Hydrogen Deformation Vibrations[1]

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Introduction

The normal vibrations of molecules can conveniently be grouped into hydrogen vibrations and skeletal vibrations[2]. Of the former the stretching vibrations are observed in the 3 μ region sufficiently separated from skeletal frequencies, whereas the deformation vibrations appear in a region in which many skeletal vibrations give infrared and Raman frequencies. Therefore, it is desirable to distinguish the hydrogen deformation vibrations from the skeletal vibrations for the interpretation of the vibrational spectra in relation to the structure of molecules[3]. The present calculation has been made with the object of aiding in the assignment of these hydrogen deformation vibrations.

Outline of the Calculation

The calculation was made by Wilson's method[4], according to which we set up a secular equation of the type:

$$|\boldsymbol{GF}-\boldsymbol{E}\lambda| = 0,$$

where $\boldsymbol{G}$ and $\boldsymbol{F}$ are, respectively, the kinetic and the potential energy matrices. In this calculation we consider only that part of a molecule which is directly connected to the CH, CH_2, and CH_3 groups under consideration, because Nakagawa has shown that there is, in general, not much coupling between the hydrogen deformation vibrations and the skeletal vibrations[5]. For example, when we calculate the CH_2 deformation frequencies of CH_3CH_2Cl, we reduce the problem to the vibrations of C–CH_2–Cl.

The symmetry coordinates $\boldsymbol{S}$ obtained from the internal coordinates $\boldsymbol{R}$ by a linear transformation:

$$\boldsymbol{S} = \boldsymbol{UR}$$

are shown in Table I. Here $\boldsymbol{U}$ is an orthogonal matrix, α is a carbon valence angle, and 1, 2, 3, and 4 (subscripts) refer to the four bonds of carbon atom (see Fig. 1). For example, α_{12} denotes the carbon valence angle formed by the first and second bonds. The mode of each hydrogen deformation vibration is understood from the mathematical expression of the corresponding symmetry coordinate shown in Table I[6].

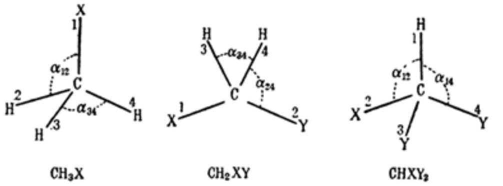

Fig. 1. Internal coordinates of CH_3X, CH_2XY and $CHXY_2$.

TABLE I

SYMMETRY COORDINATES OF HYDROGEN DEFORMATION VIBRATIONS

Molecule	Vibrational mode	Symmetry coordinate
CH_3X	CH_3 degenerate	$\begin{cases}\Delta(2\alpha_{34}-\alpha_{23}-\alpha_{24})/\sqrt{6}\\ \Delta(\alpha_{23}-\alpha_{24})/\sqrt{2}\end{cases}$
	CH_3 symmetric	$\Delta(\alpha_{12}+\alpha_{13}+\alpha_{14}-\alpha_{23}-\alpha_{24}-\alpha_{34})/\sqrt{6}$
	CH_3 rocking	$\begin{cases}\Delta(2\alpha_{12}-\alpha_{13}-\alpha_{14})/\sqrt{6}\\ \Delta(\alpha_{13}-\alpha_{14})/\sqrt{6}\end{cases}$
CH_2X_2, CH_2XY	CH_2 bending	$\Delta(4\alpha_{34}-\alpha_{13}-\alpha_{14}-\alpha_{23}-\alpha_{24})\sqrt{20}$
	CH_2 wagging	$\Delta(\alpha_{13}+\alpha_{14}-\alpha_{23}-\alpha_{24})/2$
	CH_2 twisting	$\Delta(\alpha_{13}-\alpha_{14}-\alpha_{23}+\alpha_{24})/2$
	CH_2 rocking	$\Delta(\alpha_{13}-\alpha_{14}+\alpha_{23}-\alpha_{24})/2$
CHX_3, $CHXY_2$	CH bending	$\begin{cases}\Delta(2\alpha_{12}-\alpha_{13}-\alpha_{14})/\sqrt{6}\\ \Delta(\alpha_{13}-\alpha_{14})/\sqrt{2}\end{cases}$

The matrices $\boldsymbol{G}_S$ and $\boldsymbol{F}_S$ in symmetry coordinates are obtained from the matrices $\boldsymbol{G}_R$ and $\boldsymbol{F}_R$ in internal coordinates through the transformations:

$$\boldsymbol{G}_S = \boldsymbol{UG}_R\boldsymbol{U}'$$
$$\boldsymbol{F}_S = \boldsymbol{UF}_R\boldsymbol{U}'$$

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[1] A part of this paper was presented at Gordon Research Conference on Infrared Spectroscopy, Meriden, New Hampshire, U.S.A. August, 1954.

