Ab Initio Calculation of Force Constants of Hydroxylamine

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Ab initio molecular orbital calculation has been applied to hydroxylamine molecule to reach a reliable set of force constants by the use of the 4-31G basis set. This approach was found to be an enlightening way to solve a problem of the so far undeterminable amino twisting frequency. For this, the value of 1250 ± 100 cm^{-1} was estimated. A few comments are also given on the theoretical and experimental values of force constants.

The amino group $-NH_2$ has three bending vibrational modes. They are scissoring, wagging, and twisting modes. The vibrational frequecies of the scissoring and wagging modes have been conclusively fixed in most of the primary amines. Figure 1 shows the established bending frequencies and approximate vibrational modes for three representative molecules. These are ammonia derivatives in each of which one of the hydrogen atoms is replaced by methyl, amino, or hydroxyl group. As are indicated in the figure, the twisting frequencies of methylamine and hydroxylamine have not been determined. In the twisting vibration, two XNH angles open and close alternately. Therefore, as long as the two NH bonds are equivalent to each other this vibration causes almost no change in the dipole moment, and only very weak absorption in the infrared spectrum. The twisiting modes of hydrazine give exceptionally strong absorptions, probably because the two NH bonds are not equivalent in this molecule.[1]

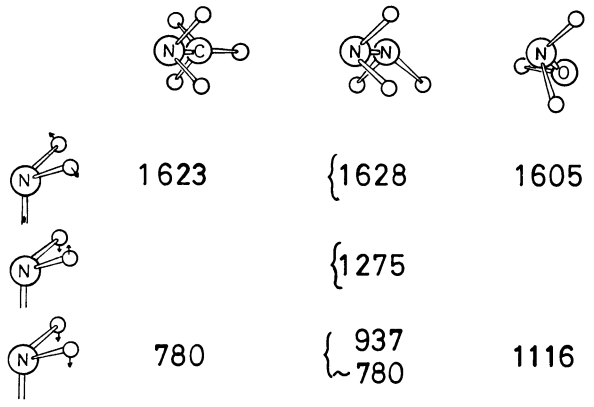

Fig. 1. Amino-scissoring, twisting, and wagging frequencies in cm^{-1}. Small circles indicate hydrogen atoms.

The weakness of the twisting bands of methylamine and hydroxylamine is one of the causes of a long-term debate[2-5] on the twisting frequency, whether it is in the vicinity of 1300 cm^{-1} or below 1000 cm^{-1}. Although there have been many normal coordinate treatments on the variety of assumptions, the results were not yet satisfactory. The off-diagonal elements of the potential energy matrix **F** for the XNH bending coordinates have never been determined on the basis of the experimental data. The infrared spectrum of hydroxylamine in gas phase was first observed by Giguere and Liu in 1952.[6] They assigned the perpendicular type band at 750 cm^{-1} to the amino twisting mode. However this band was shown later to be the first overtone of torsional vibration at 390 cm^{-1}.[7] Thus, the amino twisting frequency is now yet to be established.

The purpose of the present work is to fix the amino twisting frequency of hydroxylamine on the basis of *ab initio* molecular orbital calculation by the use of the 4-31 G basis set.[8]

Much effort has been made to obtain the meaningful set of force constants through various applications of molecular orbital theory. Unfortunately the semiempirical method such as the CNDO/2 method[9] has given the values two to three times as great as the experimental ones, and was scarcely fit for practical purpose, except for a work of estimating an order of magnitude of a vibrational frequency.[10] *Ab initio* molecular orbital calculations, on the other hand, have recently proved to be more reliable in estimating force constants of some small molecules. Particularly the "force method" developed by Pulay[11] seems to be the most useful in terms of both precision and computing time. The examples of its application are nicely reviewed by Duncan.[12]

Calculations of force constants using the 4-31 G basis set have been done by Bernhard-Schlegel *et al.*[13] The estimated error of the diagonal elements of stretching force constants is about 6%, and that of bending force constants is about 15% when the bonds involve hydrogen and second- or third-row elements. This means that the errors in frequencies are 3 and 8% for stretching and bending modes, respectively. In general, an advantage of application of *ab initio* calculation to a force field problem is that we can estimate the off-diagonal elements with the same precision as that for the diagonal elements. By experimental ways, off-diagonal elements of **F** matrix are often hard to evaluate even for small molecules.

Calculation

In this study, we used the 4-31 G split valence shell basis set in the Gaussian 70 program system.[14] The calculations were performed with a HITAC 8700/8800 in the computer center, University of Tokyo.

