STRUCTURE OF FORMAMIDE AND ITS FORCE CONSTANTS

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I. Introduction

Formamide is the simplest of the molecules in the group of amides and polypeptides. The structure of formamide has been a matter for discussion for some time, as to whether the molecule is planar or non-planar and one with a certain low symmetry C_s. Some results based on microwave data[1] indicate that the molecule does not possess any symmetry. On the basis of infra-red and Raman data Evans[2] has attempted to assign all the fundamental frequencies of formamide.

The molecule is considered to be a non-planar one having C_s symmetry with HCO and N atoms in one plane and the NH_2 group oriented in such a way that the two hydrogen atoms are symmetrically disposed about the O $\diagdown$ $\diagup$ C—N plane, one above and the other below. But the X-ray studies H of the crystalline formamide by Ladell and Post[3] indicate that the molecule possesses a planar or nearly planar structure. The study of the microwave spectra of four isotopic species carried out by Kurland and Wilson[4] showed that the molecule has completely planar structure. But more accurate studies of seven isotopic species of formamide by Costain and Dowling[1] have resulted in a new model which is slightly non-planar and has no symmetry.

Treating the molecule as having a triatomic bent structure Thomas[5] has confirmed the non-planar structure for the vapour by evaluating the force constants with a mixed valence force symmetry co-ordinates. Later assuming a potential function of Urey-Bradley type and treating the molecule as a three-body problem Miyazawa, Shimanouchi and Mizushima[6] have calculated the three skeletal frequencies and the ratios of amplitudes. They have recently[7] applied the same treatment to the molecule taking it as a six-body problem.

The object of the present investigation is to calculate the fundamental frequencies of formamide by subjecting the molecule to normal co-ordinate

treatment using a most general quadratic potential function and thus to evaluate the force constants. A comparison of the observed and calculated frequencies has helped the authors to check the earlier assignments and to some extent confirm the slightly non-planar structure of the molecule.

II. SYMMETRY CONSIDERATIONS

To start with, the molecule was treated as an unsymmetrical planar molecule as proposed by Kurland and Wilson. Later the entire molecule was considered as one having C_s symmetry. This procedure did not yield correct results. The slightly non-planar structure with only a part of the molecule possessing a C_s symmetry was an adequate assumption and the values of the frequencies obtained on this basis were found to agree with the observed ones to a close degree. The model assumed by the authors is similar to that given by Costain and Dowling[1] but with the alterations that the N—H bond lengths are taken as equal and the three angles at the N atom are considered as equal. According to Costain and Dowling the

four atoms in $\overset{\displaystyle O}{\underset{\displaystyle H}{\diagdown}}C-N$ are co-planar and the NH_2 group is oriented in such

a way that the H_2N—C group forms a shallow pyramid analogous to that of ammonia and methylamine. The molecule as a whole does not possess

any symmetry. But when split into two groups one being $H_2N-C\overset{\displaystyle H}{\underset{\displaystyle O}{\diagup\diagdown}}$

and the other $\overset{\displaystyle H}{\underset{\displaystyle H}{\diagdown}}N-R$ where R is CHO group, each one of these parts

belongs to C_s symmetry group, the former having a planar structure and the latter pyramidal. During the first part of the calculations, NH_2 is considered as a single mass and thus the plane of symmetry is the plane of the molecule itself. For the second part CHO is considered as single mass R and the plane o f the symmetry would be the plane passing through N—R and bisecting the angle H—N—H. The molecule is represented in Fig. 1 and its two parts are shown in Figs. 2 and 3.
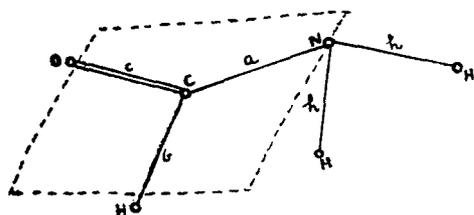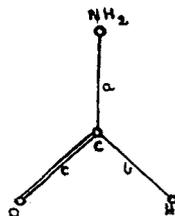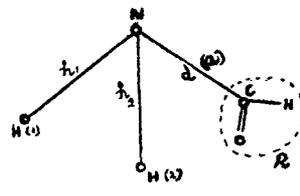

FIG. 1.   FIG. 2.   FIG. 3.

III. Normal Co-ordinate Treatment

A normal co-ordinate treatment was carried out by the Wilson's F–G matrix method. The planar part of the molecule will have six fundamentals with the distribution $5A' + 2A''$ and the pyramidal part with a distribution $4A' + 2A''$. All the fundamentals are active both in infra-red and Raman. In the planar part A'' belongs to CH out of plane mode and in the pyramidal part out of the two A'' vibrations one is asymmetric stretch and the other is a twisting mode. The symmetry co-ordinates which are orthonormal linear combinations of the internal co-ordinates are given below.