[2] See, e.g., S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press, New York (1954 ; I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).

[3] As to previous researches on hydrogen deformation vibrations, see, e.g., N. Sheppard, *J. Chem. Phys.*, **16**, 690 (1948); **17**, 74 (1949); R.S. Rasmussen, *J. Chem. Phys.*, **16**, 712 (1948).

[4] E.B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[5] I. Nakagawa, *J. Chem. Soc. Japan*, **75**, 178, 535 (1954).

[6] The modes of these deformation vibrations are shown diagramatically in reference 5.

where U' is the transpose of U.

The diagonal terms G_{SS} of G-matrices are shown in Table II, where μ_C, μ_H, μ_X and μ_Y are the reciprocals of masses of the C, H, X and Y atoms, and r_H, r_C, r_X and r_Y are the reciprocals of the C–H, C–C, C–X and C–Y bond lengths. Furthermore, all the carbon valence angles are assumed to be tetrahedral. The underlined parts of the expressions of G_{SS} are independent of X and Y and contain μ_H which makes the diagonal terms much larger than the cross terms containing the reciprocals of masses of heavier atoms. Therefore, we may neglect the cross terms of G-matrices in the approximate calculation of hydrogen deformation frequencies.

In the case of F-matrices the ratio of diagonal terms to cross terms depends on the nature of the potential function. We used the function of the Urey-Bradley type[7], from which the diagonal terms of F-matrices are calculated as shown in Table II, where

$$J_{HH}=R_H^2(H_{HCH}+2/5F_{H\ldots H}),$$
$$J_{HX}=R_HR_X(H_{HCX}+c_{HX}F_{H\ldots X}).$$

and

$$c_{HX}=tt_1+1/10\,ss_1$$
$$t=(2\sqrt{2}/3)R_X/q_{HX},$$
$$t_1=(2\sqrt{2}/3)R_H/q_{HX},$$
$$s=(1/q_{HX})(R_H+1/3\,R_X),$$
$$s_1=(1/q_{HX})(R_X+1/3\,R_H),$$
$$q_{HX}=(R_H^2+R_X^2+2/3\,R_HR_X)^{\frac{1}{2}}.$$

Here H_{HCH} and H_{HCX} are force constants for the deformation of the HCH and HCX angles, $F_{H\ldots H}$ and $F_{H\ldots X}$ those for the changes of distances between the two nonbonded H atoms and between the nonbonded H and X atoms, R_H and R_X the C–H and C–X bond lengths, and k's the intramolecular tensions[7]. The values of force constants and intramolecular tensions are shown in Table III[2,8].

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[7] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

[8] See also T. Shimanouchi, *J. Chem. Soc. Japan*, **74**, 266 (1953); I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **22**, 759 (1954); I. Nakagawa, *J. Chem. Soc. Japan*, **76**, 540 (1955).

