A New Approach to Vibrational Analysis of Large Molecules by Density Functional Theory: Wavenumber-Linear Scaling Method†

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Normal vibration calculations were performed on 164 basic organic and inorganic compounds by the density functional method of B3LYP/6-311+G** using the wavenumber-linear scaling (WLS) method, in which essentially only one parameter is involved for the whole wavenumber region. The average deviation of the WLS-scaled calculated wavenumbers from the observed wavenumbers for a total of 1223 normal modes was 3.4%. The present results and the previous results on 205 compounds have shown the high performance of the WLS method in vibrational analysis of a variety of compounds. The effect of anharmonicity on the observed wavenumbers was examined on the basis of the calculated wavenumbers for 224 diatomic molecules and ions in comparison with their experimental harmonic wavenumbers. The results indicate that the larger positive deviations of the unscaled calculated wavenumbers from the observed values at higher wavenumbers are attributed almost exclusively to the neglect of anharmonicity in the calculated wavenumbers. To generalize and simplify the WLS method for more convenient use, the wavenumber-linear scale factors were derived from 17 well-defined wavenumbers of liquid indene at different calculation levels. The application of the derived scale factors to vibrational analysis of *all-trans*-1,3,5,7,9-decapentaene yielded results in close agreement with the experimental data. This WLS indene calibration method is a convenient technique to obtain vibrational wavenumbers of large molecules with high accuracy.

Introduction

Analysis of infrared and Raman spectra of polyatomic molecules has played an important role for a long time in determining molecular structures and intramolecular and intermolecular forces. A great number of vibrational analyses were performed using empirical molecular force fields until the 1970s and have contributed significantly to the development of vibrational spectroscopy.[1] A huge number of empirical force constants have been obtained through these vibrational analyses, and the accumulated force constants have been compiled as a database.[2,3] Although the vibrational analyses using empirical force fields have been successful in many cases,[4] a number of substantial difficulties have been often encountered.[5−7]

The difficulties with the empirical force fields were overcome by the introduction of ab initio quantum mechanical method of calculations.[8,9] The theoretical development of the gradient techniques for obtaining the derivatives of the molecular energies[10,11] and the rapid progress in computer facilities have enabled us to perform a priori quantum mechanical calculations of force fields for relatively large molecules. The wavenumbers[12] calculated ab initio by the Hartree−Fock (HF) method were, however, consistently higher than the experimental wavenumbers of fundamentals by about 10% because of the neglect of electron correlation and anharmonicity effects. To solve these problems, the scaled quantum mechanical (SQM) method was proposed by Pulay et al.[13,14] In this method, the force constants of similar chemical fragments share the same scale factor. The values of scale factors are optimized by minimizing the weighted mean-square deviations of the calculated wavenumbers from the observed wavenumbers. Although the SQM method has become one of the most useful techniques in vibrational analysis of medium-sized molecules in the 1980s, several problems were raised in accurate interpretation of experimental spectra. For example, the off-diagonal force constants for polyenes were ill-determined by the HF-based SQM method.[15] To obtain more accurate predictions of vibrational spectra, more sophisticated methods including electron correlation, such as the second-order Møller−Plesset perturbation theory (MP2), have been put forward as post-HF methods. The MP2-based SQM method was actually applied to polyenes, resulting in more satisfactory results than with the HF-based SQM method.[16] The post-HF methods are, however, applicable only to relatively small molecules, as these methods require more CPU time and more memory resources than the HF method.

The evolution of density functional theory (DFT),[17] which includes electron correlation in an alternative way, has afforded opportunities of performing vibrational analysis of moderately large molecules as a cost-effective procedure in the 1990s.[18] Systematic comparison of the results from various DFT theories with the results of experiments and the molecular orbital theories has been conducted by Rauhut and Pulay,[19] Scott and Radom,[20] Baker et al.,[21] and Yoshida et al.[22] The comparison in these studies has shown that the methods using Becke's three-parameter hybrid functional (B3)[23] with correlation functionals such as the one proposed by Lee, Yang, and Parr (LYP)[24] are the most promising in providing correct vibrational wavenumbers. Although all of these studies have shown the excellence of the B3 functional, the scaling procedures for the calculated wavenumbers were different in these studies. Scott and Radom[20] used the uniform scaling method, while Pulay et al.[19,21] used the SQM method. Yoshida et al.,[22] on the other hand, adopted

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TABLE 1: The 164 Compounds Used in the Calculation[a]

