



Density functional vibrational analysis using wavenumber-linear scale factors

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Abstract

Normal coordinate calculations were performed by the density functional method of B3LYP/6-311 + G** on 205 basic organic and inorganic compounds taken from the 'Tables of Molecular Vibrational Frequencies' (T. Shimanouchi, 1972). The calculated wavenumbers, ν_{calc} , of 1729 vibrational modes were correlated with the observed wavenumbers, ν_{obs} , by a single least-squares fitting. The relationship obtained, after omitting the vibrational modes that give deviations of more than 10%, is $\nu_{\text{obs}}/\nu_{\text{calc}} = 1.0087 - 0.0000163 (\nu_{\text{calc}}/\text{cm}^{-1})$. The wavenumber-linear scaling method with this relationship predicts vibrational wavenumbers with high accuracy and is applicable to any compounds, except for the compounds for which the effect of dispersion forces is significant. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In the long history of vibrational spectroscopy, normal coordinate analysis has played an important role in interpretation of infrared and Raman spectra, in particular, for making precise assignment of the observed bands. It has also been used extensively to determine molecular structures and molecular potential surfaces for a variety of compounds. A great number of normal coordinate analyses have in fact been performed by using empirical molecular force fields and have contributed significantly to the development of vibrational spectroscopy [1]. In result, a huge number of empirical force constants have been accumulated and the force constants for fundamental organic compounds have been compiled as a database

[2–4]. Although normal coordinate analysis using empirical force fields has been successful in many cases, several difficulties with the force field have been encountered in other cases [5–7].

The difficulties in the traditional method of vibrational analysis using empirical force fields have been overcome by the introduction of ab initio quantum mechanical method of calculations [8–10]. The ab initio calculations by the Hartree–Fock method generally overestimate vibrational wavenumbers by about 10% because of the neglect of electron correlation and anharmonicity effects. The problem of the overestimation was later solved practically by the use of a scaled quantum mechanical method [11,12]. This method has then become one of the most useful techniques in vibrational analysis, especially when inexpensive calculations are preferred. To get more accurate ab initio molecular force fields, more sophisticated methods of calculations including elec-

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tron correlation, such as the second-order Møller–Plesset perturbation theory, have to be used. Since these methods require more CPU time and more memory resources than the Hartree–Fock method, they are applicable only to relatively small molecules.

The recent evolution of density functional theory (DFT) [13], which includes electron correlation in an alternative way, has afforded opportunities for performing normal coordinate analysis of moderately large molecules. Among various types of density functionals available, those which use Becke's three-parameter hybrid functional [14] with large basis sets such as 6-311 + G** have been found to be the most promising in providing excellent results of vibrational wavenumbers [15–21]. The DFT method has thus been used in normal coordinate calculations on a great number of compounds. Nevertheless, the accuracy of calculated wavenumbers for the compounds that involve high-periodic elements or isotopes is still not unambiguous.

Recent vibrational analyses by the DFT method on 1,2-dimethoxyethane and *N*-methylthiourea have indicated that no scaling of calculated wavenumbers is necessary in effect in reproducing the experimental wavenumbers [19,20]. A more recent DFT study has shown that there is a linear relationship between the scale factor and the vibrational wavenumbers for pyridine and picolines [21]. Such a linear relationship has also been found for propanesulfonate ion in our previous study of the second-order Møller–Plesset perturbation theory [22].

In the present work, we have systematically performed normal coordinate calculations by the DFT method on 205 basic organic and inorganic compounds, for which the vibrational assignments had been established. This work aims at examining calculation accuracy in normal coordinate analysis by the DFT method and at confirming and proposing a single linear relationship between the scale factor and the calculated wavenumbers for a large variety of compounds.

