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Quadratic scaling functions for obtaining Normal vibrational wavenumbers from the B3LYP calculation

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Abstract

The normal vibrations were calculated for 256 molecules, whose 3803 normal vibrations were reasonably assigned, with the Gaussian03 program based on the B3LYP method using the basis sets of 6-311++G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-31G(d,p) and 6-31G(d). Detailed analysis of the plots of the assigned vibrational wavenumbers against the calculated wavenumbers indicates that the relation between the calculated and observed vibrational wavenumbers is well expressed by a quadratic scaling function. The agreement between the observed and scaled wavenumbers by the proposed quadratic scaling function is satisfactory well.

Keywords: *Normal vibrations, ab initio MO, B3LYP calculation, Scaling of wavenumbers*

1. Introduction

Pulay and Meyer[1] expressed in the early 1970's that ab initio molecular orbital calculation has become a most useful procedure for the calculation of the normal vibrations of molecules through optimization of the molecular geometries and explicit computation of the valence force fields. The reliability of the calculated vibrational wavenumbers has been remarkably improved with highly enhanced calculational procedures[2] as well as rapid progress in performance of computer. Application of the density functional theory (DFT) to the calculation considerably improved the accuracy of the molecular force fields[3-7].

The calculated vibrational wavenumbers are generally higher by about 10% than the corresponding experimentally determined wavenumbers. However, the overestimation of the calculated wavenumbers is relatively uniform for over all calculated molecules and thus the scaling of the calculated wavenumbers could be made successfully. Systematic empirical scaling for the force constants derived from ab initio calculations was proposed by Botschwina[8,9], Blom et al.[10,11], Fogarasi et al.[12], Török et al.[13], Fogarasi and Pulay[14] and Blom et al.[15,16]. Based on their pioneering works, Pulay et al.[17] determined the optimum scale factors for the force constants through comparing the vibrational wavenumbers calculated with the HF method to the experimental data and obtained the reliable molecular force fields. Rauhut and Puley[4] derived the scale factors in the same way and found almost linear diagonal relation between the scaled and observed vibrational wavenumbers. The similar works were made by Hirata et al.[18], Panchenko et al.[19] and El-Azhary and Suter[5]. Baker et al.[20] calculated the normal vibrations for 30 molecules and determined the scale factors for individual force constants, and calculated the normal vibrations of the other set of 30 molecules using these scaled force constants. The vibrational wavenumbers calculated by this scaling procedure gave the average percentage error of less than 1% for the observed values.

On the other hand, Pople et al.[21] scaled directly the vibrational wavenumbers calculated with the HF and MP2 methods so that the scaled wavenumbers agreed well with the observed values. Scott and Radom[6] calculated 1066 normal vibrations of 122 molecules with the HF, MP2, QCISD and DFT methods and determined the scale factors for the wavenumber correction for each method of calculations. Scott and Radom also evaluated the root-mean-square (rms) errors of the scaled wavenumbers for each calculational method and found that the B3LYP and B3PW91 methods gave the smallest rms errors. The similar work was made by Wong[7].

Kudoh et al.[22] calculated the normal vibrations for pyridine and its derivatives with B3LYP/6-31++G(d,p) method and determined the usual scale factor. They also proposed a new type of scale factor expressed by a quadratic equation for wavenumber scaling, where the equation gives the curve passing through the origin of the coordinates. Their new scaling procedure showed that the agreement between the scaled and observed wavenumbers is much better than that given by the usual scaling procedures.

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Yoshida et al.[23] calculated the normal vibrations for 205 molecules with the B3LYP/6-311+G(d,p) method and proposed similar quadratic scale factor. In order to confirm the reliability of this scaling procedure, Yoshida et al.[24] also calculated the normal vibrations for additional 164 molecules and scaled the calculated wavenumbers using the proposed quadratic scale factor. The agreement between the scaled and observed wavenumbers was excellent.