The internal coordinates are defined as shown in Fig. 2. There are six A′ modes and three A″ modes.

Starting from the experimental values determined by microwave spectroscopy,[15] one of the six internal coordinates belonging to the A′ symmetry species was changed, and we find the optimized point to

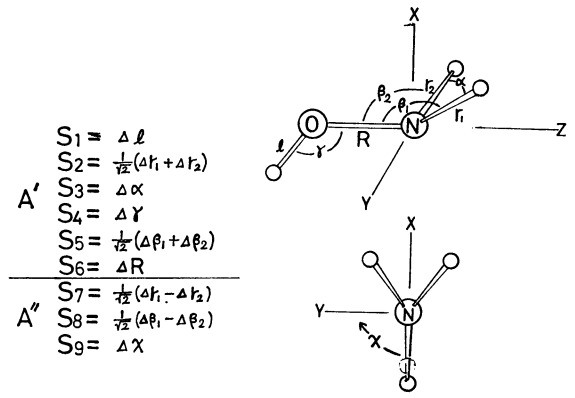

Fig. 2. Denotations of the bond lengths, bond angles, and internal rotation angle (χ); and definitions of symmetry coordinates **S** for the hydroxylamine molecule.

minimize the total energy. This procedure was repeated stepwise for other five coordinates to reach a calculated equilibrium structure (Process I).

From the process of geometry optimization we can estimate approximate values of diagonal force constants. To obtain off-diagonal force constants (or coupling constants), we need to calculate total energies at various combinations of six internal coordinates in question. A special attention was paid to have important coupling constants determined effectively (Process II).

Totally 77 sets of coordinates were chosen. Among them, the maximum deviations were ±0.04 Å in the bond lengths, and ±5° in the bond angles from the calculated equilibrium geometry. The 77 values of the total energy were used to obtain, by the least squares fit, the elements F_{ij} of the potential energy matrix in the expression,

$$V = V_0 + \sum_{i,j} \frac{1}{2} F_{ij}(R_i - R_i^0)(R_j - R_j^0), \qquad (1)$$

where R are internal coordinates (for which the total energy was calculated) and R^0 are those for the equilibrium geometry. By this procedure, we can obtain the minimum total energy (V_0), 6 parameters (R_j^0) of the "final" equilibrium geometry, and 21 force constants (F_{ij}) belonging to the A′ symmetry species.

A few comments will now be given below on the results of the calculations, so far described.

1) The total energy −130.791865(9) Hartrees at the equilibrium geometry is less than −130.78729 Hartrees obtained by Radom *et al.*[16] using the same computing program. This means that our optimization is better than theirs. (The figure given in the parenthesis gives the standard deviation in the unit corresponding to the last significant figures).

2) As shown in Table 1, the equilibrium geometry calculated by Process I is significantly different from that calculated by Process II. In the Process I, only one coordinate is changed with others fixed in finding the coordinate value that gives energy minimum. In the Process II, on the other hand, several coordinates are changed simultaneously with a proper assumption

Table 1. Equilibrium geometry of the NH_2OH molecule

	Calculated		Observed(r_0)
	Process I	Process II	
NO	1.4636(Å)	1.4432(4)[a]	1.453(2)[a]
OH	0.9528	0.9519(3)	0.962(5)
∠HON	104.98(deg)	106.00(6)	101.37(50)
∠HNH	110.86	111.28(7)	107.1(5)
NH	0.9987	0.9992(1)	1.016(8)
∠ONH	105.2	105.84(2)	103.25(50)

a) The figure in the parenthesis gives 1σ (standard deviation) in the unit corresponding to the last significant figure.

on the coupling among the coordinates. Probably, the most reliable geometry is reached by repeating the Process I in a systematic manner, but this will take a great amount of computer time.

3) The optimized structural parameters (Table 1) are found to be within the stated precision.[17,18] It should be realized that the calculated geometry is that for equilibrium or the geometry in which the total energy is minimized, while the experimental set of values determined by microwave spectroscopy, for example, are often that for vibrational ground state and for $J=K=0$ level. The former corresponds to the so-called r_e-structure, while the latter r_0-structure. Table 2 gives some examples, showing the differences of r_e- and r_0-structures. Taking probale differences between the r_e and r_0 structures of NH_2OH into account, it may be concluded that our *ab initio* calculations could reproduce the bond lengths quite satisfactorily, but the calculated bond angles are all larger than the experimental angles by about 5°.