TABLE II

DIAGONAL TERMS OF G- AND F-MATRICES, G_{SS} AND F_{SS}

Molecule	Vibrational mode	G_{SS}	F_{SS}
CH_3X	CH_3 degenerate	$\underline{[(5/2)\mu_H+(8/3)\mu_C]r_H^2}$	$J_{HH}+(1/2\sqrt{2})k_1$
	CH_3 symmetric	$\underline{[2\mu_H+(16/3)\mu_C]r_H^2}$	$(1/2)(J_{HH}+J_{HX})+(3/2\sqrt{2})k_1$
	CH_3 rocking	$\underline{[\mu_H+(1/6)\mu_C]r_H^2}+(3/2)\mu_X r_X^2+\mu_C[(3/2)$ $\times r_X^2+r_Hr_X]$	$J_{HX}+(1/2\sqrt{2})k_1$
CH_2X_2	CH_2 bending	$\underline{[(5/2)\mu_H+(10/3)\mu_C]r_H^2}+(1/10)\mu_Xr_X^2$ $+(2/15)\mu_Cr_X^2-(4/3)\mu_Cr_Hr_X$	$(4/5)J_{HH}+(1/5)J_{HX}+(3/10\sqrt{2})k_2$
	CH_2 wagging	$\underline{[(3/2)\mu_H+3\mu_C]r_H^2}+(1/2)\mu_Xr_X^2+\mu_C[(1/3)r_X^2$ $+2r_Hr_X]$	$J_{HX}+(3/2\sqrt{2})k_2$
	CH_2 twisting	$\underline{(3/2)\mu_Hr_H^2}+(3/2)\mu_Xr_X^2$	$J_{HX}-(1/2\sqrt{2})k_2$
	CH_2 rocking	$\underline{[(1/2)\mu_H+(1/3)\mu_C]r_H^2}+(3/2)\mu_Xr_X^2+\mu_C(3r_X^2$ $+2r_Hr_X)$	$J_{HX}+(3/2\sqrt{2})k_2$
CH_2XY	CH_2 bending	$\underline{[(5/2)\mu_H+(10/3)\mu_C]r_H^2}+(1/20)(\mu_Xr_X^2$ $+\mu_Yr_Y^2)+(1/20)\mu_C(r_X^2+r_Y^2)$ $+(1/30)\mu_Cr_Xr_Y-(2/3)\mu_C(r_Hr_X+r_Hr_Y)$	$(4/5)J_{HH}+(1/10)(J_{HX}+J_{HY})$ $+(3/10\sqrt{2})k_2$
	CH_2 wagging	$\underline{[(3/2)\mu_H+3\mu_C]r_H^2}+(1/4)(\mu_Xr_X^2+\mu_Yr_Y^2)$ $+(1/4)\mu_C(r_X^2+r_Y^2)-(1/6)\mu_Cr_Xr_Y$ $+\mu_C(r_Hr_X+r_Hr_Y)$	$(1/2)(J_{HX}+J_{HY})+(3/2\sqrt{2})k_2$

Molecule	Vibrational mode	G_{SS}	F_{SS}
	CH_2 twisting	$\underline{(3/2)\mu_H r_H^2}+(3/4)(\mu_X r_X^2+\mu_Y r_Y^2)+(3/4)\mu_C(r_X^2+r_Y^2)-(3/2)\mu_C r_X r_Y$	$(1/2)(J_{HX}+J_{HY})-(1/2\sqrt{2})k_2$
	CH_2 rocking	$\underline{[(1/2)\mu_H+(1/3)\mu_C]r_H^2}+(3/4)(\mu_X r_X^2+\mu_Y r_Y^2)+(3/4)\mu_C(r_X^2+r_Y^2)+(3/2)\mu_C r_X r_Y+\mu_C(r_H r_X+r_H r_Y)$	$(1/2)(J_{HX}+J_{HY})+(3/2\sqrt{2})k_2$
CHX_3	CH bending	$\underline{[(3/2)\mu_H+(3/2)\mu_C]r_H^2}+\mu_X r_X^2+\mu_C[(1/6)r_X^2+r_H r_Y]$	$J_{HX}+(1/2\sqrt{2})k_3$
$CHXY_2$	CH bending (A′)	$\underline{[(3/2)\mu_H+(3/2)\mu_C]r_H^2}+(2/3)\mu_X r_X^2+(1/3)\mu_Y r_Y^2+\mu_C[(2/3)r_H r_X+(1/3)r_H r_Y+(2/3)r_X^2-(10/9)r_X r_Y+(11/18)r_Y^2]$	$(2/3)J_{HX}+(1/3)J_{HY}+(1/2\sqrt{2})k_3$
	CH bending (A″)	$\underline{[(3/2)\mu_H+(3/2)\mu_C]r_H^2}+\mu_Y r_Y^2+\mu_C[(1/6)r_Y^2+r_H r_Y]$	$J_{HY}+(1/2\sqrt{2})k_3$
CH_3–CH_3*	CH_3 degenerate	$\underline{(G_{SS})_0}$	$J_{HH}+(1/2\sqrt{2})k_1$
	CH_3 symmetric	$\underline{(G_{SS})_0}$	$(1/2)(J_{HH}+J_{HC})+(3/2\sqrt{2})k_1$
	CH_3 rocking	$(G_{SS})_0\pm\mu_C(3r_C^2+r_C r_H)\cos\theta$	$J_{HC}+(1/2\sqrt{2})k_1$
XCH_2 –CH_2X**	CH_2 bending	$(G_{SS})_0\pm[-2\mu_C\{(2/3)r_C r_H-(1/10)r_C^2-(1/30)r_C r_X\}\cos\theta]$	$(4/5)J_{HH}+(1/10)(J_{HX}+J_{HC})+(3/10\sqrt{2})k_2$
	CH_2 wagging	$(G_{SS})_0\pm(1/2)\mu_C[r_C^2+2r_C r_H-(1/3)r_C r_X]\cos\theta$	$(1/2)(J_{HX}+J_{HC})+(3/2\sqrt{2})k_2$
	CH_2 twisting	$(G_{SS})_0\pm[-(3/2)\mu_C(r_C^2-r_C r_X)\cos\theta]$	$(1/2)(J_{HX}+J_{HC})-(1/2\sqrt{2})k_2$
	CH_2 rocking	$(G_{SS})_0\pm[-(3/2)\mu_C\{r_C^2+r_C r_X+(2/3)r_C r_H\}\cos\theta]$	$(1/2)(J_{HX}+J_{HC})+(3/2\sqrt{2})k_2$