Halls et al.[25] calculated 900 normal vibrations for 111 molecules with the HF and various DFT methods using SadlejpVTZ basis set and proposed two types of the scale factors. One is the usual uniform scale factor good for the over all wavenumber regions and the other is the dual scale factors good for the wavenumber regions below and above 1800 cm^{-1}. The dual scale factors clearly indicate that the relation between the calculated and observed wavenumbers is not linear. The numerical values of the scale factors and the quadratic scale factors determined by the above workers for the vibrational wavenumbers calculated with the B3LYP method using the basis sets of 6-31G(d) and 6-31++G(d,p) are listed in Table 1.

This paper is intended to propose a new type of scale factors and scaling functions for the wavenumber correction. Reasonably assigned normal vibrations of 256 molecules were calculated with the B3LYP method using the typical basis sets. The relation between the calculated and observed wavenumbers was investigated in detail and an optimum scaling function for wavenumbers was derived. The reasonability of the proposed scaling procedure was discussed through comparison with those proposed by previous workers.

2. Calculation

The normal vibrations were calculated with the Gaussian 03 program based on the DFT method using the basis sets of 6-311++G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-31G(d,p) and 6-31G(d). The calculations were carried out for 256 molecules whose 3803 normal vibrations were reasonably assigned. The assigned wavenumbers, modes and symmetry species for these normal vibrations were taken from the works made by Shimada et.al.[26-30] and the tables given by Herzberg[31] and compiled by Shimanouchi[32-35]. In these vibrations, 338 vibrations of 20 bromo-substituted molecules were unable to calculate using the basis sets of 6-31++G(d, p), 6-31G(d,p) and 6-31G(d). These vibrations were calculated using the 6-311++G(d,p) and 6-311G(d,p) basis sets. Molecules having intra- and intermolecular hydrogen bonds such as salicylic aldehyde and formic acid, molecules whose fundamental vibrations have high anharmonicity such as H_2 and unstable molecular species such as ions and radicals were excluded for the calculations.

The calculations of the normal vibrations were performed at the B3LYP level because the vibrational wavenumbers calculated with the B3LYP method agree well with the observed wavenumbers[3-7,20,22-25], and also the B3LYP methods were widely used. Special care was taken to the input molecular geometry for calculation. The input geometry was so chosen that the molecule gives the lowest total energy. The symmetry of the molecular geometry was ignored sometimes even if the molecule is expected to have, because the symmetry is kept unchanged throughout the calculation. For example, the methyl group of 2-methylpyrimidine molecule is considered to be π-hyperconjugated to the diazine ring so that the molecular geometry

Table 1
Scale factors and quadratic scale factors for the vibrational wavenumbers calculated with B3LYP method and the rms errors for the scaled wavenumbers

Basis set	Scale factor	rms Error
6-31G(d)	0.9614 [a]	34
6-31G(d)	0.9613 [b]	34
6-31++G(d, p)	0.9626 [c]	21†
Basis set	Quadratic scale factor*	
6-31++G(d, p)	$-0.0000104\ \nu_{calc}^2+0.9894\ \nu_{calc}$ [c]	13†

* $\nu_{scal}=a\ \nu_{calc}^2+b\ \nu_{calc}$, where ν_{scal} and ν_{calc} are reffered to as the scaled and calculated wavenumbers, respectively.
[a] After Ref. 6), [b] After Ref. 7), [c] After Ref. 22).
† The values of the rms errors were determined using the scaled vibrational wavenumbers calculated for pyridine, 2-picoline, 4-picoline and their corresponding Dewar isomers by Kudoh et al.[22]. Small rms errors may be due to the fact that the calculations were made for a series of the pyridine derivatives.

belongs to the point group C_S. However, the calculation shows that the geometry belonging to the C_S symmetry gives higher energy than the energy for the geometry belonging to the C_1 symmetry. This fact indicates that the methyl group is twisted slightly about the C-C-C pivot axis and the symmetry plane vanishes in the optimized molecular structure.

The vibrational modes were determined with the MolStudio R4 program. Assignments of the calculated vibrational wavenumbers to the normal vibrations were made according to the vibrational wavenumbers, modes and symmetry species referring to the previous works.