2. Compounds treated

The compounds treated in this work were taken from the 'Tables of Molecular Vibrational Frequencies' [23], where the experimental wavenumbers of

infrared and Raman bands for 223 basic organic and inorganic compounds including their isotopic species are critically evaluated. We used for the present normal coordinate analysis only the experimental wavenumbers classified in ranks A (uncertainty 0–1 cm⁻¹, observed in the gas phase), B (1–3 cm⁻¹, gas phase) and C (3–6 cm⁻¹, gas, solid or liquid phase) [23]. The compounds that involve the fifth or higher periodic elements were excluded from the analysis because of unknown performance of the basis function on these compounds. Liquid methanol, which forms intermolecular hydrogen bonding, and poly(methylene) were also excluded. Therefore, we used a total of 205 compounds for the present analysis. The 18 compounds excluded are SbH₃, SbD₃, SiI₄, SnCl₄, SnBr₄, SiCl₃I, SiClI₃, MoF₆, WF₆, UF₆, Cl₄, CH₃I, CD₃I, CH₃OH (liquid), CH₃OD (liquid), CD₃OH (liquid), (CH₂)_n and (CD₂)_n. A list of the compounds treated in this analysis and the results of calculations are available on request from the corresponding author.

3. Calculations

Normal coordinate calculations were performed on 205 compounds taken from Ref. [23] by the DFT method using Becke's three-parameter hybrid functional [14] combined with the Lee–Yang–Parr correlation functional [24] (abbreviated as B3LYP). The basis set used was 6-311 + G**. The computations were performed with the GAUSSIAN 98 program [25]. The input data for the GAUSSIAN 98 program were prepared by using the graphical molecular modeling program Molda [26,27].

4. Results and discussion

4.1. Scale factor

The ratios of the observed wavenumbers to the unscaled calculated wavenumbers, $\nu_{\text{obs}}/\nu_{\text{calc}}$, for 1729 vibrational modes of 205 compounds are plotted against the unscaled calculated wavenumbers in Fig. 1. This ratio is denoted as the wavenumber scale factor. The plot shows that most of the values of scale factors are within 1.00 ± 0.05 although several

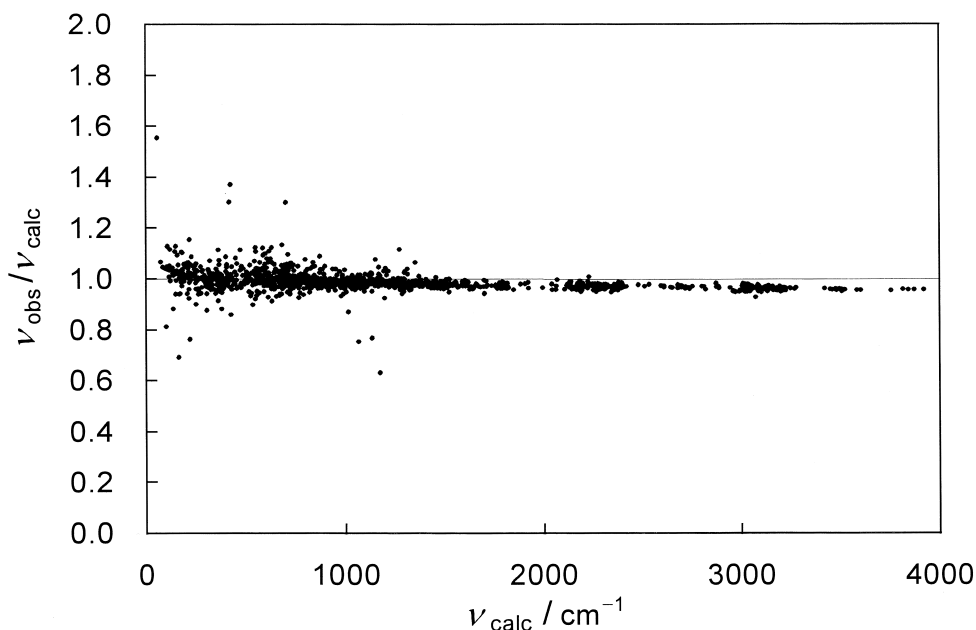


Fig. 1. Plot of the ratios of the observed wavenumbers to the unscaled calculated wavenumbers, $\nu_{\text{obs}}/\nu_{\text{calc}}$, against the unscaled calculated wavenumbers.

