Infrared Spectra and Normal Vibrations of N-Methylformamides $HCONHCH_3$, $HCONDCH_3$, $DCONHCH_3$ and $DCONDCH_3$

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A number of investigations have been made of the molecular structure and the vibrational spectra of the *N*-methylformaide, $HCONHCH_3$[1-5], which is the simplest molecule containing an NH–CO group. It has been shown that the Raman and infrared spectra of *N*-methylformamide and *N*-deuterated *N*-methylformamide in the liquid state can be interpreted solely in terms of the trans planar model for the molecule[1-4]. The vibrational assignments for the observed frequencies proposed by various

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[1] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 121, 321, 529, 619 (1956).

[2] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956).

[3] D. E. DeGraaf and G. B. B. M. Sutherland, ibid., **26**, 408 (1957).

[4] R. L. Jones, *J. Mol. Spectroscopy*, **2**, 581 (1958).

[5] R. A. Rusell and H. W. Thompson, *Spectrochim. Acta*, **8**, 138 (1956).

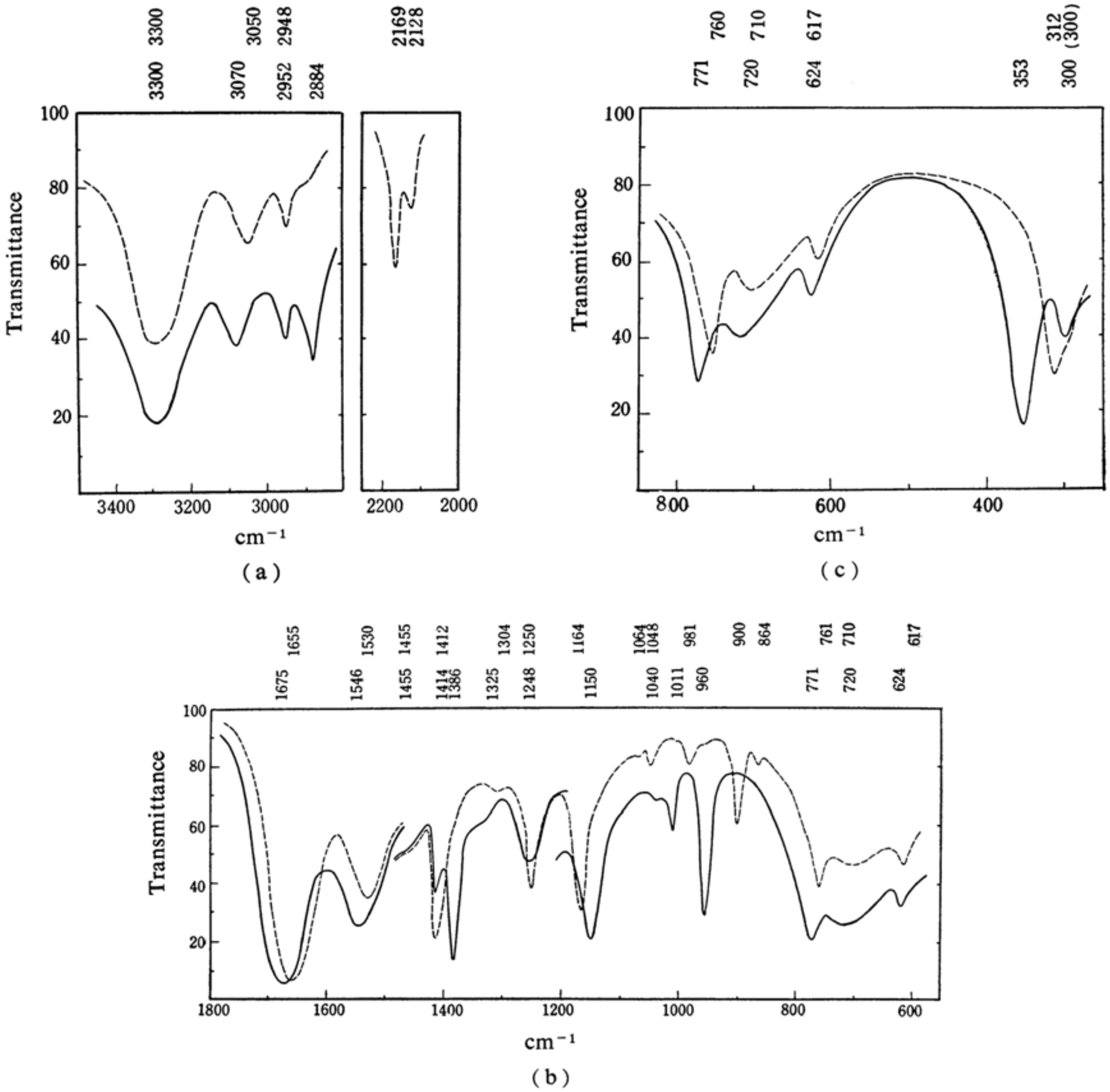

Fig. 1. Infrared spectra of $HCONHCH_3$ and $DCONHCH_3$ in the liquid state; (a) 3500~2000 cm^{-1}, (b) 1800~550 cm^{-1}, (c) 850~250 cm^{-1}, —— $HCONHCH_3$, ---- $DCONHCH_3$.

authors differ somewhat, particularly for the bands found in the region below 1100 cm^{-1}.

In order to eliminate ambiguities in the vibrational assignment and to make a detailed analysis of the nature of the normal vibrations of this molecule, the present author has prepared three other deuterated *N*-methylformamides, i. e., $HCONDCH_3$, $DCONHCH_3$ and $DCONDCH_3$, as well as $HCONHCH_3$, and has measured the infrared spectra of these compounds in the region from 3600 to 260 cm^{-1}. Furthermore, the in-plane and out-of-plane normal vibrations of this molecule have been calculated for all of the isotopic species as a nine-body problem, assuming the trans planar configuration (C_s). The Urey-Bradley force field has been employed in the calculation of the in-plane vibrations[6]. To compute the out-of-plane vibrations, this field has been modified by introducing six other force constants associated with the CH and NH out-of-plane and the torsional coordinates. Twenty-seven force constants have been determined, so that all the observed frequencies (sixty-four in number, excepting the hydrogen stretching vibrations) are explained. With these force constants, the vibrational mode and the potential energy distribution among the symmetry coordinates have been calculated for each normal vibration.