The symmetry co-ordinates for A' types of vibrations in the planar parts are:

$$R_1 = \triangle a$$
$$R_2 = \triangle b$$
$$R_3 = \triangle c$$
$$R_4 = 1/\sqrt{6}\,(2\triangle ab - \triangle ac - \triangle bc).$$
$$R_5 = 1/\sqrt{2}\,(\triangle bc - \triangle ac).$$

For A'' type

$$R_6 = k\triangle \gamma$$

where a, b and c are the changes in the bond distances of the bonds $C-NH_2$, $C-H$ and $C=O$ respectively and ab, bc and ca are the changes in the interbond angles $\langle$ N—C—H, $\langle$ H—C=O and $\langle$ O=C—N respectively.

The most general quadratic potential energy function used has the coefficients given in Table I.

TABLE I

	$\triangle a$	$\triangle b$	$\triangle c$	$\triangle ab$	$\triangle bc$	$\triangle ca$
$\triangle a$	f_a					
$\triangle b$	f_a^b	f_b				
$\triangle c$	f_a^c	f_b^c	f_c			
$\triangle ab$	f_a^{ab}	f_b^{ab}	f_c^{ab}	f_{ab}		
$\triangle bc$	f_a^{bc}	f_b^{bc}	f_c^{bc}	f_{ab}^{bc}	f_{bc}	
$\triangle ca$	f_a^{ca}	f_b^{ca}	f_c^{ca}	f_{ab}^{ca}	f_{bc}^{ca}	f_{ca}

According to the notations used in the symmetry co-ordinates and the force constants 'f' used in Table I, an example of the possible types of potential constants of various interactions is given below.

f_a = C—N stretching constant.

f_a^b = C—N and C—H bond-bond interaction constant.

f_a^{bc} = C—N and ⟨ O=C—H bond ⟨ angle interaction constant.

f_{ab}^{ca} = ⟨ N—C—H and ⟨ N—C=O angle-angle interaction constant.

In the pyramidal part the symmetry co-ordinates for the A′ type are:

$R_1 = \triangle d$

$R_2 = 1/\sqrt{2} (\triangle h_1 + \triangle h_2)$

$R_3 = 1/\sqrt{6} (2 \triangle a - \triangle \beta_1 - \triangle \beta_2)$

$R_4 = 1/\sqrt{3} (\triangle a + \triangle \beta_1 + \triangle \beta_2)$

For A″ type

$R_5 = 1/\sqrt{2} (\triangle h_1 - \triangle h_2)$

$R_6 = 1/\sqrt{2} (\triangle \beta_1 - \triangle \beta_2)$

where

$h_1 = h_2 = $ N—H bond distance and $d = $ N—C bond distance, $a = $ ⟨ H—N—H and $\beta_1 = \beta_2 = $ ⟨ H—N—C.

The coefficients of the general type of quadratic potential function for the pyramidal part are given in Table II.

TABLE II

	$\triangle d$	$\triangle h_1$	$\triangle h_2$	$\triangle a$	$\triangle \beta_1$	$\triangle \beta_2$
$\triangle d$	f_d					
$\triangle h_1$	$f_{h_1}^d$	f_{h_1}				
$\triangle h_2$	$f_{h_2}^d$	$f_{h_2}^{h_1}$	f_{h_2}			
$\triangle a$	f_a^d	$f_a^{h_1}$	$f_a^{h_2}$	f_a		
$\triangle \beta_1$	$f_{\beta_1}^d$	$f_{\beta_1}^{h_1}$	$f_{\beta_2}^{h_2}$	$f_{\beta_1}^a$	f_{β_1}	
$\triangle \beta_2$	$f_{\beta_2}^d$	$f_{\beta_2}^{h_1}$	$f_{\beta_2}^{h_2}$	$f_{\beta_2}^a$	$f_{\beta_2}^{\beta_1}$	f_{β_2}

N.B.—Since $f_i^j = f_j^i$ the elements above the diagonal are not written in Tables I and II.

From the potential energy matrices and the matrices formed from the coefficients contained in the symmetry co-ordinates the F matrix elements are obtained for both the planar and the pyramidal parts. The elements of the G matrix for both the parts of the molecule are obtained separately with the help of Decius Tables.[8] The values of the bond distances and interbond angles and masses of different atoms used in the calculations of G matrices are given in Table III.