KrF_2	$^{14}NO_2$	$^{15}NO_2$	$^{16}O_3$	$^{18}O_3$
$H_2{}^{18}O$	$S^{18}O_2$	SCl_2	$GeCl_2$	$^{16}O^{14}NF$
$^{16}O^{15}NF$	$^{18}O^{14}NF$	$^{18}O^{15}NF$	$^{16}O^{14}NCl$	$^{16}O^{15}NCl$
$^{18}O^{14}NCl$	$^{18}O^{15}NCl$	$^{16}O^{14}NBr$	$^{16}O^{15}NBr$	$^{18}O^{15}NBr$
HOF	HOCl	DOCl	NSF	NSCl
$^{10}BF_3$	$^{11}BF_3$	SO_3	NT_3	$^{15}NF_3$
$AlCl_3$	AsF_3	*trans*-N_2F_2	$F^{14}NO_2$	$F^{15}NO_2$
$Cl^{14}NO_2$	$Cl^{15}NO_2$	ClF_3	BrF_3	H_2O_2
H_2S_2	F_2S_2	HN_3	DN_3	NF_2H
$NClF_2$	NCl_2F	SOF_2	$SOCl_2$	$SOBr_2$
$TiCl_4$	$TiBr_4$	NSF_3	$SiHF_3$	$SiDF_3$
$SiHCl_3$	$SiDCl_3$	$SiHBr_3$	POF_3	$POCl_3$
$POBr_3$	PSF_3	$PSCl_3$	$^{35}ClO_3F$	$VOCl_3$
MnO_3F	GeH_3F	GeD_3F	GeH_3Cl	GeD_3Cl
GeH_3Br	GeD_3Br	$GeHCl_3$	$GeHBr_3$	SO_2F_2
SO_2Cl_2	SiH_2Cl_2	SiD_2Cl_2	SiH_2Br_2	SeO_2F_2
$H^{14}NO_3$	$D^{14}NO_3$	$H^{15}NO_3$	$D^{15}NO_3$	$FO^{14}NO_2$
$FO^{15}NO_2$	$ClO^{14}NO_2$	$ClO^{15}NO_2$	$POCl_2F$	$POBr_2F$
$PSClF_2$	$PSCl_2F$	PF_5	PCl_3F_2	PCl_5
VF_5	AsF_5	$SClF_5$	GeH_3GeH_3	GeD_3GeD_3
FCN	COF_2	$COCl_2$	$COBr_2$	SCF_2
$CSCl_2$	HNCO	DNCO	COClF	COBrCl
CSBrCl	CDF_3	$CClF_3$	$CBrF_3$	CCl_3F
CBr_3F	CCl_2F_2	CBr_2F_2	$CBrCl_2F$	CBr_2ClF
$^{10}BH_3CO$	$^{10}BD_3CO$	$^{11}BH_3CO$	$^{11}BD_3CO$	CH_3SiH_3
CH_3SiD_3	CH_3GeH_3	CD_3GeH_3	C_2N_2	C_2Cl_2
C_2Br_2	C_2BrCl	CF_3CN	*trans*-CHFCHF	*trans*-CHFCDF
trans-CDFCDF	$C_2H_2O_2$	C_2HDO_2	$C_2D_2O_2$	CH_3COF
CD_3COF	CH_3ZnCH_3	CD_3ZnCD_3	*trans*-CH_3NNCH_3	*trans*-CD_3NNCD_3
C_3O_2	C_3S_2	ClCCCN	BrCCCN	CH_2CCHCl
CH_2CCHBr	CF_3CCH	CF_3CCD	CF_3CCCl	CF_3CCBr
$CHCCH_2F$	$CHCCH_2Cl$	$CHCCH_2Br$	ClCCCCH	BrCCCCH
$C_4H_8O_2$	$(HCC)_2CO$	NCCCCCCN	$Cr(^{12}C^{16}O)_6$	

[a] Taken from ref 33.

TABLE 2: The 224 Diatomic Molecules and Ions Used in the Calculation[a]

Al_2	AlBr	AlCl	AlF	AlH	AlD	AlO	AlS
AlSe	As_2	AsCl	AsF	AsN	AsO	AsO^+	AsP
AsS	AsS^+	AsSe	B_2	BBr	BCl	BF	BH
BD	BN	BO	BS	BeBr	BeCl	BeF	BeH
BeD	BeT	BeH^+	BeD^+	BeO	BeS	Br_2	$Br_2{}^+$
BrCl	BrF	BrO	C_2	$C_2{}^-$	CCl	CCl^+	CF
CH	CD	CH^+	CN	CN^+	CO	CO^+	CP
CS	CSe	Ca_2	CaBr	CaCl	CaF	CaH	CaO
CaS	Cl_2	$Cl_2{}^+$	ClF	ClO	CoD	CrH	CrO
CrS	Cu_2	CuBr	CuCl	CuF	CuGa	CuH	CuD
CuO	CuS	CuSe	F_2	$F_2{}^+$	FO	FeCl	GaBr
GaCl	GaF	GaH	GaO	GeBr	GeCl	GeF	GeH
GeD	GeO	GeS	GeSe	H_2	HD	HT	D_2
DT	T_2	$H_2{}^+$	$T_2{}^+$	HBr	DBr	TBr	HBr^+
DBr^+	HCl	DCl	TCl	HCl^+	DCl^+	HF	DF
TF	HF^+	DF^+	K_2	KBr	KCl	KF	KH
KD	Li_2	LiBr	LiCl	LiF	LiH	LiD	LiNa
LiO	Mg_2	MgBr	MgCl	MgF	MgH	MgD	MgH^+
MgD^+	MgO	MgS	MnBr	MnF	MnH	MnD	MnO
N_2	$N_2{}^+$	NBr	NCl	NF	NH	ND	NO
NO^+	NO^-	NS	NS^+	NSe	Na_2	NaBr	NaCl
NaF	NaH	NaK	NiH	NiD	O_2	$O_2{}^+$	$O_2{}^-$
OH	OD	OH^+	OD^+	P_2	$P_2{}^+$	PF	PF^+
PH	PD	PN	PO	PO^+	PS	PS^+	S_2
$S_2{}^-$	SH	SD	SO	ScCl	ScF	ScS	Se_2
$Se_2{}^-$	SeBr	SeO	SeS	SeS^-	Si_2	SiBr	$SiBr^+$
SiCl	SiF	SiH	SiD	SiH^+	SiN	SiO	SiS
SiSe	ZnBr	ZnCl	ZnF	ZnH	ZnD	ZnH^+	ZnD^+