From his analysis of the band contours of

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

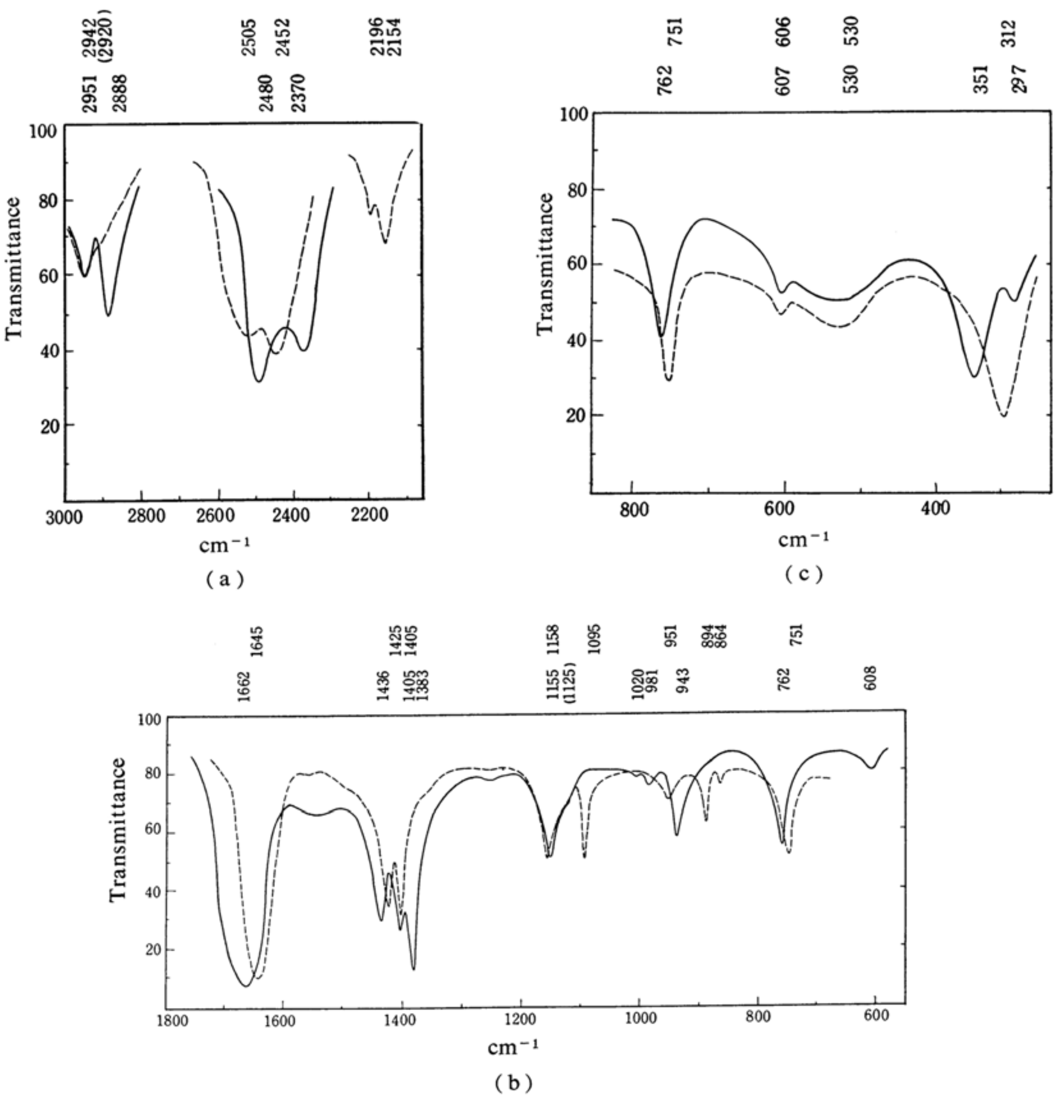

Fig. 2. Infrared spectra of $HCONDCH_3$ and $DCONDCH_3$ in the liquid state; (a) 3000~2000 cm⁻¹, (b) 1800~550 cm⁻¹, (c) 850~250 cm⁻¹, ——$HCONDCH_3$, ----, $DCONDCH_3$.

N-methylformamide in the vapor phase, Jones reached the conclusion that this molecule takes the cis form in the vapor phase[4)][*1]. It is, therefore, interesting to calculate the normal vibrations of the cis form and to see how each normal mode changes in these two isomeric forms. Such a calculation has been made for the in-plane vibrations of the cis form; the values of the force constants are taken to be the same as those of the trans form.

The present paper contains the results of these measurements and calculations and a detailed discussion of the nature of the normal vibrations of the molecule. The transferability of the values of the force constants between related molecules is also discussed.

Experimental

***N*-Methylformamide $HCONHCH_3$.**—This compound was prepared by the reaction of methylformate and methylamine dissolved in methanol, and it was purified by distillation several times under reduced pressure. B. p. 61°C/3.5 mmHg.

***C*-Deuterated *N*-Methylformamide $DCONHCH_3$.**—This compound was prepared from $DCOOCH_3$ and methylamine dissolved in methanol. $DCOOCH_3$ was obtained from heavy formic acid and methanol by the method shown in Ref. 8.

[*1] The structure is still a subject of controversy. Miyazawa has pointed out that the spectra in the vapor phase may be explained by assuming the molecule to be predominantly in the trans form[7)].

7) T. Miyazawa, *J. Mol. Spectroscopy*, **4**, 155 (1960).

8) R. F. Curl, Jr., *J. Chem. Phys.*, **30**, 1529 (1959).

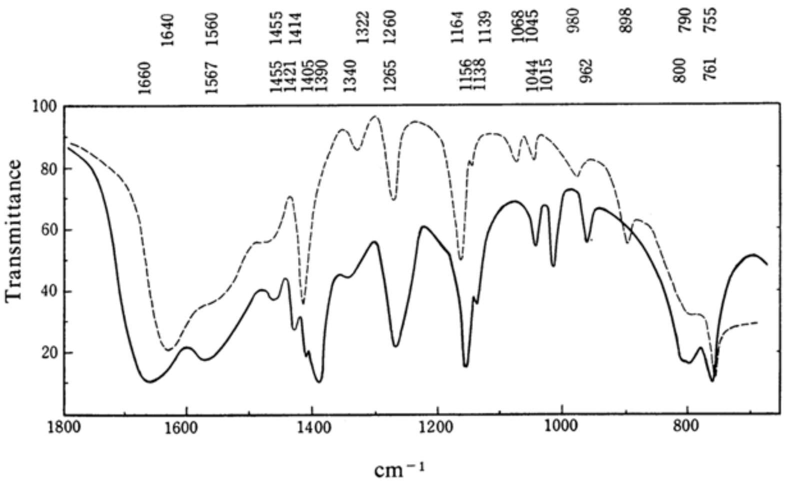

Fig. 3. Infrared spectra of $HCONHCH_3$ and $DCONHCH_3$ in the solid state;
—— $HCONHCH_3$, ---- $DCONHCH_3$.

The exchange reaction with deuterium oxide was used to replace the amide hydrogen atom by deuterium.

Infrared Spectra. — The infrared spectra in the liquid state were measured in the region from 3600 to 525 cm^{-1} with a Perkin-Elmer grating spectrophotometer model 112G equipped with a potassium bromide foreprism[9], and in the region from 800 to 260 cm^{-1} with a Nippon Bunko grating spectrophotometer equipped with a cesium bromide foreprism. The spectra of $HCONHCH_3$ and $DCONHCH_3$ in the solid state were obtained with a low temperature cell[10] at the temperature of liquid nitrogen and were recorded in the region from 1800 to 650 cm^{-1} by a Hitachi EPI infrared spectrophotometer with sodium chloride optics.