TABLE III

Structural parameters and masses of different atoms of formamide

Bond	Bond length	Interbond angle	Mass
N—H	1·014 Å	$\langle$ N—C=O 123° 48'	$M_c = 12\cdot01$ awu.
N—C	1·376 Å	$\langle$ N—C—H 113° 14'	$M_o = 16\cdot00$ awu.
C—H	1·102 Å	$\langle$ O=C—H 122° 58'	$M_H = 1\cdot008$ awu.
C=O	1·190 Å	all angles at N 118° 53'	$M_N = 14\cdot008$ awu.

The force constants used in the present calculations were transferred from the related molecules in the first instance and appropriate variations in their values were made so that they might lead to a close fit between the observed and the calculated values of the fundamental frequencies of formamide. The force constants for the planar and the pyramidal parts are given in Table IV.

The secular equation $FG - E\lambda = 0$ for the A' type of the planar part has the dimensionality of five and that of the pyramidal part four. The determinants were expanded by Denielewsky's method. The frequencies of the planar part are not sensitive to the bond-angle interaction force constants. It has also been observed that among the elements of F matrices F_{45} of the planar part and F_{34} of the pyramidal part are very critical.

The observed and the calculated values of the fundamental frequencies of the planar part are given in Table V. The observed frequencies given in this paper are taken from Evans.[2] He has given the infra-red frequencies for the vapour phase. The Raman frequencies for the liquid phase are taken from Puranik and Venkata Ramiah.[9]

Table IV

Force constants for formamide*

Planar part		Pyramidal part	
f_a	7·30	f_d	7·30 and 9·30
$f_a{}^b$	1·50	$f_d{}^{h_1}$	0·58
$f_a{}^c$	0·40	$f_d{}^\alpha$	−0·20
f_b	10·50	$f_d{}^{\beta_1}$	0·10
$f_b{}^c$	0·40	$f_d{}^{\beta_2}$	0·10
f_c	4·50	f_h	6·80 ($h_1 = h_2 = h$)
f_{ab}	1·48	f_β	1·14 ($\beta_1 = \beta_2 = \beta$)
f_{bc}	0·81	$f_\alpha{}^{\beta_1}$	0·68 ($f_\alpha{}^{\beta_1} = f_\alpha{}^{\beta_2}$)
f_{ca}	0·47	$f_{\beta_2}{}^{\beta_1}$	0·605

* Bond-bond interaction constants are in md/A, bond-angle interaction constants in md/rad and angle-angle ones are given in mdA/rad.[2]

Table V

Fundamental frequencies of the planar part (in cm.$^{-1}$)

Mode	Observed		Calculated
	Infra-red	Raman	
ν_1 (δ_{OCN})	660	610	666
ν_2 (ν_{C-N})	1253	1312	1253
ν_3 (δ_{C-H})	1378	1391	1396
ν_4 ($\nu_{C=O}$)	1740	1716	1721
ν_5 (ν_{C-H})	2852	2883	2864

IV. Wagging and Twisting Modes

For the pyramidal part of the molecule although the force constant of the bond-bond interaction are comparable with the other related mole-

cules, the angle and the angle-angle interaction terms are considerably high. This was necessitated to enhance the value of the wagging frequency which consistently remained below 300 cm.$^{-1}$ Even with such an alteration it was found difficult to obtain a value of the order of 1060 cm.$^{-1}$, which has been assigned to a wagging mode by Evans. Therefore the authors propose to assign a lower value of the order of 600 cm.$^{-1}$ to the wagging mode. The bending, wagging and twisting modes of the molecule are represented in Fig. 4.

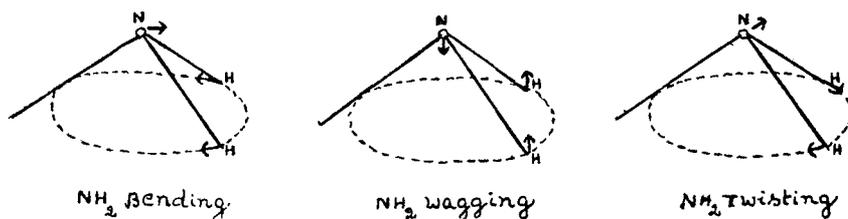NH$_2$ Bending.   NH$_2$ wagging   NH$_2$ Twisting

Fig. 4.

This assignment is further justified by the fact that in most of the peptide link compounds, the out-of-plane NH deformation is of the order of 600–800 cm.$^{-1}$ Kessler and Sutherland[10] have assigned the broad band from 800–650 cm.$^{-1}$ with a maximum at 700 cm.$^{-1}$ to the NH deformation vibration in which the hydrogen atom moves perpendicular to the plane of the peptide group. Moreover, in all these cases the wagging modes are found to be strong in infra-red and weak in Raman effect. On the contrary the band at 1065 cm.$^{-1}$ in formamide is found to be of considerable intensity in Raman effect and weak in infra-red spectrum as recorded by Puranik and Venkata Ramiah.[9] Therefore, the 1065 cm.$^{-1}$ band in the infra-red and 1096 cm.$^{-1}$ line in Raman could be more appropriately assigned to the twisting mode, rather than the 1190 cm.$^{-1}$ as assigned by Evans. The 1190 cm.$^{-1}$ band is very weak in infra-red in liquid formamide and in solutions of CH$_3$CN. The recent workers[9] in the field have not recorded even a trace of this band in infra-red. If the band exists in the spectrum of the vapour as reported by Evans as a very weak band, it might be due to a combination tone.