Next, the internal symmetry coordinates belonging to the A″ symmetry species were subjected to our examination. After the equilibrium coordinates were determined, the three A″ internal coordinates were changed within the range of distortion where anharmonicities do not become influential. Six force constants were obtained from 15 data sets in a similar way to those of the A′ symmetry species.

Table 2. A few examples of the r_e- and r_0-structures actually found in some small molecules

Molecule	Bond or bond angle	r_e-Structure	r_0-Structure
HF[a]	HF	0.9170(Å)	0.9257
OH[a]	OH	0.9707	0.9800
$^{12}C^{16}O$[a]	CO	1.1282	1.1309
NH_3[a]	NH	1.0124	1.0136
	∠HNH	106.68 (deg.)	107.05
HNO(Ã)[b]	HN	1.020	1.036
	NO	1.239	1.241
	∠HNO	114.42	116.25

a) W. Gordy and R. Cook, "Microwave Molecular Spectra," Wiley (1970). b) Landolt-Börnstein, New Series Vol. 7, Springer-Verlag (1976).

TABLE 3. CALCULATED FORCE CONSTANT MATRIX ELEMENTS[a]

	S_1(OH)	S_2(NH)	$S_3(\alpha)$	$S_4(\gamma)$	$S_5(\beta)$	S_6(NO)	S_7(NH)	$S_8(\beta)$	$S_9(\chi)$
S_1	8.042(226)[b]	0.002(108)	−0.048(53)	−0.011(64)	0.100(50)	−0.224(134)			
S_2		8.077(86)	0.302(34)	0.039(49)	0.195(19)	0.062(69)			
S_3			0.743(8)	−0.018(10)	−0.027(6)	−0.049(27)			
S_4				1.000(6)	0.181(12)	0.754(53)			
S_5					1.054(7)	0.837(25)			
S_6						5.427(106)			
S_7							7.894(37)	0.021(7)	0.042(8)
S_8								1.027(10)	0.061(4)
S_9									0.072(5)

a) Units are as follows. str.-str.: 10^5 (dyn/cm), str.-bend.: 10^{-3} (dyn), bend.-bend.: 10^{-11} (dyn cm). b) The figure in the parenthesis gives 1σ (standard deviation) in the unit corresponding to the last significant figure.

Force Constants and Normal Frequencies

Table 3 shows the force constants obtained for the two symmetry species. Some off-diagonal elements are not found to be determinable from our 77 sets. All of these, however, are taken to be actually very small judged from their physical meanings. The coupling constant between S_3 and S_5 has been found to be as small as -0.03×10^{-11} dyne cm. The corresponding off-diagonal element of methylamine was once estimated to be as big as 0.123×10^{-11} dyne cm[2] (see Table 4). This should now be revised; an *ab initio* study on methylamine by Pulay and Török[19] also gave a very small value to this off-diagonal element.

In the process of experimental force-constant determination, the definitions of non-totally symmetrical coordinates are sometimes ambiguous. Particularly the physical meanings of off-diagonal elements and their signs are not usually the subject of investigation. On the other hand, in the case of calculation using molecular orbital theory as in this study, the definitions of coordinates and related force constants with their signs are determined unambiguously in principle. This is another merit of such a theoretical study.

The calculated normal frequencies, ω, are shown in Table 5, where experimental geometry was used to calculate **G**-matrix (inverse kinetic energy matrix). We have no data of experimental normal frequencies to compare, except for torsional oscillation. Here a rather nice agreement has been obtained, *i.e.* $\omega_{obsd}=407$ cm^{-1} [7] while $\omega_{calcd}=457$ cm^{-1}.

In comparing the observed and calculated frequencies, the frequency difference between the normal and fundamental frequencies, which is caused by anharmonicity, should be taken into account. For a correction, Pulay & Török[19] reduced 10% of diagonal stretching force constants and 20% of diagonal bending force constants, with off-diagonal force constants fixed. With this correction to include the anharmonicity effectively, they reproduced the observed frequencies within the deviation of 40 cm^{-1} for the fundamental frequencies below 2000 cm^{-1}. We adopted the same empirical way in changing the calculated normal frequencies into "calculated fundamental frequencies." The results are given in Table 5 (see also Table 4).

