6-31G**	75	25	15

(1) Calculated wavenumbers. (2) Scaled wavenumbers with an overall factor. (3) Scaled wavenumbers with the scaling equations.

Table 21

Absolute error in the scaled wavenumbers of 2-thiouracil and 5-bromouracil using the scaling equations

No.	2-TU				5-BrU			
	HF	BLYP	B3P86	B3LYP	HF	BLYP	B3P86	B3LYP
3	−1	28	22	19	6	22	17	18
5	−6	19	13	8				
6	−3	17	9	6	−2	13	7	9
7					−8	10	3	6
8	1	22	22	12	−15	29	25	21
9	8	25	19	12	−2	29	21	21
10	35	27	33	24				
12	−37	−6	−7	−18				
14	−27	−17	0	−18	−8	−15	−7	−10
15					59	−6	−2	5
17	−17	3	7	−7	−18	−31	−16	−24
18	−11	−24	−2	−19	−28	−40	−5	−15
19	−13	−11	−8	−27	2	−31	−18	−25
20	15	−19	−16	−25	2	−18	−17	−14
21	7	−21	−2	−21	21	−19	−28	−24
22	1	−19	−3	−25	−3	−48	−18	−22
23	18	−19	−2	−20	13	−23	−9	−13
24	19	−22	−2	−22	19	−29	−9	−14
25	61	−9	31	1	63	−9	24	14
26					45	3	28	18
27	−28	30	26	−7	−8	53	26	34
29	30	33	48	8	25	30	26	25
30	22	22	39	−2	13	20	17	16
rms	24	21	21	16	25	27	18	19

terior in precision to the P86 and PW91 functionals. Thus combining the most accurate exchange with the correlation functional leads to B3-LYP, which gives the lowest errors in benzene and uracil molecules (and derivatives), and is therefore the recommended method.

6.2.3. With a specific scale factor for each mode

It is well known that in organic molecules many of the vibrational modes are localized and that many functional groups have characteristic wavenumbers that do not vary much between different molecules. Therefore, considering the groups with analogous molecules, scaling factors can be calculated as

$$\lambda = \frac{\nu^{\text{experimental}}}{\omega^{\text{calculated}}}$$

which bring the computed wavenumbers in line with the available experimental data. That is, the procedure is based on the assumption that the ratios between the experimental and computed wavenumbers are fairly constant for each type of characteristic wavenumber, such as C–H stretch, C–Cl stretch, and NH₂ torsion etc. It is then possible to derive, for known experimental spectra, a correction factor for each characteristic wavenumber by taking the average of the ratios between the experimental and computed wavenumbers, λ , and to use them for predicting or assigning unknown spectra.

The introduction of different scale factors for distinct types of vibrational modes, instead of using an uniform correction factor for all the modes, removes the error which is systematic and associated with the same mode in the related molecules, and therefore remarkably improves the

accuracy of the methods in predicting the wavenumbers, particularly the semiempirical.

The difference between the computed and the experimental characteristic wavenumbers may be owing to various effects that are usually not even considered in theory such as anharmonicity, errors in the computed geometry, Fermi resonance, or even solvent effects. The introduction of a scaling factor for a single characteristic wavenumber is capable of accounting for most of these various effects and leads to a more precise prediction for specific characteristic wavenumbers that are of special interest.

It should be noted that certain types of vibrational modes are much more readily identified than the others, e.g. the stretchings. On the other hand, many of the torsion and out-of-plane

modes are delocalized throughout a wide low-wavenumber range, and it is difficult to identify these modes or to differentiate among them. Thus, the scale factors obtained for these modes are not so transferable, and should be considered with caution.

This procedure of scaling is especially recommended to be used with semiempirical methods, reducing the rms error to ca. 25. Earlier it was applied to several organic molecules with biological and pharmacological applications, with errors lower than 3% in the majority of the cases [9]. For the ring modes of these molecules specific scale factors were obtained [64] from benzene. For uracil derivatives, Table 22 outlines the scale factors determined in the uracil molecule [27]. The absolute errors calculated with AM1 and SAM1 are similar to those obtained in benzene.