[a] Taken from ref 34.

another approach called the wavenumber-linear scaling (WLS) method, which is based on the linear relationship between the scale factor and the vibrational wavenumbers.[25,26]

In our previous work,[22] we performed normal vibration calculations by the DFT method on 205 basic organic and inorganic compounds that contain elements from the fourth or lower periods of the periodic table. Through the systematic calculations, we obtained a single linear relationship between the scale factor and the calculated wavenumbers for a total of 1729 normal modes of the 205 compounds, for which the vibrational assignments had been established.[27] The aim of the present study is to confirm the performance of the WLS method[22] on additional 164 basic organic and inorganic compounds and to examine the effect of anharmonicity on the observed wavenumbers by performing systematic normal vibration calculations on 224 diatomic molecules and ions. We also propose in this work a simpler and thereby more practical WLS method, using the well-calibrated and well-assigned observed wavenumbers of liquid indene, and apply this method to a linear polyene, *all-trans*-1,3,5,7,9-decapentaene, whose force field has been argued about for a long time.[5−7,28−32]

Calculations

Compounds. As a continuation of the systematic normal vibration calculations,[22] we have carried out in this work the calculations on 164 basic organic and inorganic compounds including their isotopic species. These compounds, listed in Table 1, were taken from *Tables of Molecular Vibrational Frequencies, Consolidated Volume II*,[33] where the experimental wavenumbers of infrared and Raman bands for 212 basic compounds are critically evaluated and ranked according to their experimental accuracy with A (uncertainty 0−1 cm^{-1}, observed in the gas phase), B (1−3 cm^{-1}, gas phase), C (3−6 cm^{-1}, gas, solid, or liquid phase), D (6−15 cm^{-1}, gas, solid, or liquid phase), and E (15−30 cm^{-1}, estimated or calculated). We excluded 48 compounds that contain elements in the fifth or higher periods from the present analysis. The compounds used in the previous calculations[22] were taken from *Tables of Molecular Vibrational Frequencies, Consolidated Volume I*.[27] Since these 205 compounds were not explicitly shown in the previous paper,[22] they are given in Table 1S (Supporting Information).

To study the effect of anharmonicity on the observed wavenumbers and accordingly on the linear relationship between the scale factor and the wavenumbers, we have calculated the wavenumbers of 224 diatomic molecules and ions, for which the harmonic wavenumbers are known, taken from Herzberg's *Constants of Diatomic Molecules*.[34] Out of more than 900 diatomic species listed in the literature,[34] we excluded the species that contain elements from the fifth or higher periods or the rare gas elements and those for which the experimental harmonic wavenumbers and the anharmonicity constants are not given. The 224 diatomic molecules and ions used in the present analysis are listed in Table 2.

Method. Normal vibration calculations in this work were carried out by the B3LYP method of DFT using Becke's three-parameter hybrid functional combined with the Lee−Yang−Parr correlation functional. The basis set 6-311+G** was used for the calculations on the 164 basic polyatomic molecules and the 224 diatomic molecules and ions, and the basis sets 6-311+G** and 6-31G* were used for the calculations on indene and *all-trans*-1,3,5,7,9-decapentaene. The computations were performed with the GAUSSIAN 98 program.[35] The input data for the GAUSSIAN 98 program were prepared by using the graphical molecular modeling program MOLDA for Windows.[36]

Results and Discussion

Wavenumber-Linear Scaling (WLS) Method. In our previous work,[22] we have calculated the wavenumbers of normal

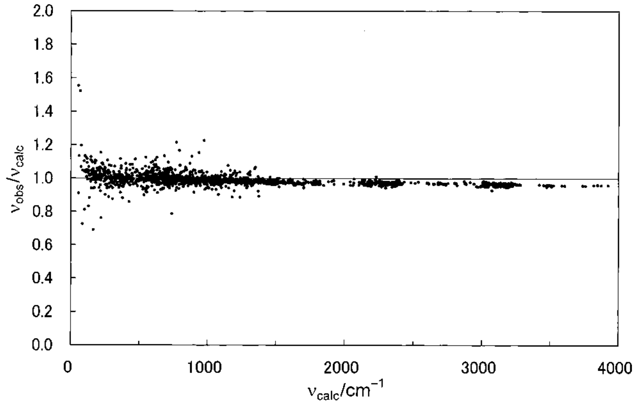

Figure 1. Ratios of the observed wavenumbers to the unscaled calculated wavenumbers, ν_{obs}/ν_{calc}, for 2157 normal modes of 205 compounds taken from ref 27, plotted against the unscaled calculated wavenumbers. The calculated wavenumbers are those by the B3LYP/6-311+G** method. Some of the band assignments have been corrected (see text).

modes for 205 organic and inorganic compounds[27] by the B3LYP/6-311+G** method and have correlated the unscaled calculated wavenumbers, ν_{calc}, with 1729 observed wavenumbers of fundamentals, ν_{obs}, with ranks A−C. The relationship obtained by a single least-squares fitting, after omitting 28 normal modes that gave deviations of ν_{obs}/ν_{calc} by more than 10%, is[22]

$$\nu_{obs}/\nu_{calc} = 1.0087(9) - 0.0000163(6)\nu_{calc} \qquad (1)$$

where ν_{obs} and ν_{calc} are given in cm^{-1}, and the errors, given in parentheses, apply to the last significant figure. The ratio ν_{obs}/ν_{calc} in eq 1 is denoted as the wavenumber scale factor to be applied to the B3LYP/6-311+G** calculation.