Infrared Spectra

The infrared spectra of $HCONHCH_3$ and $DCONHCH_3$ in the liquid state are shown in Figs. 1(a)–(c), and those of $HCONDCH_3$ and $DCONDCH_3$, in Figs. 2(a)–(c). The infrared spectra of $HCONHCH_3$ and $DCONHCH_3$ in the solid state are shown in Fig. 3. The values of the observed frequencies for $HCONHCH_3$ and $HCONDCH_3$ agree within a few wave numbers with those give previously by the other authors. In this section, the effects of the *C*-deuteration on the spectra are mainly described. As seen from Figs. 1 and 2, the bands at 2884 and 1386 cm^{-1} of $HCONHCH_3$, which are assigned to the CH stretching and in-plane deformation vibrations ν(CH) and δ(CH) respectively, disappear on *C*-deuteration, and a new band corresponding to the CD stretching vibration is found at 2169 cm^{-1}. It is not easy to identify the band chiefly associated with the CD in-plane deformation vibration. The bands found in the region 1100∼900 cm^{-1} are more or less affected by the *C*-deuteration; this fact suggests that the CD deformation motion takes part in each normal mode appearing in this region. In $DCONDCH_3$, the amide III′ band also falls in this region. The nature of these bands will be described more quantitatively in the following section on the basis of the results of the calculation of the normal vibrations.

It is of interest to determine which band is associated chiefly with the CH out-of-plane motion. The 771 cm^{-1} band of $HCONHCH_3$ was assigned to the CH out-of-plane vibration by DeGraaf and Sutherland[3] and by Jones[4], while Miyazawa[1,2] assigned this band to the amide IV (NCO bending) vibration. The fact that the 771 cm^{-1} band of $HCONHCH_3$ is insensitive to the *C*-deuteration excludes the possibility of assigning this band to the CH out-of-plane mode. Considering that the CH out-of-plane vibrations occurs at 1056 cm^{-1} in $HCONH_2$[11], at 1083 cm^{-1} in HCOOH[12], and at 1069 cm^{-1} in $HCOO^-$ [13], it seems reasonable to assign the 1011 cm^{-1} band of $HCONHCH_3$ to this mode. (In $HCONDCH_3$ it is found at 1021 cm^{-1}.) At 864 cm^{-1}, a band with a comparatively weak intensity is found both in $DCONHCH_3$ and $DCONDCH_3$. Since no vibrational mode other than the CD out-of-plane mode, is expected to occur in this region, the 864 cm^{-1} band is assigned to the CD out-of-plane vibration. This assignment is consistent

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[9] S. Mizushima et al., A Report on the Perkin-Elmer Grating Spectrophotometer Model 112G, The Perkin-Elmer Corp. (1959).

[10] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 821 (1955).

[11] I. Suzuki, This Bulletin, **33**, 1359 (1960).

[12] T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.*, **30**, 1076 (1959).

[13] O. Thomas, *Discussions Faraday Soc.*, **9**, 339 (1950).

with the above assignment of the CH out-of-plane vibration.

A band with a strong intensity is found at 353 cm^{-1} in $DCONHCH_3$; this band is hardly affected by the *N*-deuteration. On the *C*-deuteration, on the other hand, the band is shifted by 41 cm^{-1} to a lower frequency. The rather large shift due to the *C*-deuteration shows that this band does not arise from one of the skeletal deformation vibrations, but from the torsional vibration about the C–N bond. This assignment is in agreement with that given by DeGraaf and Sutherland³⁾.

Calculation of Normal Vibrations

The calculation of the normal vibration was made according to Wilson's method¹⁴⁾. It was assumed that the molecule is planar (point group C_s) except for two hydrogen atoms attached to the methyl carbon atom (see Fig. 4). Thus, the normal vibrations can be classified into 14 in-plane (A′) and 7 out-of-plane (A″) vibrations. The structural parameters used in this calculation are shown in Table I[*2].

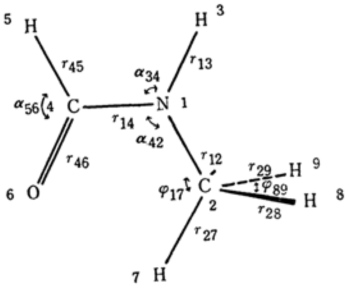

Fig. 4. Molecular structure and internal coordinates of *N*-methylformamide; the H_8 and H_9 atoms lie respectively, above and below the plane determined by the peptide group.

TABLE I. STRUCTURE PARAMETERS*

$r_{C-H}=r_{C'-H}=1.07$ Å $r_{C'-N}=1.47$ Å
$r_{N-H}=1.04$ Å $r_{C=O}=1.21$ Å
$r_{C-N}=1.32$ Å
$\alpha_{ij}{}^0=120°$ (Bond angles around the C and N atoms)
$\varphi_{ij}{}^0=109°28'$ (Bond angles around the C′ atom)

* Since no structural analysis has yet been reported for $HCONHCH_3$, the values of the bond lengths are taken from those of $HCONH_2$ ¹⁵,¹⁶⁾ and $CH_3CONHCH_3$⁷⁾.

In-plane Vibrations.—The potential function employed in the calculation is of the Urey-Bradley type⁶⁾:

$$2V=\sum K_i(\varDelta r_i)^2+\sum H_{ij}r_i{}^0r_j{}^0(\varDelta\alpha_{ij})^2 +\sum F_{ij}(\varDelta q_{ij})^2+\text{linear terms}$$

where r_i and r_j are bond lengths with equilibrium values of $r_i{}^0$ and $r_j{}^0$, α_{ij}'s are bond angles, and q_{ij}'s, distances between nonbonded atoms. *K*, *H* and *F* are stretching, bending and repulsive force constants respectively. In addition, the intramolecular tension, κ, appears in the elements of the $\boldsymbol{F}$ matrix when the linear terms are eliminated by a redundancy condition⁶⁾.

To simplify the computation, the lower frequencies are separated from the four higher frequencies in the region from 3000 to 2000 cm^{-1} ¹⁴⁾. The symmetry coordinates used in the calculation are shown in Table II (a).

The values of the force constants were transferred from formamide¹¹⁾ and methylamine molecules¹⁸⁾ and were slightly modified so as to obtain a better frequency agreement. The final set of the values of the force constants are given in Table III (a).