Table 22
Calculated scale factors, $\omega^{\text{cal}}/\nu^{\text{exp.}}$, in the uracil molecule

No.	AM1	SAM1	HF	BLYP	B3P86	B3LYP
2	1.2252	1.2091	1.0335	1.1212	1.0819	1.0882
3	1.0182	0.9560	0.9178	1.0625	1.0156	1.0156
4	1.0734	1.0734	0.9207	1.0395	0.9950	0.9975
5	0.9922	0.9481	0.9127	1.0220	0.9865	0.9865
6	0.9693	0.9537	0.9039	1.0328	0.9871	0.9908
7	0.9270	0.9286	0.9179	1.0429	0.9982	1.0018
8	1.1720	1.0322	0.9269	1.0037	0.9545	0.9680
9	1.0963	0.9720	0.9041	0.9910	0.9524	0.9607
10	1.0482	1.0947	0.8929	1.0228	0.9795	0.9835
11	1.0543	1.0955	0.8782	1.0692	0.9960	1.0066
12	0.8806	0.8777	0.9433	1.0553	1.0013	1.0129
13	0.9134	1.0101	0.8862	1.0256	0.9853	0.9865
14	0.8881	0.8981	0.9041	1.0337	0.9764	0.9865
15	1.0189	1.0611	0.8757	1.0531	1.0010	1.0021
16	0.9099	0.9041	0.9201	1.0366	0.9960	1.0000
17	0.9101	0.9363	0.9132	1.0229	0.9772	0.9835
18	0.9135	0.9630	0.8974	1.0362	0.9686	0.9783
19	0.8589	0.9310	0.8812	0.9950	0.9573	0.9643
20	0.9391	0.9805	0.8863	1.0249	0.9769	0.9812
21	0.9240	0.9429	0.8925	1.0335	0.9788	0.9858
22	0.9144	0.9085	0.8992	1.0189	0.9804	0.9845
23	0.8985	0.8980	0.8871	1.0111	0.9612	0.9701
24	0.9071	0.9026	0.8885	1.0130	0.9630	0.9710
25	0.8538	0.8865	0.8727	1.0104	0.9514	0.9629
26	0.8811	0.9232	0.8728	0.9949	0.9400	0.9518
27	0.9809	1.0707	0.9063	0.9812	0.9511	0.9550
28	0.9726	1.0540	0.9110	0.9836	0.9521	0.9571
29	0.9968	0.9988	0.8895	0.9792	0.9432	0.9492
30	1.0040	1.0052	0.8929	0.9822	0.9462	0.9524

Table 23

Scaled wavenumbers obtained using specific scale factors for each mode, and experimental ones in 2-TU and 5-BrU

No.	2-TU						5-BrU				
	HF	BLYP	B3P86	B3LYP	Exp. ^a	Exp. ^b	HF	BLYP	B3P86	B3LYP	Exp ^c
1							120	123	122	121	
2	184	183	183	182							
3	270	274	275	274	269(2)	271(3)	401	399	403	401	390
4							395	388	391	390	
5	530	528	531	530	530(2)	531(4)					
6	488	491	488	487	491(2)	492(4)	531	530	531	531	532
7							597	599	599	599	594
8	622	598	606	592	604(5)	635(3)	548	548	548	548	548
9	705	686	690	682	694(11)	714(5)	656	651	652	653	656
10	739	727	738	730	727(1)	744(5)					
12	724	732	734	720	710(1)	717(6)	792	784	785		760
14	885	897	912	890	907(1)	906(1)	960	958	958	958	962
15	972	973	974	973			941	924	928	930	906
16	1001	1002	1010	999	986(2)	994(4)					
17	1061	1070	1075	1060	1060(1)	1062(1)	1047	1022	1039	1030	1055
18	1180	1195	1195	1174	1191(24)	1197(32)	1126	1139	1150	1144	
19	1189	1193	1204	1185	1223(5)	1225(10)	1170	1138	1159	1153	1192
20	1362	1368	1363	1357	1363(1)	1372(6)	1313	1331	1328	1328	1327
21	1377	1392	1398	1377	1376(6)	1396(13)	1392	1395	1370	1376	1397
22	1435	1431	1451	1431	1430(2)	1432(7)	1391	1358	1397	1389	1400
23	1536	1528	1541	1515	1534(100)	1541(100)	1456	1445	1449	1448	1463
24	1640	1632	1646	1619	1634(5)	1635(5)	1640	1626	1632	1630	1635
25	1753	1749	1768	1728	1738(87)	1732(49)	1746	1740	1742	1741	1729
26							1760	1758	1758	1758	1761
27	3081	3081	3092	3066			3090	3095	3089	3090	3058 ^d
28	3127	3131	3142	3109							
29	3427	3427	3445	3404	3415(13)	3399(41)	3432	3434	3432	3432	3413
30	3473	3469	3490	3447	3457(24)	3439(58)	3479	3482	3481	3480	3459

^a In Ar matrix, from Ref. [34].^b In nitrogen matrix, from Ref. [34].^c In argon matrix, from Ref. [35].^d From Ref. [67].