We found previously that the ratios ν_{obs}/ν_{calc} for several normal modes deviate greatly from the linear relationship given by eq 1.[22] Some of these deviations were reasonably ascribed to improper assignments of the observed bands in the literature.[27] After revising these assignments and the additional ones to be mentioned below, we have plotted in Figure 1 the ratios ν_{obs}/ν_{calc} for the 1729 normal modes with wavenumber-accuracy ranks A−C, plus the ratios for 428 normal modes with rank D. The revisions of the band assignments we have made on the basis of our calculations are described below.

The improper assignments of the bands for cyclobutane and methylamine have been discussed previously.[22] In addition to these, obvious misassignments were found for acetaldehyde and acetic acid. The experimental wavenumbers for the CH_3 (or CD_3) rocking mode (a″ species) of three isotopic species of acetaldehyde, CH_3CHO, CH_3CDO, and CD_3CDO, are listed as 867, 802, and 573 cm^{-1}, respectively, in the literature.[27] The calculations gave, however, considerably higher wavenumbers 1132, 1064, and 968 cm^{-1} (1121, 1055, and 961 cm^{-1} after scaling with eq 1) for these isotopic species. These vibrations have already been reassigned to the bands at 1107, 1043, and 948 cm^{-1}, respectively,[37] in agreement with the calculated wavenumbers. For acetic acid, the experimental wavenumbers for the CCO deformation mode (a′ species) of CH_3COOH and CH_3COOD are listed as 581 and 543 cm^{-1}, respectively.[27] The calculations gave much lower wavenumbers 424 and 417 cm^{-1} (425 and 418 cm^{-1} after scaling with eq 1) for these isotopic species. In a matrix-isolation infrared study,[38] new assignments of these vibrations have in fact been proposed to the bands at 428 and 418 cm^{-1}, respectively, in excellent agreement with the calculated results.

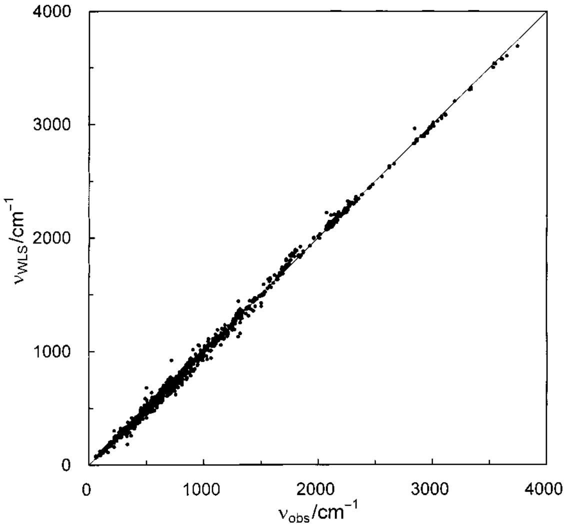

Figure 2. Correlation between the WLS-scaled calculated wavenumbers, ν_{WLS}, and the observed wavenumbers, ν_{obs}, for 1223 normal modes of 164 compounds taken from ref 33. The calculated wavenumbers are those by the B3LYP/6-311+G** method.

Performance of the WLS Method for Additional Compounds. To confirm the performance of the WLS method, we carried out normal vibration calculations on additional 164 basic organic and inorganic compounds available in *Tables of Molecular Vibrational Frequencies, Consolidated Volume II*.[33] The wavenumbers calculated by the B3LYP/6-311+G** method were scaled by the WLS method using eq 1. The calculated results and the observed data are given in Table 2S (Supporting Information).

The correlation between the WLS-scaled calculated wavenumbers, ν_{WLS}, and the observed wavenumbers, ν_{obs}, with ranks A−D of 1223 normal modes for the 164 compounds is shown in Figure 2. As seen in this figure, the WLS-scaled calculated wavenumbers agree excellently with the observed wavenumbers. The average deviation of ν_{WLS} from ν_{obs}, i.e., the average value of $|\nu_{WLS} - \nu_{obs}|/\nu_{obs}$ for all of the 1223 normal modes is 3.4%. The great majority of the normal modes, namely, 93% of the total, give deviations less than 10%, and 77% of the total give deviations less than 5%. The deviations larger than 15% are found for 24 normal modes of 18 compounds: ClF_3, F_2S_2, $^{35}ClO_3F$, SeO_2F_2, PCl_5, $SClF_5$, GeD_3GeD_3, $CSCl_2$, C_2Cl_2, CD_3ZnCD_3, *trans*-CH_3NNCH_3, *trans*-CD_3NNCD_3, C_3O_2, C_3S_2, ClCCCN, ClCCCCH, BrCCCCH, and NCCCCCCN. These compounds mostly contain a number of halogen atoms or have linear molecular structures. The large deviations of wavenumbers for halogen-containing compounds have been found in the previous calculations.[22] Theoretical development to solve this problem is necessary to obtain more reliable results on these compounds, although several attempts have already been made.[39] The present calculations have also revealed the difficulty of vibrational analysis of linear molecules. The large deviations of wavenumbers for these molecules are due most probably to the coupling between the bending vibration and the molecular rotation. Another remark we should make here is that, in our calculation on C_3O_2, we assumed a quasi-linear structure with C_{2v} symmetry[40] instead of a linear structure as described in the literature.[33]