of them, especially those in the low-wavenumber region, deviate appreciably from 1.0. It is noted that the deviations of the calculated wavenumbers from the observed wavenumbers of rank A are all within 8%. It is also shown that the deviations are larger for lower wavenumbers. The vibrational modes that give large deviations are mostly of the compounds that contain many halogen atoms (e.g., SF_6 , SeF_6 , CF_3CF_3 , CCl_3CCl_3 and CBr_3CBr_3). These deviations can be explained by the effect of the London dispersion force generated by the halogen atoms, which may influence the wavenumbers of the halogen-involved vibrational modes. In a previous study on the London dispersion force [28], the local and gradient-corrected local (semilocal) DFT failed to describe the dispersion interaction properly. A more sophisticated treatment is necessary to elucidate the effect of dispersion forces.

In the wavenumber region higher than 1000 cm^{-1} , the distribution of the scale factor $\nu_{\text{obs}}/\nu_{\text{calc}}$ is small and the averaged value of the scale factor decreases with increasing wavenumber. Most of the vibrations in the $2000\text{--}4000\text{ cm}^{-1}$ region are associated with

the C–H and C–D stretching modes. Since the amplitudes of these vibrations involving H and D atoms are large, significant vibrational anharmonicity is expected for these modes. Accordingly, the normal coordinate calculations under the harmonic approximation give rise to an overestimation of wavenumbers for these modes. The effect of anharmonicity thus explains the lower values of the scale factor for the modes in the $2000\text{--}4000\text{ cm}^{-1}$ region than the modes with lower wavenumbers. The calculated wavenumbers for the C–H and C–D bending modes in the $1000\text{--}1500\text{ cm}^{-1}$ region are also lower than the observed wavenumbers, giving scale factors of about 0.98. This result is consistent with uniform scale factors, which were justified in previous discussions [18,19]. A relationship between the scale factor and vibrational anharmonicity has been explicitly described by Kudoh et al. [21].

The present results of the calculated wavenumbers for 1729 vibrational modes of 205 compounds were correlated with the observed wavenumbers by a single least-squares fitting. The 28 vibrational modes that give deviations of $\nu_{\text{obs}}/\nu_{\text{calc}}$ by more than 10%

Table 1
Observed and calculated wavenumbers of four isotopic species of methylamine

	Sym. species	Approximate type of mode	ν_{obs}^a	$\nu_{\text{calc}}^{\text{unscaled } b}$	$\nu_{\text{calc}}^{\text{scaled } b,c}$	$\nu_{\text{calc}}^{\text{SQM } d}$
CH ₃ NH ₂	A'	NH ₂ s-stretch	3361 (B)	3508	3338	3398
		CH ₃ d-stretch	2961 (B)	3057	2931	2968
		CH ₃ s-stretch	2820 (B)	2962	2845	2840
		NH ₂ scis	1623 (B)	1668	1637	1624
		CH ₃ d-deform	1473 (B)	1498	1474	1467
		CH ₃ s-deform	1430 (B)	1460	1438	1430
		CH ₃ rock	1130 (A)	1164	1152	1147
	A''	CN stretch	1044 (A)	1056	1047	1059
		NH ₂ wag	780 (A)	822	818	785
		NH ₂ a-stretch	3427 (C)	3585	3407	3442
		CH ₃ d-stretch	2985 (C)	3093	2964	3000
		CH ₃ d-deform	1485 (D)	1517	1493	1508
		NH ₂ twist	1419 (D)	1343	1325	1325
		CH ₃ rock	1195 (D)	974	967	954
Torsion	268 (B)	306	307	274		
CH ₃ ND ₂	A'	ND ₂ s-stretch	2479 (B)	2535	2452	2445
		CH ₃ d-stretch	2961 (B)	3057	2931	2970
		CH ₃ s-stretch	2817 (B)	2962	2845	2847
		ND ₂ scis	1234 (B)	1246	1232	1222
		CH ₃ d-deform	1468 (B)	1498	1474	1467
		CH ₃ s-deform	1430 (B)	1461	1439	1430
		CH ₃ rock	1117 (A)	1148	1137	1140
	A''	CN stretch	997 (A)	1011	1003	1001
		ND ₂ wag	625 (A)	642	641	615
		ND ₂ a-stretch	2556 (B)	2643	2552	2538
		CH ₃ d-stretch	2985 (C)	3093	2964	2981
		CH ₃ d-deform	1485 (D)	1514	1490	1506
		ND ₂ twist	1058 (E)	793	790	773
		CH ₃ rock	1187 (C)	1223	1209	1216
Torsion	228 (C)	253	254	225		
CD ₃ NH ₂	A'	NH ₂ s-stretch	3361 (B)	3508	3338	3398
		CD ₃ d-stretch	2203 (B)	2251	2188	2195
		CD ₃ s-stretch	2077 (A)	2140	2084	2048
		NH ₂ scis	1624 (B)	1666	1635	1622
		CD ₃ d-deform	1065 (D)	1078	1068	1056
		CD ₃ s-deform	1142 (A)	1160	1148	1146
		CD ₃ rock	913 (A)	944	938	902
	A''	CN stretch	973 (B)	990	983	978
		NH ₂ wag	740 (A)	767	764	761
		NH ₂ a-stretch	3427 (C)	3585	3407	3442
		CD ₃ d-stretch	2236 (C)	2294	2228	2211
		CD ₃ d-deform	1077 (C)	1091	1081	1087
		NH ₂ twist	1416 (C)	1269	1254	1238
		CD ₃ rock	926 (D)	794	791	784
Torsion	247 (D)	278	279	249		
CD ₃ ND ₂	A'	ND ₂ s-stretch	2477 (B)	2535	2452	2445
		CD ₃ d-stretch	2202 (B)	2251	2188	2195
		CD ₃ s-stretch	2073 (B)	2139	2083	2048
		ND ₂ scis	1227 (B)	1243	1229	1211