* $(G_{SS})_0$ signifies G_{SS} of CH_3X for X=C. The signs + and − refer, respectively, to the symmetric (A) and the anti-symmetric (B) vibrations to the C_2 axis. The azimuthal angle θ is taken as zero for the trans position.

** $(G_{SS})_0$ signifies G_{SS} of CH_2XY for Y=C.

TABLE III

VALUES OF FORCE CONSTANTS H AND F IN 10^5 dyn./cm. AND INTRAMOLECULAR TENSION k IN 10^{-11} dyn. cm.

Deformation constant H		Repulsion constant F		Intramolecular tension k							
H–C–H	0.40	H..(C)..H	0.10							CH_4	0.00
H–C–F	0.06	H..(C)..F	1.15	CH_3F	0.10	CH_2F_2	0.20	CHF_3	0.35	CF_4	0.45
H–C–Cl	0.05	H..(C)..Cl	0.80	CH_3Cl	0.05	CH_2Cl_2	0.10	$CHCl_3$	0.20	CCl_4	0.26
H–C–Br	0.04	H..(C)..Br	0.65	CH_3Br	0.03	CH_2Br_2	0.07	$CHBr_3$	0.15	CBr_4	0.25
H–C–I	0.04	H..(C)..I	0.52	CH_3I	0.02	CH_2I_2	0.04	CHI_3	0.10		
H–C–CX_3	0.15	H..(C)..CX_3	0.40	CH_3CX_3	0.05						
H–C–CH_3	0.25	H..(C)..CH_3	0.50					$CH(CH_3)_3$	0.03	$C(CH_3)_4$	0.04
H–C–C(≡)	0.21	H..(C)..C(≡)	0.50	CH_3CN	0.04	$CH_2(CN)_2$	0.07				
H–C–N	0.20	H..(C)..N	0.60	CH_3NC	0.05						

Although the diagonal terms of F-matrices are not always large as compared with the cross terms, approximate calculations of hydrogen deformation frequencies have been made from the product $G_{SS}F_{SS}$ of the diagonal terms shown in Table II. The difference between the computed and the observed frequencies has been found to be less than 5%[9].

In the higher approximations we have taken into account the effect of the cross terms in the following form:

$$(GF)_{SS}=G_{SS}F_{SS}+a,$$
$$\lambda=(GF)_{SS}+b,$$

where a and b are the correction terms[9].

Results for CH Deformation Frequencies

The calculations have been made for many molecules, including those of methane and ethane derivatives and their deuterated compounds. The computed values have been shown to be in good agreement with those observed[10]. The frequency ranges of hydrogen deformation vibrations thus obtained are shown in Table IV, where those of fluorine compounds have been omitted, because they show abnormal values[10].