The present results of normal vibration calculations on 164 compounds, together with the previous results,[22] have thus ensured the high performance of the WLS method in vibrational analysis of a variety of compounds. The important point is that, although the WLS method employs essentially only one

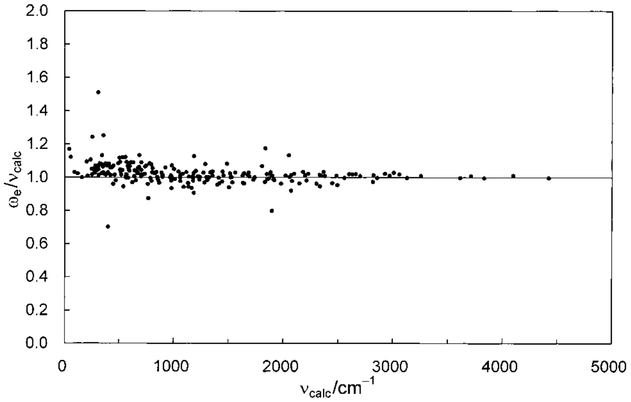

Figure 3. Ratios of the experimental harmonic wavenumbers to the unscaled calculated wavenumbers, ω_e/ν_{calc}, for 224 diatomic molecules and ions taken from ref 34, plotted against the unscaled calculated wavenumbers. The calculated wavenumbers are those by the B3LYP/6-311+G** method.

parameter to scale wavenumbers in the whole region, it reproduces the experimental wavenumbers excellently except those for peculiar types of compounds.

Effect of Anharmonicity. The effect of anharmonicity on the observed wavenumbers was examined on the basis of the calculated wavenumbers for diatomic molecules and ions in comparison with their experimental harmonic wavenumbers. The observed wavenumber of a fundamental, ν_{obs}, for the vibrational transition between $v = 0$ and $v = 1$ for a diatomic molecule is expressed as[41]

$$\nu_{obs} = \omega_e - 2\omega_e x_e + ... \quad (2)$$

where ω_e is the harmonic wavenumber and $\omega_e x_e$ is the anharmonicity constant. If the unscaled calculated wavenumber, ν_{calc}, is really the harmonic wavenumber, the ratio ω_e/ν_{calc} should be unity. In this work, we calculated the vibrational wavenumbers for 224 diatomic molecules and ions available in Herzberg's *Constants of Diatomic Molecules*.[34] The experimental harmonic wavenumbers (ω_e), the unscaled calculated wavenumbers (ν_{obs}), and their ratios are given in Table 3S (Supporting Information). The ratios ω_e/ν_{calc} for these diatomic species are plotted against the unscaled calculated wavenumbers in Figure 3. The results show that the ratios are actually 1.0 with deviations less than ±0.1 for 92% of the diatomic species examined. The molecules and ions that show the deviations larger than ±0.1 are AsSe, BN, BrO, Ca_2, Cu_2, H_2^+, T_2^+, Mg_2, P_2^+, S_2^-, ScCl, ScS, SeS^-, SiH^+, ZnBr, ZnCl, and ZnF. It may be stated that converged wavenumber values were not obtained for FeF, MnS, N_2^-, ScO, TiO, and VO.

The results obtained for diatomic molecules and ions demonstrate that the wavenumbers calculated by the DFT method can be represented as harmonic wavenumbers and that the decrease of the ratios ν_{obs}/ν_{calc} with increasing wavenumber as noted for polyatomic molecules (see Figure 1) is attributed almost exclusively to the neglect of anharmonicity in the calculated wavenumbers. The wavenumber-linear scale factor is thus substantially a correction for anharmonicity, and hence the proposed scaling procedure of the WLS method is theoretically validated. A relation between the scale factor and anharmonicity has been discussed previously by Kudoh et al.[26]

Calibration of the Calculated Wavenumbers by the Raman Spectrum of Indene. Although the WLS method using a simple relationship predicts the observed wavenumbers with high accuracy, the wavenumber scale factors, such as eq 1, are applicable only to the results obtained by the same calculation method. For more practical applications of the WLS method to vibrational analysis of organic compounds in particular, we propose to use the well-calibrated and well-assigned observed wavenumbers of liquid indene, instead of using a great number of observed wavenumbers for diverse compounds, to obtain the scale factors for different calculation methods. Indene was chosen for this purpose because it is one of the most typical organic compounds that give many prominent Raman and infrared bands and that the high-quality spectra for spectrometer calibration are available. This method of wavenumber scaling or "calibration" using the indene wavenumbers will be called the WLS indene calibration (WLS/IC) method.