Table 1 (continued)

Sym. species	Approximate type of mode	$\nu_{\text{obs}}^{\text{a}}$	$\nu_{\text{calc}}^{\text{unscaled}}^{\text{b}}$	$\nu_{\text{calc}}^{\text{scaled}}^{\text{b,c}}$	$\nu_{\text{calc}}^{\text{SQM}}^{\text{d}}$
A'	CD ₃ d-deform	1065 (D)	1077	1067	1057
	CD ₃ s-deform	1123 (B)	1141	1130	1123
	CD ₃ rock	880 (B)	914	908	890
	CN stretch	942 (A)	948	942	940
	ND ₂ wag	601 (A)	617	616	600
	ND ₂ a-stretch	2556 (C)	2643	2552	2538
	CD ₃ d-stretch	2238 (C)	2293	2227	2210
	CD ₃ d-deform	1077 (C)	1093	1083	1093
	ND ₂ twist	1072 (D)	1056	1047	1043
	CD ₃ rock	910 (B)	700	698	684
Torsion	201 (C)	218	219	194	

^a Ref. [23]. Ranks of the observed wavenumbers are given in parentheses.

^b Calculated in this work by the B3LYP/6-311 + G** method.

^c Scaled with Eq. (1).

^d Calculated and scaled by the HF/4-31G and SQM methods [31].

were omitted from the fitting. (The data for these modes are yet included in Fig. 1.) The relationship thus obtained for 1701 vibrational modes is

$$\begin{aligned} \nu_{\text{obs}}/\nu_{\text{calc}} \\ = 1.0087(9) - 0.0000163(6)(\nu_{\text{calc}}/\text{cm}^{-1}), \end{aligned} \quad (1)$$

where the errors, given in parentheses, apply to the last significant figures. The relationship derived in this work may be compared with the previous relationship derived from 139 vibrational modes of pyridine, 2-picoline, 4-picoline and the corresponding Dewar isomers [21]:

$$\begin{aligned} \nu_{\text{obs}}/\nu_{\text{calc}} \\ = 0.9894(10) - 0.0000104(6)(\nu_{\text{calc}}/\text{cm}^{-1}). \end{aligned} \quad (2)$$

This formula (2) deviates slightly from Eq. (1). The deviation may be ascribed to the difference in the basis sets used, 6-311 + G** in Eq. (1) and 6-31 + G** in Eq. (2), and to the fact that only the data for pyridine and picolines were used to derive Eq. (2). The present relationship (1) has been derived from the experimental wavenumbers covering a wider range of wavenumbers using a number of compounds that contain a variety of chemical elements. Both relationships show that the scale factor, $\nu_{\text{obs}}/\nu_{\text{calc}}$, is extrapolated to nearly 1.0 at zero

wavenumber, where the effect of vibrational anharmonicity is negligible.