The inspection of the expressions of G_{SS} and F_{SS} shown in Table II, together with the numerical values given in Table IV, gives us information on the specific features of hydrogen deformation vibrations, which are useful in the assignment of these vibrations. Some of these features are listed in the following:

TABLE IV

THE FREQUENCY RANGES OF HYDROGEN DEFORMATION VIBRATIONS IN cm^{-1}

Molecule*	Vibrational mode	Frequency range
CH_3X	CH_3 degenerate	ca. 1450
	CH_3 symmetric	1250–1400
	CH_3 rocking	900–1150
CH_2X_2 & CH_2XY	CH_2 bending	1350–1450
	CH_2 wagging	1100–1350
	CH_2 twisting	1000–1300
	CH_2 rocking	700–1000
CHX_3 & $CHXY_2$	CH bending	1100–1350
CH_3CX_3	CH_3 degenerate	ca. 1450
	CH_3 symmetric	1370–1390
	CH_3 rocking	1000–1100
CH_3CHX_2 & CH_3CH_2X	CH_3 degenerate (A' & A'')	ca. 1450
	CH_3 symmetric	1370–1390
	CH_3 rocking (A' & A'')	1000–1100
CH_3COX	CH_3 degenerate (A' & A'')	ca. 1420
	CH_3 symmetric	ca. 1360
	CH_3 rocking (A' & A'')	1000–1100
$(CH_3)_2CHX$	CH_3 degenerate (A' & A'')	ca. 1450
	CH_3 symmetric (A' & A'')	1370–1390
	CH_3 rocking (A' & A'')**	900–1150
	C–C stretching**	870–890 (A'), 1120–1140 (A'')
	CH bending	variable (A'), 1320–1340 (A'')
$(CH_3)_3CX$	CH_3 degenerate (A_1 & E)	ca. 1450
	CH_3 symmetric (A_1 & E)	1370–1390
	CH_3 rocking (A_1 & E)**	900–1150
	C–C stretching (A_1 & E)**	800–810 (A_1), 1220–1240 (E)
XCH_2CH_2X	CH_2 bending	1400–1450
	CH_2 wagging	1150–1350
	CH_2 twisting	1000–1300
	CH_2 rocking	700–1000 $B_g > A > B > A_u$

* Fluorine compounds are excluded.

** The C–C stretching and CH_3 rocking vibrations are coupled with each other considerably in these cases.

(1) The CH_3 degenerate deformation vibrations and the CH_2 bending vibrations appear in narrow frequency regions. Furthermore, these regions are separated from those of other hydrogen deformation vibrations.

(2) The CH_3 symmetric deformation vibrations also appear in a narrow frequency range, when this group is directly connected to a carbon atom as CH_3–C–.

(3) The frequency values of the hydrogen deformation vibrations in the same series (e.g. CH_3X, CH_2X_2 and CHX_3) decrease in the following order: CH_3 degenerate deformation $>CH_2$ bending$>CH_3$ symmetric deformation $>CH_2$ wagging$>$CH bending$>CH_2$ twisting $>CH_3$ rocking $>CH_2$ rocking. In some cases

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[9] I. Nakagawa, *J. Chem. Soc. Japan*, **75**, 1259 (1954).

[10] I. Nakagawa, ibid., **76**, 540 (1955).

the order of the CH_2 wagging frequency and the CH_3 symmetric deformation frequency may be reversed.

(4) The CH bending frequencies of CHX_3 and CHY_3, which are degenerate, are split into two frequencies A' and A'' in $CHXY_2$ where A'' has nearly the same frequency as the degenerate frequency of CHY_3 and A' has a value lying between those of CHX_3 and CHY_3 but closer to that of CHX_3.

(5) According to the result of the similar calculation made for molecules of the type, $XH_2C{-}CH_2X$, the two deformation frequencies, one symmetric and the other antisymmetric to the C_2 axis, are not much different from each other and are not sensitive to the change of azimuthal angle of the internal rotation about the C–C axis, except for the CH_2 rocking frequencies. Furthermore, the selection rules for the rocking frequencies are quite different for the trans, gauche and cis forms. The frequency values of the rocking vibrations decrease in the following order: B_g(*trans*) > *A*(*gauche*) > *B*(*gauche*) > A_u (*trans*). The observation of rocking frequencies provides important experimental data of the optical isomerism of a new type described in previous notes[11].