3. Results and discussion

The wavenumbers of the experimentally assigned normal vibrations were plotted against the wavenumbers calculated with the B3LYP method using the basis sets of 6-311++G(d,p), 6-311G(d,p), 6-31++G(d,p) and 6-31G(d,p) and the results were shown in Fig. 1. The calculation made with the 6-31G(d) basis set gave almost the same plot as that obtained by the 6-31G(d,p) calculation. The plots shown in Fig. 1 appear to be almost straight lines, although some points are scattered from the plotting lines. The vibrational modes corresponding to these points indicate that the scattering is to be caused by the vibration-vibration interaction, which is not taken into account in the harmonic approximation.

In order to clarify the problem that the plots shown in Fig. 1 are straight lines or curves, the values of $\Delta\nu_{obs}/\Delta\nu_{calc}$ calculated with the B3LYP/6-311++G(d,p) method were plotted against the calculated wavenumbers, where $\Delta\nu_{obs}$ is the difference of the observed wavenumbers read at intervals of 125cm^{-1} in the plot and $\Delta\nu_{calc}$ is that of the calculated wavenumbers. The result was shown in Fig. 2 together with the regression line calculated with the least-squares fitting method for the plot. If the relation between the calculated and observed wavenumbers is linear, the values of $\Delta\nu_{obs}/\Delta\nu_{calc}$ are to be constant over all wavenumber regions and the regression line is to be a horizontal line. The slanting regression line indicates that the plot is not expressed by the straight line but curve. The calculation made with the other basis sets gave the same results as that obtained by the 6-311++G(d,p) calculation.

Linear, quadratic, cubic, quartic, quintic and sextic regression equations expressing the plotted curves shown in Fig. 1 were derived by the least-squares fitting method. These equations expressing the relation between the calculated and observed vibrational wavemunbers could be reasonably used for the scaling of the calculated vibrational wavenumbers and thus the equations will be called as scaling functions here after. It should be noted that the curves expressed by these equations do not pass through the origin of the coordinates. The values of the usual scale factors were also calculated for the plotted curves.

The calculated vibrational wavenumbers of the 3465 (3803 for the calculations made with the 6-311++G(d,p) and 6-311G(d,p) basis sets) normal vibrations were scaled using the derived scaling functions and scale factors. The rms errors of the scaled wavenumbers for all of the normal vibrations, which are the measure of the reasonability for the proposed scaling procedures, were calculated according to the method given by Scott and Radom[6]. The relations among the values of the rms errors, the basis sets used for the calculation and the degrees of the scaling functions were represented in Fig. 3. The figure shows that the rms errors for the wavenumbers scaled by the scaling functions are much less than the errors for the wavenumbers scaled by the

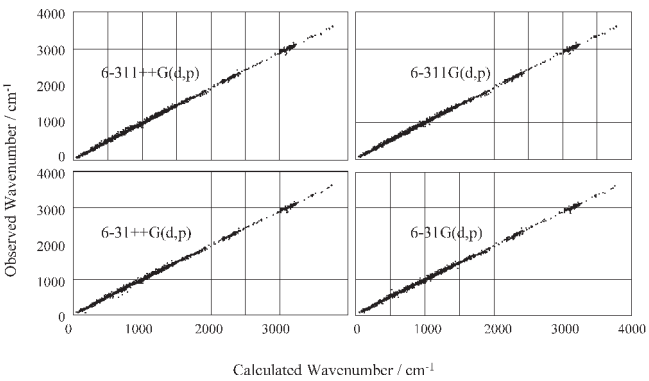

Fig. 1 Plots of the observed vibrational wavenumbers against the wavenumbers calculated with the B3LYP methods.

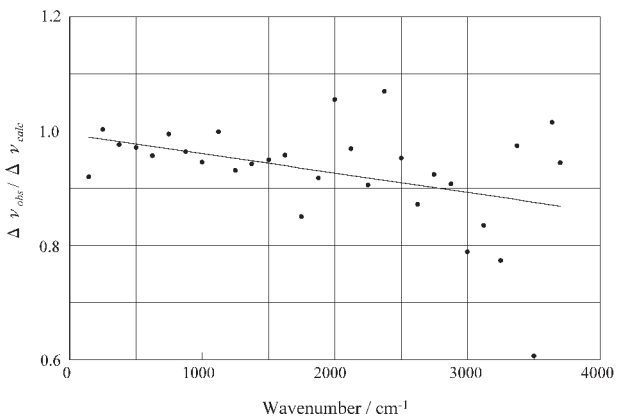

Fig. 2 Plots of values of $\Delta\nu_{obs}/\Delta\nu_{calc}$ against the vibrational wavenumbers calculated with the B3LYP/6-311++G(d,p) methods.