Out-of-plane Vibrations. — The type of the internal coordinates associated with the N–CH_3 part of the molecule, as well as the form of the potential function, is the same as that used for the calculation of the in-plane vibrations. Besides these six internal coordinates, Ω_1, Ω_4, τ_{25}, τ_{26}, τ_{35} and τ_{36} are introduced for the complete description of the out-of-plane modes, where Ω_i is $(\rho_{ij}\sin\alpha_{kil}+\rho_{ik}\sin\alpha_{lij}+\rho_{il}\sin\alpha_{jik})$ times the distance between the central atom *i* and the plane of atoms *j*, *k* and *l*, which surround the atom *i*, $(\rho_{ij}=1/r_{ij})$, and τ_{ij} is $\sin\alpha_{i14}\sin\alpha_{14j}$ times the dihedral angle (θ_{ij}) between the planes determined by atoms *i*, 1, 4 and 1, 4, *j* respectively¹²⁾. Six symmetry coordinates, three of which are redundant, are obtained by the linear combinations of these internal coordinates; these are given in Table II(b). The potential function of the out-of-plane vibrations as a whole is in the following form:

$$2V=\text{Urey-Bradley type for } S_1{}', S_2{}' \text{ and } S_3{}' +f_{44}S_4{}'^2+f_{55}S_5{}'^2+f_{66}S_6{}'^2+2f_{56}S_5{}'S_6{}' +2f_{46}S_4{}'S_6{}'+2f_{45}S_4{}'S_5{}'$$

The values of the Urey-Bradley type force constants are taken to be the same as those used in the in-plane vibrations. Since few data are available for the out-of-plane and torsional force constants, f_{44}, f_{45}, etc., they are determined from the observed frequencies by

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

[*2] C and C′ denote carbonyl and methyl carbon atoms respectively.

15) C. Post and J. Ladell, *Acta Cryst.*, **7**, 559 (1954).

16) R. A. Krombrout and G. B. Mohlton, *J. Chem. Phys.*, **25**, 35 (1956).

17) M. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953).

18) A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1105 (1959).

TABLE II. SYMMETRY COORDINATES

(a) In-plane vibrations

	Symmetry coordinate	Vibrational mode	Abbr.
S_1	Δr_{46}	C=O Stretching	ν(C=O)
S_2	Δr_{14}	C-N Stretching	ν(CN)
S_3	Δr_{12}	C′-N Stretching	ν(C′N)
S_4	$(\Delta\alpha_{23}-\Delta\alpha_{34})/\sqrt{2}$	NH Deformation	δ(NH)
S_5	$(\Delta\alpha_{15}-\Delta\alpha_{56})/\sqrt{2}$	CH Deformation	δ(CH)
S_6	$(2\Delta\alpha_{42}-\Delta\alpha_{23}-\Delta\alpha_{34})/\sqrt{6}$	CNC′ Deformation	δ(CNC′)
S_7	$(2\Delta\alpha_{61}-\Delta\alpha_{15}-\Delta\alpha_{56})/\sqrt{6}$	NCO Deformation	δ(NCO)
S_8	$(\Delta\varphi_{17}+\Delta\varphi_{18}+\Delta\varphi_{19}-\Delta\varphi_{78}-\Delta\varphi_{79}-\Delta\varphi_{89})/\sqrt{6}$	CH_3 Sym. deformation	$\delta_s(CH_3)$
S_9	$(2\Delta\varphi_{17}-\Delta\varphi_{18}-\Delta\varphi_{19})/\sqrt{6}$	CH_3 Rocking	$r(CH_3)_i$
S_{10}	$(2\Delta\varphi_{89}-\Delta\varphi_{78}-\Delta\varphi_{79})/\sqrt{6}$	CH_3 Asym. deformation	$\delta_a(CH_3)_i$
S_R	$(\Delta\alpha_{42}+\Delta\alpha_{23}+\Delta\alpha_{34})/\sqrt{3}$	Redundant	
$S_{R'}$	$(\Delta\alpha_{15}+\Delta\alpha_{56}+\Delta\alpha_{61})/\sqrt{3}$	Redundant	
$S_{R''}$	$(\Delta\varphi_{17}+\Delta\varphi_{18}+\Delta\varphi_{19}+\Delta\varphi_{78}+\Delta\varphi_{79}+\Delta\varphi_{89})/\sqrt{6}$	Redundant	

(b) Out-of-plane vibrations

	Symmetry coordinate	Vibrational mode	Abbr.
S_1	$(\Delta r_{28}-\Delta r_{29})/\sqrt{2}$	CH_3 Anti. stretching	$\nu_a(CH_3)_o$
S_2	$(\Delta\varphi_{18}-\Delta\varphi_{19})/\sqrt{2}$	CH_3 Rocking	$r(CH_3)_o$
S_3	$(\Delta\varphi_{79}-\Delta\varphi_{78})/\sqrt{2}$	CH_3 Asym. deformation	$\delta_a(CH_3)_o$
S_4	$(\Delta\tau_{25}+\Delta\tau_{26}+\Delta\tau_{35}+\Delta\tau_{36})/2$	CN Torsion	τ(CN)
S_5	$(2\Delta\Omega_1-\Delta\tau_{25}-\Delta\tau_{26}+\Delta\tau_{35}+\Delta\tau_{36})/\sqrt{8}$	NH Out-of-plane	π(NH)
S_6	$(2\Delta\Omega_4-\Delta\tau_{25}+\Delta\tau_{26}-\Delta\tau_{35}+\Delta\tau_{36})/\sqrt{8}$	CH Out-of-plane	π(CH)
S_r	$(-\Delta\tau_{25}+\Delta\tau_{26}+\Delta\tau_{35}-\Delta\tau_{36})/2$	Redundant	
$S_{r'}$	$(\Delta\Omega_1+\Delta\Omega_4+\Delta\tau_{25}-\Delta\tau_{36})/2$	Redundant	
$S_{r''}$	$(\Delta\Omega_1-\Delta\Omega_4+\Delta\tau_{26}-\Delta\tau_{35})/2$	Redundant	

TABLE III. VALUES OF FORCE CONSTANTS

(a) Urey-Bradley type (in md./A)

$K_{C=O}$	8.80	$H_{CNC'}$	0.35	$F_{C\cdots C'}$	0.30
K_{CN}	6.15	$H_{HNC'}$	0.25	$F_{H\cdots C'}$	0.36
$K_{C'N}$	3.15	H_{HNC}	0.30	$F_{H\cdots C}$	0.46
		H_{NCH}	0.18	$F_{N\cdots H}$	0.72
		H_{HCO}	0.20	$F_{H\cdots O}$	0.92
		H_{NCO}	0.37	$F_{N\cdots O}$	1.50
		$H_{NC'H}$	0.28	$F_{N(C')H}$	0.52
		$H_{HC'H}$	0.43	$F_{H\cdots H}$	0.03

$\kappa_{(CH_3)}=-0.04$ (md.·A)
$F'=-0.1F$

(b) General quadratic type for A″ species (md.·A)

f_{44}	0.169	f_{55}	0.106	f_{66}	0.290
f_{45}	0	f_{46}	0.052_3	f_{56}	0.005

the method of least squares[19,20]. The final values of these force constants are given in Table III(b). The methyl torsional vibration lies beyond the limit of the present measurements and is omitted from the calculation.

Results of Calculations. — With the aforementioned force constants given in Tables III (a) and (b), the normal vibrations have been calculated. In Tables IV (a)–(d), the observed and calculated frequencies, percent deviations, the potential energy distributions among the symmetry coordinates for each normal mode, and the signs of the corresponding ***L***-matrix elements are given for the in-plane normal vibrations. In Tables V (a)–(d), those for the out-of-plane vibrations are given.

To visualize the feature of a given normal mode, it is preferable to compute the atomic displacement vectors, which can be obtained

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19) T. Miyazawa, ibid., **76**, 1132 (1955).