We used for the WLS/IC method the wavenumbers of the most prominent bands of liquid indene obtained from the high-quality Raman spectra of Klots.[42] Using 20 selected fundamentals ranging from 3111 to 382 cm^{-1} (ν_2, ν_4, ν_7, ν_8, ν_9, ν_{16}, ν_{18}, ν_{22}, ν_{23}, ν_{25}, ν_{27}, ν_{28}, ν_{29}, ν_{30}, ν_{36}, ν_{38}, ν_{40}, ν_{41}, ν_{42}, and ν_{43}), the wavenumbers calculated by the B3LYP/6-311+G** and B3LYP/6-31G* methods were correlated with the observed wavenumbers by a respective single least-squares fitting, where we assumed that the ratio ν_{obs}/ν_{calc} is extrapolated to exactly 1.0 at zero wavenumber because the effect of anharmonicity is negligible at this point. The relationships obtained from the 20 fundamentals (calibration A) are

$$\nu_{obs}/\nu_{calc} = 1.0-0.00001356\nu_{calc} \quad (3)$$

for the B3LYP/6-311+G** method and

$$\nu_{obs}/\nu_{calc} = 1.0-0.00001692\nu_{calc} \quad (4)$$

for the B3LYP/6-31G* method.

The wavenumbers of indene calculated by the B3LYP/6-311+G** and B3LYP/6-31G* methods and scaled by the WLS/IC method ($\nu_{WLS/IC}$) using eqs 3 and 4, respectively (calibration A), are given in Table 3, where the observed wavenumbers (ν_{obs}), the unscaled calculated wavenumbers (ν_{calc}), and the wavenumbers calculated by the B3LYP/6-311+G** method and scaled by eq 1 (ν_{WLS}) are also given. The good agreement between $\nu_{WLS/IC}$ and ν_{WLS} calculated by the B3LYP/6-311+G** method indicates that the scaling using only a single compound of indene suffices for general vibrational analysis. The results in Table 3 show, however, that the deviations of $\nu_{WLS/IC}$ from ν_{obs} in the wavenumber region higher than 2800 cm^{-1} are appreciably larger than those in the region below 1700 cm^{-1} in both the B3LYP/6-311+G** and B3LYP/6-31G* methods.

For practical purposes of applying vibrational analysis to structural chemistry of organic compounds, the vibrations in the fingerprint region are particularly important. To obtain the scale factors that reproduce the observed wavenumbers in the fingerprint region accurately, the relationship between the observed and calculated wavenumbers was obtained from 17 fundamentals of indene in the region below 1610 cm^{-1} (ν_8, ν_9, ν_{16}, ν_{18}, ν_{22}, ν_{23}, ν_{25}, ν_{27}, ν_{28}, ν_{29}, ν_{30}, ν_{36}, ν_{38}, ν_{40}, ν_{41}, ν_{42}, and ν_{43}) (calibration B). The relationships obtained are

$$\nu_{obs}/\nu_{calc} = 1.0-0.00001838\nu_{calc} \quad (5)$$

for the B3LYP/6-311+G** method and

$$\nu_{obs}/\nu_{calc} = 1.0-0.00002520\nu_{calc} \quad (6)$$

for the B3LYP/6-31G* method.

The calculated wavenumbers of indene after scaling by the WLS/IC method ($\nu_{WLS/IC}$) using the 17 fundamentals (calibration

TABLE 3: Observed and Calculated Wavenumbers (cm^{-1}) of Indene

			B3LYP/6-311+G**						B3LYP/6-31G*				
					calibration A[a]		calibration B[b]			calibration A[a]		calibration B[b]	
sym	mode	ν_{obs}[c]	ν_{calcd}[d]	ν_{WLS}[e]	$\nu_{WLS/IC}$[f]	dev[g]	$\nu_{WLS/IC}$[h]	dev[g]	ν_{calcd}[d]	$\nu_{WLS/IC}$[i]	dev[g]	$\nu_{WLS/IC}$[j]	dev[g]
a′	ν_2	3111[k]	3189.3	3051.3	3051.4	−1.92	(3002.4)	(−3.49)	3211.1	3036.7	−2.39	(2951.3)	(−5.13)
	ν_4	3054[k]	3173.8	3037.2	3037.2	−0.55	(2988.7)	(−2.14)	3192.2	3019.8	−1.12	(2935.4)	(−3.88)
	ν_7	2891.5[k]	3015.7	2893.7	2892.4	0.03	(2848.5)	(−1.49)	3030.6	2875.2	−0.56	(2799.2)	(−3.19)
	ν_8	1609.6	1647.4	1617.5	1610.6	0.06	1597.5	−0.75	1666.5	1619.5	0.61	1596.5	−0.81
	ν_9	1587.9	1631.4	1602.2	1595.3	0.47	1582.5	−0.34	1654.3	1608.0	1.27	1585.3	−0.16
	ν_{16}	1287.8	1314.2	1297.4	1290.7	0.23	1282.4	−0.42	1327.4	1297.6	0.76	1283.0	−0.37
	ν_{18}	1205.1	1226.2	1212.4	1205.9	0.06	1198.6	−0.54	1240.0	1214.0	0.74	1201.3	−0.32
	ν_{22}	1067.8	1088.3	1078.5	1072.3	0.42	1066.6	−0.12	1095.2	1074.9	0.67	1065.0	−0.26
	ν_{23}	1018.9	1040.7	1032.1	1026.0	0.70	1020.8	0.19	1051.0	1032.3	1.31	1023.1	0.42
	ν_{25}	861.5	872.8	868.0	862.5	0.11	858.8	−0.31	877.0	864.0	0.29	857.6	−0.45
	ν_{27}	730.6	743.9	741.4	736.4	0.80	733.7	0.43	744.1	734.7	0.56	730.1	−0.07
	ν_{28}	592.2	604.5	603.8	599.6	1.24	597.8	0.95	603.2	597.0	0.81	594.0	0.30
	ν_{29}	534.4	541.6	541.5	537.6	0.60	536.2	0.34	542.9	537.9	0.66	535.5	0.21
	ν_{30}	381.9	387.9	388.8	385.9	1.04	385.2	0.85	387.5	385.0	0.80	383.7	0.47
a″	ν_{36}	915.5	937.6	931.5	925.7	1.12	921.5	0.65	932.3	917.6	0.23	910.4	−0.56
	ν_{38}	768.4	783.6	780.4	775.3	0.89	772.3	0.51	790.4	779.8	1.49	774.7	0.82
	ν_{40}	695	705.9	703.9	699.1	0.59	696.7	0.25	710.4	701.9	0.99	697.7	0.39
	ν_{41}	551.5	562.4	562.2	558.1	1.20	556.6	0.92	564.1	558.8	1.31	556.1	0.84
	ν_{42}	420.5	425.5	426.2	423.0	0.60	422.2	0.40	431.3	428.2	1.82	426.6	1.46
	ν_{43}	393.2	395.4	396.3	393.3	0.02	392.5	−0.17	398.1	395.5	0.57	394.1	0.24