scale factors. The rms errors decrease very gradually with increase of the degrees of the scaling functions, and the values are kept almost constant for higher than second degree of the functions. This fact suggested that the scaling functions higher than second degree are unnecessary and the quadratic scaling function is the most favorable function for the scaling of the calculated wavenumbers. The determined values and coefficients of the scale factors, linear and quadratic scaling functions are listed in Table 2 together with the rms errors, whose values were rounded to the integers, for the overall scaled wavenumbers. It should be noticed that the rms errors for the vibrational wavenumbers scaled by linear and quadratic scaling functions are much small compared with the rms values given by Scott and Radom[6].

Scott and Radom[6] gave 0.9614 for the value of the scale factor for the 6-31G(d) calculation whereas we gave 0.9629, and Kudoh et al.[22] gave the value of 0.9626 for the 6-31++G(d,p) calculation whereas we gave 0.9688. Kudoh et al.[22] also gave the quadratic scale factor:

$$\nu_{scal} = -0.0000104\nu_{calc}^2 + 0.9874\nu_{calc}, \quad (1)$$

whereas we proposed the quadratic scaling function:

$$\nu_{scal} = -0.0000086\nu_{calc}^2 + 0.9786\nu_{calc} + 13.84, \quad (2)$$

for the 6-31++G(d,p) calculation. Here ν_{scal} and ν_{calc} are the scaled and calculated vibrational wavenumbers, respectively. In order to compare the validity of the scaling procedures proposed in this work with those proposed by Scott and Radom[6] and Kudoh et. al.[22], the wavenumbers calculated for the 3465 normal vibrations of 236 molecules were scaled according to their scaling procedures. The overall rms errors for these scaled wavenumbers were evaluated and the results were given in Table 3 together with the errors for the corresponding scaled wavenumbers given in Table 2. It should be noted that the value of the rms error of 28 shown in Table 3 for the scaled wavenumbers using the scale factor proposed by Scott and Radom[6] is smaller than the corresponding value of 34 shown in Table 1. This fact suggests that the vibrational assignments made for 3465 vibrations are quite reasonable. The table also shows that the values of the rms errors obtained by the scaling procedures proposed by Scott and Radom[6] and Kudoh et al.[22] are nearly equal to the values we proposed.

The main difference between the quadratic scale factor (1) proposed by Kudoh et al.[22] and the scaling function (2) proposed in this work is the fact that the curve given by equation (1) passes through the origin of the coordinates but the curve given by the function (2) does not. Therefore, it should be interested to compare the values of rms errors for the two scaling procedures in the low wavenumber region.

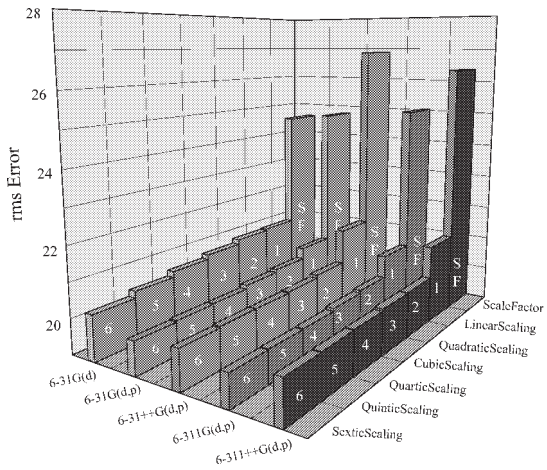

Fig. 3 The rms errors of the vibrational wavenumbers scaled by scale factor and scaling functions.
The vibrational wavenumbers were calculated with the B3LYP methods.