NH_2 stretching and wagging have deviations as much as 100—200 cm^{-1}. The anharmonicity for the former might be underestimated, and that for the latter overestimated. These discrepancies may be removed by including polarization functions and or by configura-

TABLE 4. SOME OF THE AMINO-DEFORMATION FORCE CONSTANTS

CH_3NH_2[a]	S_2(NH_2 str.)	S_3(NH_2 sci.)	S_5(NH_2 wag.)
$S_2(\nu_2=3360$ cm$^{-1})$	6.444	0.305	0.034
$S_3(\nu_3=1623$ cm$^{-1})$		0.453	0.123
$S_5(\nu_5=780$ cm$^{-1})$			0.774
NH_2OH[b]	S_2	S_3	S_5
$S_2(\nu_2=3297$ cm$^{-1})$	7.269	0.302	0.195
$S_3(\nu_3=1605$ cm$^{-1})$		0.594	−0.027
$S_5(\nu_5=1115$ cm$^{-1})$			0.843

a) Determined by Hirakawa *et al.*[2] b) Calculated in the present work, and corrected on the basis of the Pulay & Török's proposal.[19]

TABLE 5. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES (ν_i) AND CALCULATED NORMAL FREQUENCIES (ω_i) OF HYDROXYLAMINE
(The potential energy distribution calculated on the force constant values obtained in the present work are also shown.)

A′	ν_i(obsd)	3656	3297	1605	1357	1115	895
	ν_i(calcd)	3602	3578	1569	1341	1021	888
	ω_i(calcd)	3797	3764	1836	1483	1125	981
S_1	OH-str.	99.6	0.2	0.1	0.2	0.0	0.5
S_2	NH-str.	0.2	99.9	0.5	0.6	1.2	0.4
S_3	HNH-bend.	0.0	0.0	61.4	24.2	15.6	1.4
S_4	NOH-bend.	0.0	0.0	3.3	55.8	42.2	16.5
S_5	ONH-bend.	0.0	0.0	28.8	3.0	64.7	26.1
S_6	NO-str.	0.0	0.0	0.0	3.0	1.3	131.2

A″	ν_i(obsd)	3350	—	386
	ν_i(calcd)	3618	1233	391
	ω_i(calcd)	3823	1409	457
S_7	NH-str.	99.9	0.0	0.5
S_8	NH_2 twist	0.1	97.6	10.8
S_9	Torsion	0.0	0.2	108.8

tion interaction calculation.

Now we can predict the twisting frequency in question. Estimating the maximum error, we predict that the frequency should be 1250±100 cm^{-1}. Giguére and Liu[6] observed, in their IR spectrum, a weak absorption at 1297 cm^{-1} on the shoulder of the OH bending band centered at 1350 cm^{-1}. They assigned this to $\nu_6+\nu_9$ combination band. In a solid state spectrum, a very weak absorption at 1287 cm^{-1} was assigned to $\nu_8+\nu_9$. It is possible, however, to assign these to the twisting mode. An *ab initio* MO study on methylamine by Pulay and Török[19] shows that NH_2 twisting mode and CH_3 rocking mode are so severely coupled to give positive combination of the two modes at 1335 cm^{-1}, and negative combination somewhere in the 880—1000 cm^{-1} region, with uncoupled original position around 1170 cm^{-1}. Therefore it is now certain that NH_2 twisting mode contributes to a band in the region of 1300 cm^{-1}.

The first order centrifugal distortion constants directly reflect the harmonic force field, and these were also calculated in our present study. The results are shown in Table 6. The most of the calculated values are in agreement with the experimental values at least in the order of magnitude.

Table 6. Centrifugal distortion constants (MHz)

	Obsd[15]	Calcd[a]
τ' aaaa	−17.306	−10.14
τ' bbbb	−0.3257	−0.263
τ' cccc	−0.2895	−0.251
T_1	−3.3744	−1.14
T_2	−0.31212	−1.78

a) Procedure II.

Dipole Moment Derivatives

The intensity of infrared fundamental band is represented by the formula,

$$A_i = \frac{N\pi g_i}{3c^2}\left|\frac{\partial^2 P}{\partial Q_i^2}\right|^2 \qquad (2)$$

where N is Avogadro's number, g_i the degeneracy of the i-th normal vibration, c the light velocity, P the dipole moment, and Q_i the normal coordinate of the i-th normal vibration. Therefore, $(\partial^2 P/\partial Q_i^2)^2$ is the experimentally determinable value. To investigate the physical meaning of the intensity we need to know $\partial P/\partial R_i$ which is related to $\partial P/\partial Q_i$ by the following formula,

$$\frac{\partial P}{\partial R_j} = \sum_i \left(\frac{\partial P}{\partial Q_i}\right) L_{ij}^{-1}, \qquad (3)$$

where $\boldsymbol{L}$ is the transformation matrix between internal (symmetry) coordinate R and normal coordinate Q, and can be obtained accurately when the vibrational analysis is completed.