[a] Least-squares fitting using 20 selected observed wavenumbers (ν_2, ν_4, ν_7, ν_8, ν_9, ν_{16}, ν_{18}, ν_{22}, ν_{23}, ν_{25}, ν_{27}, ν_{28}, ν_{29}, ν_{30}, ν_{36}, ν_{38}, ν_{40}, ν_{41}, ν_{42}, and ν_{43}) of liquid indene. [b] Least-squares fitting using 17 selected observed wavenumbers (ν_8, ν_9, ν_{16}, ν_{18}, ν_{22}, ν_{23}, ν_{25}, ν_{27}, ν_{28}, ν_{29}, ν_{30}, ν_{36}, ν_{38}, ν_{40}, ν_{41}, ν_{42}, and ν_{43}) of liquid indene. [c] Raman wavenumbers of indene in the liquid phase.[42] [d] Unscaled calculated wavenumbers. [e] Scaled by the WLS method using eq 1. [f] Scaled by the WLS/IC method using eq 3. [g] Deviations in % of the scaled calculated wavenumbers from the observed wavenumbers. [h] Scaled by the WLS/IC method using eq 5. [i] Scaled by the WLS/IC method using eq 4. [j] Scaled by the WLS/IC method using eq 6. [k] Not used for a least-squares fitting for calibration B.

B) are given in Table 3 for the B3LYP/6-311+G** and B3LYP/6-31G* methods. Overall agreement between $\nu_{WLS/IC}$ and ν_{obs} for the 17 fundamentals is good with a mean error of 0.48% for both calculation methods. The results of the present calculations thus indicate that the WLS/IC method proposed in this study is applicable to most of common organic compounds. To confirm this, we applied the WLS/IC method to a linear polyene as described below.

Vibrational Analysis of *all-trans*-1,3,5,7,9-Decapentaene by the WLS/IC Method. Linear polyenes $(-CH{=}CH-)_n$ have attracted much attention of spectroscopists and theoretical chemists for many years because of their importance as the simplest model compounds that contain conjugated π electron systems and as models of polyacetylene which shows high electric conductivity upon doping.[43] Polyenes are also the models of biological pigments such as retinoids and carotenoids. Vibrational analysis of linear polyenes is a prototypical example for examining the performance of quantum mechanical calculations, because the force constants of conjugated π electron systems were difficult to estimate empirically.[5−7]

In this work, we performed vibrational analysis of a polyene, *all-trans*-1,3,5,7,9-decapentaene [$CH_2{=}CH(-CH{=}CH)_3-CH{=}CH_2$], by the B3LYP/6-311+G** and B3LYP/6-31G* methods. The calculated wavenumbers were scaled by the WLS/IC method using eq 5 for B3LYP/6-311+G** and eq 6 for B3LYP/6-31G* (calibration B). The observed wavenumbers and the scaled calculated wavenumbers are given in Table 4, where the previous results[16] calculated by the HF/6-31G* and MP2/6-31G* methods and scaled by the SQM method are also given.

As seen in Table 4, the calculated results by the four methods agree satisfactorily with the observed data, except for the wavenumbers of the C=C stretching modes calculated by the HF method. The HF/6-31G* calculation (SQM) gave the ν_8 (a_g) and ν_{47} (b_u) wavenumbers 45 and 18 cm^{-1} higher than the observed wavenumbers, 1593 and 1626 cm^{-1}, respectively. The MP2/6-31G* (SQM), B3LYP/6-311+G** (WLS/IC), and B3LYP/6-31G* (WLS/IC) calculations, on the other hand, gave the scaled wavenumbers for the ν_8 and ν_{47} modes in good agreement with the observed values. It should be remarked that, while the MP2/6-31G* (SQM) calculation used 11 empirical parameters for scaling,[16] the present WLS/IC method uses only one empirical parameter (eqs 5 and 6). The present exemplified calculations on *all-trans*-1,3,5,7,9-decapentaene have demonstrated that the WLS/IC method is a convenient technique to obtain vibrational wavenumbers of large molecules with high accuracy.