The vibrational wavenumber region of $0cm^{-1} \sim 4000cm^{-1}$ was divided into four regions and the rms errors for each regions were calculated and the results are listed in Table 4. The table shows that the agreement between the scaled and observed vibrational wavenumbers made in this work is better than that gave by Kudoh et al.[22] in the lower wavenumber region. These facts indicate that the quadratic scaling functions given in Table 2 are to be reasonably used for the scaling of the vibrational wavenumbers calculated with the B3LYP method using the basis sets of 6-311++G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-31G(d,p) and 6-31G(d). Table 2 and Fig. 3 show that the linear scaling function may be also usable for the scaling of the vibraional wavenumbers.

In the course of calculations it was found that the Gaussian 03 program could not recognize the symmetry species of the degenerate vibrations of molecules belonging to the point groups C_{3v}, D_3, D_{3h}, D_{3d} and D_{5h}, such as chloroform, triaminobenzene, trihalobenzenes, cyclohexane, iodine heptafluoride, respectively. The wavenumber of degenerate vibration splits into two different wavenumbers although the difference of wavenumbers is small.

4. Conclusion

The normal vibrations were calculated for 256 molecules, whose 3803 normal vibrations were reasonably assigned, with the Gaussian 03 program based on the B3LYP method using the basis sets of 6-311++G(d,p), 6-311G(d,p), 6-31++G(d,p), 6-31G(d,p) and 6-31G(d). The plots of the as-

Table 2
Scale factors and linear and quadratic scaling functions for wavenumbers calculated with B3LYP method and the rms errors for the scaled wavenumbers

Basis set	Scale factor	rms Error
6-311++G(d, p)	0.9724	26
6-311G(d, p)	0.9713	25
6-31++G(d, p)	0.9688	27
6-31G(d, p)	0.9656	25
6-31G(d)	0.9629	25
	Linear scaling function*	
6-311++G(d, p)	$0.9552\ \nu_{calc} + 28.10$	21
6-311G(d, p)	$0.9557\ \nu_{calc} + 25.33$	21
6-31++G(d, p)	$0.9506\ \nu_{calc} + 29.83$	21
6-31G(d, p)	$0.9501\ \nu_{calc} + 25.40$	21
6-31G(d)	$0.9486\ \nu_{calc} + 23.57$	21
	Quadratic scaling function**	
6-311++G(d, p)	$-0.0000081\ \nu_{calc}^2 + 0.9813\ \nu_{calc} + 13.50$	20
6-311G(d, p)	$-0.0000070\ \nu_{calc}^2 + 0.9783\ \nu_{calc} + 12.68$	20
6-31++G(d, p)	$-0.0000086\ \nu_{calc}^2 + 0.9786\ \nu_{calc} + 13.83$	20
6-31G(d, p)	$-0.0000047\ \nu_{calc}^2 + 0.9655\ \nu_{calc} + 16.60$	20
6-31G(d)	$-0.0000013\ \nu_{calc}^2 + 0.9529\ \nu_{calc} + 21.08$	21

* $\nu_{scal} = b\ \nu_{calc} + c$
** $\nu_{scal} = a\ \nu_{calc}^2 + b\ \nu_{calc} + c$

Table 3
Comparison between the rms errors for wavenumbers scaled by this and previous workers for the 3465 vibrational wavenumbers of the 236 molecules

Scaling	Basis set	6-31++G(d,p)		6-31G(d)	
	Workers	KTN[a]	This work	SR[b]	This work
Scale factor		28[a]	27	25[b]	25
Quadratic scaling function		21[a]	20	—	21

[a] After Ref. 22), [b] After Ref. 6)

Table 4
The rms errors of scaled wavenumbers by quadratic function and quadratic scaling

Wavenumber region*	rms Error	
	This work	KTN[a]
0−500	18	20
500−1500	20	21
1500−2500	21	21
2500−4000	24	24

* in cm^{-1} units
[a] After Ref. 22)

signed vibrational wavenumbers against the calculated wavenumbers appear to be almost straight line. Careful observation of the plots indicates that the "line" bends slightly downward with increase of vibrational wavenumbers, and does not pass through the origin of the coordinates. Through detailed analysis of the plots it was concluded that the relation between the calculated and observed vibrational wavenumbers could be well expressed by a quadratic equation containing constant term. These quadratic equations, which refer to as quadratic scaling functions, were listed in Table 2. It was shown that the quadratic scaling functions proposed in this work gave satisfactory well agreement between the scaled and observed vibrational wavenumbers.

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