The high value of the interaction constants can be attributed to the large amount of coupling between different modes of vibration. The observed and the calculated values of the frequencies for the pyramidal part using $f_d = 7\cdot3$ md/A are given in Table VI.

Table VI

Fundamental frequencies (cm.$^{-1}$) of the pyramidal part

Mode	Type	Observed		Calculated
		Infra-red	Raman	
ν_1 (δ_{NH_2}) wagging	A′	..	..	664
ν_2 (ν_{C-N})	A′	1253	1313	1108
ν_3 (δ_{NH_2})	A′	1572	1599	1575
ν_4 (ν_{N-H})	A′	3450	3456	3433
ν_5 (δ_{NH_2}) Twisting	A″	1065	1096	1064
ν_6 (ν_{N-H}) assym. str.	A″	3545	..	3557

The calculations for the pyramidal part are based upon the assumption that the group COH acts as a solid mass. Therefore the C—N frequency calculated for the planar part corresponds to just C—N whereas in the pyramidal part it corresponds to HOC—N. It is seen from Tables V and VI that with $f_d = 7 \cdot 3$ md/A in the two cases the frequency is reduced from 1253 cm.$^{-1}$ in the planar to 1108 cm.$^{-1}$ in the pyramidal part. In order to ascertain the effect of mass M_R linked to the nitrogen atom, on the various frequencies, three sets are worked out with different values of M_R. A comparison of the values thus obtained is given in Table VII.

Table VII

Effect of mass on the frequencies

Mode	$f_d = 7 \cdot 3$ md/A			$f_d = 9 \cdot 3$ md/A
	$M_R = 12 \cdot 01$ (C)	$M_R = 29$ (COH)	$M_R = \infty$	$M_R = 29$ (COH)
δ_{NH_2} (wagging)	669	664	650	665
ν_{R-N} (stretch)	1348	1108	906	1246
δ_{NH_2} (bending)	1576	1575	1575	1580
ν_{N-H} (stretch)	3434	3433	3433	3433

From Table VII it is evident that except for the R—N stretching where R is CHO, the other frequencies remain unaltered with the change of mass M_R. It follows that taking the aggregate mass of CHO group at point C is not valid as far as C—N frequency is concerned, when the force constant is transferred from the planar part. In order to arrive at the observed frequency by this process of evaluation it is seen from Table VII that the effective mass is reduced from the aggregate one and lies in between the values $M_R = 29$ which is the aggregate mass and $M_R = 12 \cdot 01$ which is the mass of C only. On the other hand, if the effective mass is assumed to be that of CHO group, the observed frequency for the R—N stretch could be arrived at by calculation using a force constant $f_d = 9 \cdot 3 \, md/A$. It is also seen from Table VII, with this enhanced force constant the variation in the magnitude of the other frequencies is negligible.

In all eleven out of twelve fundamental frequencies of formamide have been calculated. Six of them $(5A' + A'')$ are for the planar part and the other six $(4A' + 2A'')$ for the pyramidal part but since C—N is common to both, only eleven have been evaluated. With the addition of torsional frequency of the NH_2 group at 765 cm.$^{-1}$—as given by Evans—all the twelve frequencies are accounted for.

V. Summary

A new procedure has been adopted in subjecting formamide—a molecule which has no symmetry—to normal co-ordinate treatment by the Wilson's F—G matrix method. The molecule is split into two parts for the purposes of calculation. One part is $\begin{smallmatrix} O \\ \diagdown \\ \diagup \\ H \end{smallmatrix}C-NH_2$ and the other is $R-N\begin{smallmatrix} \diagup H \\ \diagdown \\ H \end{smallmatrix}$ where R is the CHO group. Both the parts have C—N bond in common. Assuming the part one to be planar and the part two to be pyramidal as suggested by Costain and Dowling, the normal co-ordinate treatment of both the parts has been carried out and the fundamental frequencies calculated. The close agreement between the observed and the calculated values confirms the non-planar structure of formamide. Among all the fundamental frequencies, the frequency due to C—N stretch alone appears to be mass sensitive. On the basis of all these considerations some of the frequencies have been assigned to the wagging and twisting modes, which are different from those that are assigned by Evans.

VI. REFERENCES

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