Since it is difficult to determine the sign of $\partial P/\partial Q_i$ experimentally, and there is in general some ambiguity in the values of the off-diagonal elements $\boldsymbol{L}_{ij}$, the determination of the size of dipole moment derivative $\partial P/\partial R_j$ and its sign by *ab initio* calculations would have some significance. For example, near-Hartree-Fock calculation on NH_3[20] and CH_4[21] by Meyer and Pulay gave satisfactory results determining a set of signs of dipole moment derivatives. They stated that the dipole moment derivatives by *ab initio* calculations for bending coordinates are fairly stable for the choise of basis set, and estimated error is 20—30%.

Table 7. Dipole moment and its derivatives at equilibrium geometry

	μ_{total}	μ_x	μ_z
Expl.	0.592	0.060	0.582
ab initio	0.9181(5)	−0.0048(5)	0.9185(3)
A′-symmetry			
$\mu'_i=\frac{\partial\mu}{\partial S_i}$	μ'_{total}	μ'_x	μ'_z
1(OH str.)	−0.616(33)	−0.727(37)	−0.544(22)
2(NH_2 str.)	0.050(18)	0.245(21)	0.088(12)
3(NH_2 sci.)	0.588(12)	−1.267(13)	0.578(8)
4(OH bend.)	−1.290(11)	0.173(12)	−1.287(7)
5(NH_2 wag.)	1.443(6)	−1.189(7)	1.409(4)
6(NO str.)	1.515(21)	0.364(23)	1.457(13)
A″-symmetry			
$\mu'_i=\frac{\partial\mu}{\partial S_i}$	μ_{total}	μ'_x	μ'_y	μ'_z
7(NH_2 str.)	0.012(12)	−0.005(6)	0.268(5)	0.006(7)
8(NH_2 twist.)	0.017(6)	−0.005(3)	0.088(3)	0.012(4)
9(torsion)	0.011(8)	−0.015(4)	−1.195(4)	−0.004(5)

We present our results on NH_2OH in Tables 7 and 8. The dipole moment μ at various sets of coordinates were calculated, and by the use of an equation,

$$\mu = \mu_0 + \sum_i \left(\frac{\partial\mu}{\partial S_i}\right)\Delta S_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2\mu}{\partial S_i \partial S_j}\right)\Delta S_i \Delta S_j, \qquad (4)$$

the values of μ_0, $\partial\mu/\partial S_i$, and $\partial^2\mu/\partial S_i\partial S_j$ were determined by a least squares fit. The third term, with the second derivatives, was included (see Table 8) because some of them were determinable from our data set. The x, y, z axes were defined as in Fig. 2.

Strong intensities of OH bending and NH_2 wagging bands are obvious, and almost no intensity for NH_2 twisting is just as expected. It would be worthwhile to give the following two comments here:

1) The derivatives of the dipole components $\partial\mu_x/\partial S_i$, $\partial\mu_y/\partial S_i$,…… can be used to determine the band type —parallel or perpendicular—of each fundamental band, or, if it is a hybrid band, to determine the amount of contribution from each type.

2) When the amplitude of a stretching mode is set greater than 10^{-2} Å, the contribution from the second derivative is found to be appreciable. This can be accurate up to a few percent. This would allow us to estimate an intensity of some overtone and combination bands. To an intensity factor of overtone or combination transitions, the electrical anharmonicity (second derivative of dipole moment) and mechanical anharmonicity (anharmonicity of potential surface) are possible to contribute. So far,

TABLE 8. EXAMPLES OF SECOND DERIVATIVES OF DIPOLE MOMENT

$\frac{1}{2}\partial^2\mu_x/\partial S_i\partial S_j$					
OH str.	NH_2 str.	NH_2 sci.	OH bend.	NH_2 wag.	NO str.
−0.47(158)	−0.81(151)	−0.02(74)	3.06(90)	−2.01(35)	−0.16(187)
	−2.00(60)	0.44(48)	1.47(68)	−0.10(27)	0.20(96)
		−0.78(6)	0.13(14)	−1.90(8)	−0.02(38)
			0.68(4)	−0.17(16)	−1.91(74)
				−1.82(5)	1.49(35)
					1.45(75)

however, no systematic investigation has been done on them. We hope that *ab initio* calculation is valuable also in this field of research.

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