20) W. T. King, I. M. Mills and B. C. Crawford, *J. Chem. Phys.*, **27**, 455 (1957).

TABLE IV. THE OBSERVED AND CALCULATED FREQUENCIES IN cm^{-1} AND POTENTIAL ENERGY DISTRIBUTIONS $(F_{ii}L_{is}^2/\lambda_s)\times 100$

(a) $HCONHCH_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
ν_1	1675	1675	0	72	27*	0	22	1	2	1*	0	1*	0*
ν_2	1546	1547	−0.1	2	32	8*	0	60	4*	0	0*	4	1
ν_3	1455	1462	−0.5	1	0*	0	0	0	4*	0	0	13	80
ν_4	1414	1417	−0.2	0	0	9*	0	0	0	0*	104	0	0*
ν_5	1384	1392	−0.6	16*	1*	0*	75	0	0*	2	0*	0	0
ν_6	1248	1246	+0.2	10*	33*	5	4*	36	0*	4	0	0*	2
ν_7	1150	1115	+3.0	1	0	18	0	0*	10*	6	0	54	13*
ν_8	960	960	0	1	12	54	1	0*	2*	0	0	22*	4
ν_9	771	739	+4.1	2	0*	11*	0*	0	18*	60	0*	5*	1
ν_{10}	297	288	+3.0	0*	1	0	0*	0*	67	27	0	1	0*

(b) $DCONHCH_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
ν_1	1655	1660	−0.3	76	32*	0	10	0	2	0*	0	1*	0*
ν_2	1530	1539	−0.6	4	26	7*	0	63	0	4*	1*	3	1
ν_3	—	1463	—	0	0*	0	0	4*	0	0	0	13	80
ν_4	1412	1416	−0.3	0	0	9*	0	1	0	0*	104	0	0*
ν_5	1250	1252	−0.2	19*	33*	2	3	30	0*	5	0	0*	2
ν_6	1164	1122	+3.6	1	0*	30	6*	1	10*	4	0	39	9*
ν_7	1048	1059	−1.0	1*	0*	12*	52	3*	0*	1	0*	25	5*
ν_8	900	914	−1.5	0	12	32	29	0	2*	2	0	13*	2
ν_9	761	727	+4.4	1	0*	13*	2*	0	17*	59	0*	4*	0
ν_{10}	(297)	288	+3.0	0*	1	0	0*	0*	68	26	0	1	0*

(c) $HCONDCH_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
ν_1	1662	1671	−0.5	72	31*	0	21	0	2	0*	0	1*	0*
ν_2	—	1476	—	6	16	4*	1	6	0	3*	1*	16	49
ν_3	1436	1434	+0.1	5*	31*	6	0*	14*	0*	6	8	1	32
ν_4	1405	1416	−0.8	0	4	13*	0	1	0	1*	96	0	1*
ν_5	1383	1392	−0.7	14*	0*	1*	77	0	0*	1	0*	0	0
ν_6	1155	1106	+4.3	1	0	15	0	0*	9*	4	0	58	13*
ν_7	981	998	−1.7	5*	23*	14*	3*	43	0	0	0	7	1*
ν_8	943	923	+2.2	0*	1	42	0	35	1*	0	0	11*	2
ν_9	762	735	+3.5	2	0	10*	0*	1	18*	61	0*	5*	1
ν_{10}	297	283	+4.7	0*	1	0	0*	0*	70	27	0	1	0*

(d) $DCONDCH_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
ν_1	1645	1658	−0.8	76	34*	0	10	0*	2	0*	0	1*	0*
ν_2	—	1472	—	6	9	2*	0	4	0	2*	0*	16	60
ν_3	1425	1434	−0.6	7*	25*	2	0*	13*	0*	4	32	0	18
ν_4	1405	1414	−0.7	3	13	18*	0	6	0	2*	73	0	5*
ν_5	1158	1123	+3.0	7	3	27	22*	5*	6*	1	0	22	6*
ν_6	1095	1087	+0.7	2*	5*	0*	28	8	3*	5	0	43	8*
ν_7	951	941	+1.1	2*	7*	3	20*	61	0	0*	0	0*	0
ν_8	891	908	−1.9	0	9	42	20	4	2*	1	0	13*	2
ν_9	751	723	+3.7	1	0*	11*	2*	1	18*	61	0*	4*	1
ν_{10}	(297)	283	+4.7	0*	1	1	0*	0	69	27	0	1	0*

$$\Delta=[(\nu_{obs}-\nu_{calcd})/\nu_{obs}]\times 100$$

* The asterisk means that the corresponding **L**-matrix element is negative.

TABLE V. THE OBSERVED AND CALCULATED FREQUENCIES IN cm^{-1} AND POTENTIAL ENERGY DISTRIBUTIONS FOR THE OUT-OF-PLANE VIBRATIONS

(a) HCONHCH$_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6
ν_1	2952	2954	−0.1	100	0*	0	0	0*	0*
ν_2	1455	1459	−0.3	1*	15	81	0	0	0*
ν_3	—	1082	—	0*	70	16*	1	4	15*
ν_4	1011	1019	−0.7	0*	15	2*	14*	2*	85
ν_5	720	706	+2.0	0	0*	0	34	54	5
ν_6	353	353	0	0*	1	0*	57	42*	0

(b) DCONHCH$_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6
ν_1	2948	2954	−0.2	100	0*	0	0	0*	0*
ν_2	1455	1459	−0.3	1*	15	81	0	0	0*
ν_3	—	1076	—	0*	82	18*	0*	3	2*
ν_4	864	865	−0.1	0*	3	0*	11*	8*	95
ν_5	710	709	+0.1	0	0*	0	33	50	8
ν_6	312	314	−0.6	0*	1	0*	63	38*	1*

(c) HCONHCH$_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6
ν_1	2951	2954	−0.1	100	0*	0	0	0*	0*
ν_2	—	1459	—	1*	15	81	0	0	0*
ν_3	—	1080	—	0*	73	16*	1	3	13*
ν_4	1020	1015	+0.5	0*	12	2*	12*	1*	90
ν_5	530	535	−1.0	0	0*	0	34	58	4
ν_6	351	356	−1.4	0*	1	0*	59	38*	0

(d) DCONDCH$_3$

Q	ν_{obs}	ν_{calcd}	Δ	S_1	S_2	S_3	S_4	S_5	S_6
ν_1	2942	2954	−0.1	100	0*	0	0	0*	0*
ν_2	—	1459	—	1*	15	81	0	0	0*
ν_3	—	1074	—	0*	83	18*	0*	2	1*
ν_4	864	859	−0.6	0*	2	0*	7*	4*	100
ν_5	530	536	−1.2	0	0*	0	34	58	3
ν_6	312	312	0	0*	1	0*	66	36*	1*

$\Delta=[(\nu_{obs}-\nu_{calcd})/\nu_{obs}]\times 100$

* The asterisk means that the corresponding $\boldsymbol{L}$-matrix element is negative.

from the $\boldsymbol{L}^x$ matrix defined, in matrix expression, as

$$\boldsymbol{X}=\boldsymbol{L}^x\boldsymbol{Q}$$

where $\boldsymbol{X}$ is the column vector of the Cartesian coordinates of the atoms involved. The $\boldsymbol{L}^x$ matrix was computed for the out-of-plane normal modes, for which vibrational features are somewhat difficult to deduce from the P. E. D. matrices. The results are shown schematically in Figs. 5 (a) and (b).