The majority of the published works with ab initio methods use a single overall correction value for the wavenumbers, with no consideration for the different modes. Sometimes a simplification is used with only two or three scale factors for the modes, e.g. 0.9 for stretches and bends and 1.0 for torsion [65]. However, a better accuracy is obtained if a specific scale factor is used for each mode and level of calculation, although this requires a slightly more computational effort. The only scale factors reported with this procedure, to our knowledge, are for the tertiary amines [29], and for the toluene molecule [66]. However, the

scale factors reported for toluene are not as detailed as the calculations carried out by us on the benzene molecule [64], and the present work on the uracil molecule.

Table 23 shows the scaled wavenumbers in 2-TU and 5-BrU using the specific scale factors in Table 22. Table 23 also gives the experimental IR wavenumbers used in 2-TU and reported in argon and nitrogen matrices [34], and the experimental values for 5-BrU in Ar matrix [35]. The relative intensity estimated for these bands are given in parentheses. Table 24 shows the absolute errors obtained with this procedure. It is noted that the

DFT methods at 6-31G** level, show a more reliable prediction for the calculated wavenumbers than with the more expensive HF and MP2 methods.

An overall conclusion is that B3-based DFT procedures provide an extremely cost-effective means of determining harmonic vibrational wavenumbers. They show fewer cases of poorer quality than do the HF- and MP2-based procedures.

7. Resume and conclusions

The accuracy of several quantum chemical methods in calculating the wavenumber of the uracil normal modes was determined. To improve the calculated wavenumbers, two procedures can be used. Although the procedure for scaling the

force constants can lead to similar or slightly lower errors than to scaling the wavenumbers directly, we recommend the use of the latter one, mainly because of its simplicity. Thus, by following the scaling of the wavenumbers, three procedures were proposed. The scaling equations procedure gives rise to a slightly greater improvement in the predicted wavenumbers, than when a single overall scale factor is used. A list with scaling equations and specific scale factors for each mode was shown to be used in uracil derivatives.

For the computed wavenumbers of the semiempirical methods the use of a single overall scale factor or a scaling equation was not recommended; instead specific scale factors for each mode should be used.

The procedure selected for scaling depends on the size of the organic molecule and the accuracy

Table 24

Absolute errors obtained in the scaled wavenumbers of 2TU and 5-BrU using specific scale factors

No.	2-TU				5-BrU			
	HF	BLYP	B3P86	B3LYP	HF	BLYP	B3P86	B3LYP
3	1	5	6	5	11	9	13	11
5	0	-2	1	0				
6	-3	0	-3	-4	-1	-2	-1	-1
7					3	5	5	5
8	18	-6	2	-12	0	0	0	0
9	11	-8	-4	-12	0	-5	-4	-3
10	29	17	28	20				
12	-3	5	7	-7				
14	-22	-10	4	-17	-2	-4	-4	-4
15					34	19	22	24
16	15	16	24	13				
17	1	10	15	0	-1	-26	-9	-18
18	-11	4	4	-17	-28	-15	-4	-10
19	-34	-30	-19	-37	-19	-50	-30	-36
20	-1	5	0	-6	-13	4	1	1
21	1	16	22	1	15	18	7	-1
22	5	0	21	1	1	-32	7	-1
23	2	-6	7	-19	-2	-13	-9	-10
24	5	-2	12	-15	5	-10	-3	-5
25	15	11	30	-10	17	11	13	12
26					-1	-3	-3	-3
27	12	13	24	-2	32	37	31	32
29	11	12	30	-11	7	9	7	7
30	16	12	33	-10	8	11	10	9
rms	14	12	17	13	15	19	13	14

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

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

With molecules larger than 20 atoms, semiempirical methods, and HF and DFT methods with small basis set, can be used for calculating the wavenumbers. However, the cost-effective ratio with HF and DFT methods is very high versus semiempirical methods, and therefore not recommended to use. In contrast, the AM1 and SAM1 semiempirical methods, when a specific scale factor for each mode is used, give good predicted wavenumbers, with error lower than 5%. There was no confirmed advantage with the relatively new SAM1 method over the AM1 method.

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