Conclusions

The vibrational analysis by DFT using the WLS method gave satisfactory results on 164 organic and inorganic compounds, in addition to 205 compounds examined in the previous work. It should be emphasized that, although the WLS method employs essentially only one parameter to scale wavenumbers in the whole region, it reproduces the experimental wavenumbers excellently except the wavenumbers for peculiar types of compounds such as those that contain a number of halogen atoms and those with linear molecular structures. The larger positive deviations of the unscaled calculated wavenumbers from the observed values at higher wavenumbers are attributed almost exclusively to the neglect of anharmonicity in the calculated wavenumbers. The wavenumber-linear scale factor is thus substantially a correction for anharmonicity. The satisfactory results obtained for a total of 369 compounds encourage us to generalize and simplify the WLS method for more convenient use. The wavenumber-linear scale factors were then derived from only 17 well-defined wavenumbers of liquid indene at different calculation levels. The application of the derived scale factors to vibrational analysis of *all-trans*-1,3,5,7,9-decapentaene yielded results in close agreement with the experimental data. These results demonstrate that the WLS indene calibration (WLS/IC) method, which is more general and simpler than

TABLE 4: Observed and Calculated Wavenumbers[a] (cm^{-1}) of *all-trans*-1,3,5,7,9-Decapentaene

sym	mode	ν_{obs}[b]	ν_{SQM}[c] (HF/ 6-31G*)	ν_{SQM}[d] (MP2/ 6-31G*)	$\nu_{\mathrm{WLS/IC}}$[e] (B3LYP/ 6-311+G**)	$\nu_{\mathrm{WLS/IC}}$[f] (B3LYP/ 6-31G*)
a_g	ν_7	1621	1622	1618	1626	1607
	ν_8	1593	1638	1593	1591	1572
	ν_9		1543	1543	1558	1540
	ν_{10}	1409	1416	1408	1408	1393
	ν_{11}	1292	1299	1296	1300	1288
	ν_{12}	1284	1288	1294	1288	1276
	ν_{13}		1282	1283	1284	1272
	ν_{14}		1248	1248	1255	1244
	ν_{15}	1177	1180	1179	1178	1168
	ν_{16}	1121	1104	1113	1125	1116
	ν_{17}	947	946	945	946	939
	ν_{18}	597	600	599	596	594
	ν_{19}	419	419	414	413	411
	ν_{20}		267	270	277	277
	ν_{21}	160	152	149	150	150
a_u	ν_{22}	1010	1022	1020	1029	1021
	ν_{23}	972	984	978	987	980
	ν_{24}	918	929	922	922	916
	ν_{25}	899	900	894	906	901
	ν_{26}	863	865	852	881	876
	ν_{27}	651	640	642	658	655
	ν_{28}		379	374	389	388
	ν_{29}		189	190	196	196
	ν_{30}		133	133	134	134
	ν_{31}		39	40	40	40
b_g	ν_{32}		1009	1005	1017	1009
	ν_{33}		954	947	951	945
	ν_{34}	900	901	894	911	905
	ν_{35}	886	890	867	902	896
	ν_{36}		820	822	841	836
	ν_{37}		626	631	643	640
	ν_{38}		281	280	292	292
	ν_{39}		237	236	249	248
	ν_{40}		103	105	106	106
b_u	ν_{47}	1626	1644	1627	1630	1611
	ν_{48}	1595	1586	1586	1598	1580
	ν_{49}	1417	1434	1422	1421	1407
	ν_{50}	1320	1308	1309	1320	1307
	ν_{51}		1285	1289	1294	1282
	ν_{52}	1279	1285	1282	1279	1267
	ν_{53}	1216	1209	1211	1218	1207
	ν_{54}	1153	1136	1141	1160	1150
	ν_{55}	1142	1113	1132	1146	1137
	ν_{56}	945	950	947	945	938
	ν_{57}		549	549	546	544
	ν_{58}	486	480	483	486	485
	ν_{59}		278	274	274	273
	ν_{60}		58	57	57	57

[a] Wavenumbers higher than 1700 cm^{-1} are not given in this table. [b] Ref 16. [c] Calculated by the HF/6-31G* method and scaled by the SQM method.[16] [d] Calculated by the MP2/6-31G* method and scaled by the SQM method.[16] [e] Calculated by the B3LYP/6-311+G** method and scaled by the WLS/IC method using eq 5. [f] Calculated by the B3LYP/6-31G* method and scaled by the WLS/IC method using eq 6.

others, is a promising technique for performing vibrational analysis of large molecules with high accuracy.

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Supporting Information Available: Table 1S: a list of 205 compounds used in the calculations in the previous work.[22] Table 2S: the observed wavenumbers, unscaled calculated wavenumbers, and WLS-scaled calculated wavenumbers for 164 compounds listed in Table 1. Table 3S: the experimental harmonic wavenumbers, unscaled calculated wavenumbers, and their ratios for 224 diatomic molecules and ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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