As mentioned above, the in-plane vibrations of the cis configuration have also been calculated with the values of the force constants given in Table III (a); the results are summarized in Tables VI (a)–(d).

The notations used throughout this paper are the same as those used for the previous paper[11]. All the numerical computations were carried out with a parametron computer PC-1, the routines and the method of calculation are given in detail in the Ref. 21 and so are not discussed here.

Discussion

The Nature of the Observed Bands. — Based on the calculated values of vibrational amplitudes and potential energy distributions shown in Tables IV and V, the nature of the observed bands will be discussed[*3].

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21) T. Shimanouchi and I. Suzuki, *J. Mol. Spectroscopy*, **6**, 277 (1961).

[*3] In this and the following sections, one of the abbreviations given in the final columns of Tables II (a) and (b) is used to refer to a given vibrational mode. For instance, $\delta_a(CH_3)_i$ is used instead of "in-plane CH$_3$ asymmetric deformation vibration".

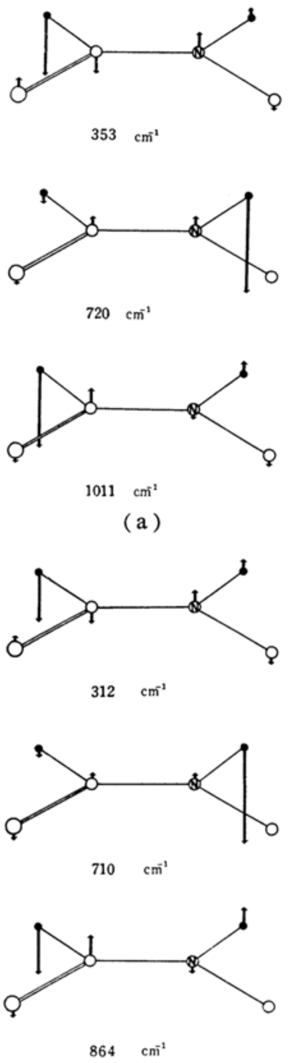

Fig. 5. Schematic representation of vibration features of the out-of-plane normal modes (a) $HCONHCH_3$, (b) $DCONHCH_3$; the movements of hydrogen atoms attached to the C′ atom are neglected; ●, ○, Ⓝ and =○ denote hydrogen, carbon, nitrogen and oxygen atoms respectively.

In the Region from 3500 to 2000 cm⁻¹. — The bands chiefly associated with the NH stretching vibration are found in the region from 3500 to 3000 cm⁻¹ and those associated with the ND motion, in the region from 2500 to 2400 cm⁻¹. The cause of the doublings of these bands has been discussed in detail by earlier workers[22,23] and so is not discussed here. The bands associated with the various CH stretching vibrations are found around 2900 cm⁻¹. The

TABLE VI. THE CALCULATED FREQUENCIES IN cm⁻¹ AND P. E. D. FOR THE IN-PLANE VIBRATIONS OF THE CIS CONFIGURATIONS

(a) $HCONHCH_3$

ν_{calcd}	P. E. D.*
1687	ν(C=O) 60, ν(CN) 34, δ(CH) 19, δ(NH) 12
1459	$\delta_a(\mathrm{CH_3})$ 50, δ(NH) 33
1441	δ(NH) 26, $\delta_a(\mathrm{CH_3})$ 26, ν(C=O) 18, $r(\mathrm{CH_3})$ 13
1416	$\delta_s(\mathrm{CH_3})$ 100
1402	δ(CH) 58, ν(C=O) 16
1328	ν(CN) 41, δ(CH) 18, δ(NH) 18
1108	ν(C′N) 46, $r(\mathrm{CH_3})$ 30
1009	$r(\mathrm{CH_3})$ 45, ν(C′N) 25
595	δ(NCO) 58, ν(C′N) 19
360	δ(C′NC) 79, δ(NCO) 18

(b) $DCONHCH_3$

ν_{calcd}	P. E. D.*
1675	ν(C=O) 62, ν(CN) 36, δ(NH) 14
1475	$\delta_a(\mathrm{CH_3})$ 32, ν(C=O) 21, $r(\mathrm{CH_3})$ 14
1460	$\delta_a(\mathrm{CH_3})$ 45, δ(NH) 35
1416	$\delta_s(\mathrm{CH_3})$ 101
1335	ν(CN) 49, δ(NH) 22, δ(NCO) 11
1120	ν(C′N) 35, $r(\mathrm{CH_3})$ 33
1030	δ(CD) 40, ν(C′N) 30
988	δ(CD) 41, $r(\mathrm{CH_3})$ 35
595	δ(NCO) 58, ν(C′N) 19
351	δ(C′NC) 78, δ(NCO) 19

(c) $HCONDCH_3$

ν_{calcd}	P. E. D.*
1675	ν(C=O) 68, ν(CH) 33, δ(CH) 21
1470	$\delta_a(\mathrm{CH_3})$ 68, $r(\mathrm{CH_3})$ 18
1419	$\delta_s(\mathrm{CH_3})$ 90
1413	ν(C=O) 24, ν(CN) 24, δ(CH) 18
1374	δ(CH) 61, ν(CN) 17
1169	ν(C′N) 35, δ(ND) 28
1060	$r(\mathrm{CH_3})$ 64, $\delta_a(\mathrm{CH_3})$ 12, δ(ND) 11
924	δ(ND) 43, ν(C′N) 34
580	δ(NCO) 56, ν(C′N) 16
355	δ(C′NC) 78, δ(NCO) 19

(d) $DCONDCH_3$

ν_{calcd}	P. E. D.*
1662	ν(C=O) 71, ν(CN) 36, δ(CD) 10
1468	$\delta_a(\mathrm{CH_3})$ 70, $r(\mathrm{CH_3})$ 18
1418	$\delta_s(\mathrm{CH_3})$ 103
1394	ν(CH) 42, $\delta_a((\mathrm{CH_3})$ 13, ν(C′N) 12
1165	ν(C′N) 34, δ(NCO) 20
1093	$r(\mathrm{CH_3})$ 45, δ(CD) 27
991	δ(CD) 62, $r(\mathrm{CH_3})$ 20
923	δ(ND) 44, ν(C′N) 35
583	δ(NCO) 86, δ(C′NC) 15
345	δ(C′NC) 77, δ(NCO) 19

* Only the important terms are given in this table.

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[22] M. Beer, H. D. Kessler and G. B. B. M. Sutherland, *J. Chem. Phys.*, **29**, 1097 (1958).

[23] T. Miyazawa, *J. Mol. Spectroscopy*, **4**, 168 (1960).

CD stretching vibrations occur at about 2150 cm^{-1}.