NH_3-Deformation Frequencies in Ammine Complexes

When the NH_3 group is coordinated about a central metal atom in coordination complexes such as $[Co(NH_3)_6]Cl_3$, we expect the appearance of three deformation frequencies similar to those of the CH_3 deformation frequencies. Actually we have found in these complexes three frequencies at about 1610, 1330 and 830 cm^{-1} and these are assigned, respectively, to the degenerate deformation, symmetric deformation and rocking vibrations as shown in a previous paper[12]. There we did not describe the procedure of the calculation at all, but it is easily seen that this is quite similar to that of the calculation of CH_3 deformation vibrations of CH_3X shown in Table I. The force constants used in this calculation are shown in Table V.

TABLE V

THE VALUES OF FORCE CONSTANTS *H* AND *F* IN 10^5 DYNES/CM. AND INTRAMOLECULAR TENSION *k* IN 10^{-11} dyn. cm.

H		*F*		*k*
H–N–H	0.54	H..(N)..H	0.06	−0.04
H–N–Co	0.18	H..(N)..Co	0.10	

It is to be noted that of these five constants H_{HNH}, $F_{H..(N)..H}$ and *k* can also be used for the calculation of the normal frequencies of ammonia, NH_3, ammonium ion, NH_4^+ and their deuteration products, ND_3 and ND_4^+. Therefore, the reasonableness of their values can be checked by the normal frequency calculations for these compounds and ions. As shown in Table VI the calculated values are in good agreement with the observed values and consequently, these constants are concluded to have reasonable values.

TABLE VI*

CALCULATED AND OBSERVED FREQUENCIES IN cm^{-1} OF NH_3, ND_3, NH_4^+ AND ND_4^+

	NH_3		ND_3	
	Calc.	Obs.	Calc.	Obs.
A_1	3333	3336	2374	2419
	951	950	724	749
E	3410	3414	2506	2555
	1630	1628	1188	1191
	NH_4^+		ND_4^+	
	Calc.	Obs.	Calc.	Obs.
A_1	3041	3041	2150	2214
E	1710	1710	1209	1215
T	3138	3138	2321	2350
	1403	1403	1049	1066

* Evidently for the calculation of these frequencies the N–H stretching force constants (6.30×10^5 dynes/cm. for NH_3 and 5.26×10^5 dynes/cm. for NH_4^+) are needed in addition to the three constants mentioned above.

Using the force constants shown in Table V, the frequencies of the NH_3 degenerate deformation, symmetric deformation and rocking vibrations of $[Co(NH_3)_6]Cl_3$ have been calculated and compared with the observed values in Table VII. The agreement between the computed and observed values is good and consequently our assign-

TABLE VII

CALCULATED AND OBSERVED DEFORMATION FREQUENCIES IN CM^{-1} OF THE NH_3 AND ND_3 LIGANDS

Vibrational mode	$[Co(NH_3)_6]Cl_3$		$[Co(ND_3)_6]Cl_3$	
	Calc.	Obs.	Calc.	Obs.
Degenerate	1579	1610	1156	1162
Symmetric	1340	1330	1021	1024
Rocking	854	835	628	outside the NaCl region

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[11] J. V. Quagliano and S. Mizushima, *J. Am. Chem. Soc.*, **75**, 6084 (1953). See also S. Mizushima, I. Nakagawa, I. Ichishima and T. Miyazawa, *J. Chem. Phys.*, **22**, 1614 (1954).

[12] S. Mizushima, I. Nakagawa and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

ment has been shown to be correct. Furthermore, this assignment has been checked by observing the isotopic shift of these frequencies[12]. As shown in the same table, the observed frequencies of the deformation vibrations of the ND_3 ligand are in good agreement with those calculated from the isotopic relations.

Some authors have explained these bands as arising from the metal-ligand vibrations of the octahedral cation[13]. However, from our calculation it has been shown that the assignment made in this paper is more reasonable.

From the result of the present research we can conclude that the metal-to-ligand bond should be fairly covalent in metal ammine complexes. If this bond were ionic, we could conclude that there are no rocking vibrations of the NH_3 group.

Summary

The CH, CH_2 and CH_3 deformation frequencies in various organic compounds and the NH_3 deformation frequencies in metal ammine complexes have been calculated based on the Urey-Bradley field. The fact that diagonal terms of G-matrices for these vibrations are much larger than the cross terms makes the approximate calculation quite easy. The frequency range of each of these vibrations has been tabulated and their specific features have been pointed out, which will aid in the assignment of the frequencies observed for many organic compounds and metal ammine complexes.

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[13] H.G. Hill and A.F. Rosenberg, *J. Chem. Phys.*, 22, 148 (1954).