4.2. Revised assignments based on the present analysis

Fig. 1 shows that there are several large deviations of $\nu_{\text{obs}}/\nu_{\text{calc}}$ from the linear relationship given by Eq. (1), besides the deviations observed for halogen-containing compounds as discussed above. The unexpected large deviations can be ascribed most probably to misassignment of the observed bands. The present normal coordinate analysis has in fact pointed out several obvious misassignments.

For cyclobutane, the experimental wavenumber for the CH₂ rocking mode (A₁ species) is listed as 741 cm⁻¹ in Ref. [23]. The present calculation gave a considerably higher wavenumber 1173 cm⁻¹ for this mode (1161 cm⁻¹ after scaling with Eq. (1)), suggesting a revision of the assignment. Actually, this mode has already been reassigned to a Raman band at 1153 cm⁻¹ [29].

Other examples of misassignments are found for methylamine. The present analysis has revealed two large deviations in $\nu_{\text{obs}}/\nu_{\text{calc}}$ for the observed wavenumbers with ranks A–C [23]. One is for the wavenumber of the NH₂ twisting mode (A' species) of CD₃NH₂ and the other for the wavenumber of the CD₃ rocking mode (A' species) of CD₃ND₂. The present calculations gave wavenumbers 1269 and

700 cm^{-1} for these modes (1254 and 698 cm^{-1} after scaling with Eq. (1)), in comparison with the listed observed wavenumbers 1416 and 910 cm^{-1} [23]. Revised assignments of these modes have already been proposed to infrared bands at 1260 cm^{-1} for CD_3NH_2 and at 670 cm^{-1} for CD_3ND_2 [30]. The wavenumbers of these reassigned bands agree well with the present scaled wavenumbers 1254 and 698 cm^{-1} . Several other revisions of assignment are found for the amino twisting and methyl rocking modes (A' species) with ranks D and E [23]. Large deviations noted for other compounds will be described elsewhere.

4.3. Wavenumber predictability by the wavenumber-linear scaling method

The predictability of vibrational wavenumbers by the wavenumber-linear scaling (WLS) method with a relationship of Eq. (1) will be discussed by illustrating the results of methylamine given in Table 1. In a previous analysis of methylamine [31], the scaled quantum mechanical (SQM) method [11,12] was used in the Hartree–Fock calculations. In this method, each of the internal coordinates, in terms of which the force constants are expressed, is differentially scaled by a least-squares method so that the calculated wavenumbers fit with the experimental wavenumbers. In the previous calculations on methylamine [31], 14 scale factors were empirically optimized, which yielded as a matter of course an excellent agreement between the observed and calculated wavenumbers as shown in Table 1.

The present results on methylamine based on the WLS method are compared with the SQM results optimized by a number of scale factors [31]. The two sets of the calculated wavenumbers for methylamine, not only for the undeuterated species but also for the deuterated species, show remarkable coincidence with each other (Table 1). Thus, the WLS method as applied in this work is found to reproduce experimental vibrational wavenumbers for a large variety of compounds, with the exception of compounds for which the effect of dispersion forces is significant. The high predictability of vibrational wavenumbers ensures that the WLS method is a powerful tool for precise normal coordinate analysis of molecules for

practically any compounds. This method is especially useful for vibrational analysis of those compounds whose scale factors are not readily transferable from other compounds.

5. Conclusion

The present DFT vibrational analysis by the WLS method on 205 organic and inorganic compounds reproduced the experimental wavenumbers. The proposed relationship of wavenumber-linear scale factor is applicable to any compounds, except for the compounds for which the effect of dispersion forces is significant, in calculations by the B3LYP/6-311 + G^{**} method. In consideration of the recent evolution of high-speed and inexpensive computers, the WLS method is undoubtedly a promising approach to ab initio vibrational analysis.

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