In the Region from 1700 to 1200 cm^{-1}.—Three characteristic bands of monosubstituted amides are found in this region. They are termed the amide I, II and III bands and are found at 1675, 1546 and 1248 cm^{-1} respectively in *N*-methylformamide. The nature of these bands has been discussed in detail for *N*-methylacetamide[24], and the present calculation gives similar results for these bands; i. e., the amide I band is chiefly associated with the ν(C=O) motion, and the amide II and III bands are chiefly due to the mixed vibrations of the ν(CN) and δ(NH). In addition, there are considerable contributions from the ν(CN) and δ(CH) vibrations to the amide I band, which may be the cause of the lowering of this band by 20 cm^{-1} by the *C*-deuteration.

Three CH$_3$ and CH deformation vibrations occur also in this region. In the undeuterated species, the bands at 1455, 1414 and 1384 cm^{-1} correspond to almost pure $\delta_a(\mathrm{CH_3})$, $\delta_s(\mathrm{CH_3})$ and δ(CH) vibrations respectively. In *N*-deuterated species, a band is found at about 1430 cm^{-1} and is termed the amide II′ band; the present calculations show that this band is rather complicated in its nature. Both $\nu_a(\mathrm{CH_3})_i$ and ν(CN) vibrations are associated with this normal mode, and in addition, the contributions of the δ(ND) and the skeletal deformation [δ(NCO) and δ(CNC′)] vibrations are not negligible. In other words, this normal vibration is not localized in the peptide linkage. On *N*-deuteration, the bands assigned to the $\delta_s(\mathrm{CH_3})$ and δ(CH) modes are hardly affected; they are found at 1405 and 1383 cm^{-1} respectively.

In the Region from 1200 to 850 cm^{-1}. — In HCONHCH$_3$, the ν(C′N), $r(\mathrm{CH_3})$ and π(CH) vibrations are expected to occur in this region. In fact, the bands at 1150 and 960 cm^{-1} can be assigned to the $r(\mathrm{CH_3})_i$ and ν(C′N) modes respectively, although there are also certain contributions from other vibrational modes. In deuterated species, the δ(CD) and/or δ(ND) vibrations couple with the aforementioned vibrations, and the nature of the bands thus becomes much more complex. As seen in Table IV (b) the 1048 cm^{-1} band of DCONHCH$_3$ is a mixed vibration of δ(CD), $r(\mathrm{CH_3})$ and ν(C′N), and the 900 cm^{-1} band is a mixed vibration of ν(C′N), δ(CD), $r(\mathrm{CH_3})_i$ and ν(CN).

A band named the amide III′ band appears at 981 cm^{-1} in HCONDCH$_3$; the δ(ND) and ν(CN) as well as ν(C′N) vibrations play an important role in this normal mode. In DCONDCH$_3$, the $r(\mathrm{CH_3})_i$, δ(CD), δ(ND) and ν(C′N) vibrational modes interact with each other, and this gives rise to four observed bands at 1158, 1095, 951 and 891 cm^{-1}. The present calculation yields the result that the δ(CD) vibration occurs in each of these normal modes in approximately the same amount, although it predominates in none of these modes.

Two types of the methyl rocking modes must be considered; one belongs to the A′ species; $r(\mathrm{CH_3})_i$, and the other to the A″ species, $r(\mathrm{CH_3})_o$, and they are expected to give different frequencies, because the way of coupling with vibrational modes is different in each symmetry species. A weak band found at 1040 cm^{-1} in NCONHCH$_3$ and at 1064 cm^{-1} in DCONHCH$_3$ may tentatively be assigned to the $r(\mathrm{CH_3})_o$ mode, but this is not certain because the present calculation shows that the average splitting of the $r(\mathrm{CH_3})_i$ and $r(\mathrm{CH_3})_o$ frequencies is about 40 cm^{-1} [*4].

As has been mentioned earlier in this paper, the π(CH) and π(CD) vibrations also occur in this region. The features of these modes are illustrated in Fig. 5.

In the Region from 850 to 260 cm^{-1}. — The bands associated with two skeletal deformation vibrations, δ(NCO) and δ(CNC′), are expected to appear in this region. Present calculation shows that an interaction occurs between the δ(NCO) and δ(CNC′) vibrations and that this gives rise to two observed bands at 771 and 297 cm^{-1} of HCONHCH$_3$. For the 771 cm^{-1} band, the energy associated with the δ(NCO) vibration is 60% of the total and that associated with the δ(CNC′) is 20%, while for the 297 cm^{-1} band the energy associated with the δ(NCO) mode is 30% and that associated with the δ(CNC′) is 70%[*5]. The way of coupling of the δ(NCO) and δ(CNC′) motions seems to be unaffected by deuteration.

In Fig. 5, the features of the normal modes of the bands found at 720 and 353 cm^{-1} are shown. It is clear that the 720 cm^{-1} band corresponds to almost pure π(NH) vibration, while the vibrational coupling occuring between the π(CH) and τ(CN) modes makes the 353 cm^{-1} band complex in its nature.

Force Constants.—*Urey-Bradley Type.* — The Urey-Bradley type of force constants have been classified into three groups after their values

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24) T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **29**, 611 (1958).

[*4] If we adopt this assignment, the observed splitting is about three times larger than the calculated. Such a deviation is rather large even though the splitting of the frequencies depends on the type of force field employed in the calculation.

[*5] This may also be the cause of the rather high frequency of the amide IV band, as compared with other amides; the value of the force constants chiefly concerned with this vibrational mode, namely H_{NCO} and $F_{\mathrm{N\cdots O}}$, are practically unchanged from those used for the evaluation of the HCONH$_2$[11] molecule, which gives the δ (NCO) vibration at about 600 cm^{1}.

had first been chosen by the following procedure:

(I) The force constants associated with the HCONH- part of the molecule, i.e. K_{CO}, K_{CN}, H_{NCH}, H_{HCO}, H_{NCO}, H_{HNC}, $F_{N\cdots H}$, $F_{H\cdots C}$, $F_{N\cdots O}$ and $F_{H\cdots C}$.—The values of the force constants belonging to group I were first transferred from the formamide molecule, for which the values of the constants had been definitely determined by an analysis of its normal vibrations[11].

(II) The force constants associated with the N–CH_3 part of the molecules, i.e. $K_{C'N}$, $H_{NC'H}$, $H_{HC'H}$, $F_{N(C')H}$, $F_{H\cdots H}$ and κ.—Their values were primarily transferred from the methylamine molecule[18]; in addition, the results of the recent investigation on methyl halides were also taken into account when the initial values of these constants were selected.

(III) The other force constants, i.e. $H_{CNC'}$, $H_{HNC'}$, $F_{C\cdots C}$ and $F_{H\cdots C'}$. — Their values were primarily transferred from *N*-methylacetamide[24], but slightly modified values were used as initial guesses because in that calculation the methyl group was approximated as a dynamic unit.

In order to obtain a better frequency agreement, the values of the force constants were refined as indicated by the elements of the Jacobian matrix $(\Delta\lambda_i/\Delta K_j)$[19,20]. Thus the final set of force constants given in Table III(a) was obtained. The force constants in group I remain almost unchanged, and an analogous result was obtained for the constants belonging to group II, the maximum change from the initial values being only 0.05 (in md./A). The constants involving hydrogen and carbon atoms only, i.e. $H_{HC'H}$, $F_{H\cdots H}$ and κ, are similar to values found for methyl halides[21]. As for the constants in group III, the deviations from the original are found to be comparatively large for some of the force constants.

The above results indicate that the Urey-Bradley type force constants, if determined carefully for a given molecule, can be used for the calculation of the normal vibrations for related molecules, even when they are relatively complicated and large in size.

General Quadratic Type for the A'' Vibrations.—As an initial set of force constants, the following values were taken: $f_{44}=0.051$, $f_{55}=0.136$, $f_{66}=0.271$, and zero for all the cross terms. The method of least squares was applied to refine these constants, and five repetitions of interaction processes give the values shown in Table III(b). The cross terms, f_{45} and f_{56}, are found to be small, while f_{46}, the cross term between the τ(CN) and π(CH) coordinates, is comparatively large. This implies that an interaction takes place between the τ(CN) and π(CH) vibrations to some degree and is quite consistent with the result of the infrared measurements; i.e., the 351 cm^{-1} band of $HCONHCH_3$ is sensitive to the *C*-deuteration while it is not to the *N*-deuteration.

The force constant, f_{44}, can be related to the barrier to internal rotation about the C–N bond[12]. This constant can be written as:

$$f_{44}=4(2V_2+\Delta E/2)/9 \qquad (1)$$

if we assume the sinusiodal potential curve of the following form:

$$V(\theta)=\Delta E(1-\cos\theta)/2+V_2(1-\cos 2\theta)/2 \qquad (2)$$

where θ is the angle of internal rotation ($\theta=0$ for the trans form) and ΔE is the energy difference between the cis and trans isomers. If we make use of the relations[12,25] $\Delta\theta=\Delta(\theta_{25}+\theta_{26}+\theta_{35}+\theta_{36})/4=2S_4/3$, and $2V(\theta)=(2V_2+\Delta E/2)(\Delta\theta)^2$ for small $\Delta\theta$, the Eq. 1 can be obtained. From the values of f_{44}, the barrier height, $V_0\fallingdotseq V_2+\Delta E/2$, is estimated as 28.5~28.0 kcal./mol. (ΔE is assumed to be 3~1 kcal./mol.). Since the height of the barrier depends on the type of the potential function used for the calculation, the value itself is not important. However, present calculation shows that the barrier height is considerable and that the internal rotation of the molecule about the C–N bond is severely restricted.

The Vibrational Modes of the cis Isomers.—The calculated frequencies and potential energy distributions, shown in Tables VI(a)–(d), were evaluated with the force constants given in Table III(a). They give the features of the normal vibrations for the cis amide; the results are summarized as follows:

(1) The amide I band is not much affected by the change in structure.

(2) In the cis amide, the δ(NH) vibration interacts with the $\delta_a(CH_3)$ rather than with the ν(CN) vibration. This interaction gives rise to two frequencies around 1450 cm^{-1} and may be a cause of the difficulty in finding the corresponding bands in some lactams[26], in which the NH–CO groups take the cis configuration.

(3) The bands associated with the δ(CH) and $\delta_s(CH_3)$ motions are not sensitive to the change in structure.

(4) The vibration chiefly associated with the ν(CN) vibration occurs around 1330 cm^{-1} in $HCONHCH_3$ and $DCONHCH_3$, and around 1400 cm^{-1} in the *N*-deuterated species. There are small contributions from the δ(CH) or δ(NH) vibration to this normal mode.

(5) In the region from 1200 to 900 cm^{-1},

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[25] T. Miyazawa, This Bulletin, **34**, 691 (1961).

[26] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen & Co., Ltd., London (1958), p. 216.

two bands which are associated with $r(CH_3)$ and $\nu(C'N)$ modes are expected to occur, and in addition, the $\delta(CD)$ and $\delta(ND)$ modes are also found in the deuterated species. The way of coupling between these vibrational modes is different from that in the trans form. This gives a frequency somewhat different from that in the trans form for each normal vibration.

(6) It is well known that skeletal deformation vibrations are quite sensitive to the structure of a given molecule. Such is also the case for *N*-methylfomamide, and the present calculation gives a value of 595 cm^{-1} to a band chiefly associated with the $\delta(NCO)$ motion (amide IV band) and a value of 360 cm^{-1} to that associated with the $\delta(CNC')$ motion. To the former vibration, there is practically no contribution from the $\delta(CNC')$ mode as there is in the trans configuration; this may be a reason for the comparatively low frequency of the vibration. To the latter band, the contribution from the $\delta(NCO)$ motion is less compared to that in the trans form. The amide IV band can be used to check the molecular configuration in the vapor phase. Miyazawa et al. showed that the amide IV band hardly moves with the change of state2). Thus, if the molecule of *N*-methylformamide takes the trans configuration in the vapor phase, the position of the amide IV band scarcely moves, while it is expected to shift towards a lower frequency if the molecule takes the cis form, as concluded by Jones4). In the spectrum of *N*-methylformamide in the vapor phase, the amide IV band is found at 785 cm^{-1}; this seems to indicate that the molecule is predominantly in the trans form, although there are some bands found in the spectrum due to the cis isomer7) coexisting as a less stable one.

(7) Although all the fundamental frequencies are correlated with the observed band, there remained a few unassigned bands for each isotopically substituted species, i. e., 1325, (1040), and 624 cm^{-1} for $HCONHCH_3$, 1304, (1064), 981 and 617 cm^{-1} for $DCONHCH_3$, 1125 and 607 cm^{-1} for $NCONDCH_3$, and (1125) and 606 cm^{-1} for $DCONDCH_3$. They may be interpreted as overtones and combination tones of the fundamentals, but there are some difficulties in assigning these bands to certain overtones and combination tones systematically throughout the four isotopic species of the molecule. In addition, it should be noted that their frequencies are in good agreement with the calculated values of the cis characteristic bands; i. e., the band around 1320 cm^{-1} for the NH species corresponds to the $\nu(CN)$ vibration*6, the band around 1120 cm^{-1} for the ND species, to the mixed vibration of the $\delta(ND)$ and $\nu(C'N)$ modes, the band at 980 cm^{-1} of $DCONHCH_3$, to the mixed one of the $\delta(CD)$ and $r(CH_3)$ and the band around 600 cm^{-1}, to the $\delta(NCO)$ motion (see Table VI). However, objections may arise in assigning these bands as those of the cis isomer, since they persist in the solid phase. This fact does not exclude the possibility of the coexistence of the cis isomer as mixed crystals because of the very high barrier hindering internal rotation, as has been described in the preceding section. Therefore, while it is not possible to give an unequivocal answer to this question at present, it is probable that these bands are arising from the cis isomer of the molecule.

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*6 The shift of the band about 20 cm^{-1} with solidification is also consistent with the above assignments.