Infrared Spectra and Normal Vibrations of Formamide; $HCONH_2$, $HCOND_2$, $DCONH_2$ and $DCOND_2$

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A number of investigations have been made on the molecular structure of formamide. The geometrical structure of the molecule was precisely determined by the studies of the microwave spectrum[1-3], X-ray diffraction[4], and nuclear magnetic resonance[5]. It was indicated that the formamide molecule is planar in the solid state and is nearly planar and of very shallow pyramidal configuration as to the C-NH_2 group in the gaseous state. The Raman and infrared spectra of $HCONH_2$ were observed by a number of investigators in the gaseous, liquid, and solid states and in solutions[6-13]. The infrared spectra of *N*-deuterated formamide, $HCOND_2$, were also observed in the liquid state and in solutions[11,13]. A normal coordinate treatment of the molecule as a three-body problem was made by Miyazawa[13]. However, a full analysis of the normal vibrations of the formamide molecule has never been attempted, and the assignments of the observed frequencies are not yet complete.

In order to clarify the nature of the normal vibrations of the formamide molecule, the present writer observed the infrared spectra of *C*-deuterated formamides; $DCONH_2$ and $DCOND_2$. The infrared spectra of undeuterated

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formamide ($HCONH_2$) and *N*-deuterated formamide ($HCOND_2$) have been remeasured.

A normal coordinate treatment has been made for all of these four molecules as a six-body problem. Fourteen force constants have been determined so that all the thirty-six observed frequencies are thereby explained. With these force constants, the vibrational mode and the potential energy distribution among the symmetry coordinates have been calculated for each normal vibration.

The purpose of this paper is to give the results of these observations and calculations and to present a complete assignment of the observed frequencies and a detailed discussion on the nature of each normal vibration of the formamide molecule.

Experimental

Formamide $HCONH_2$.—The sample used was obtained from a commercial source, and was purified several times by vacuum distillation; b. p. 86°C (5 mmHg).

***C*-Deuterated Formamide $DCONH_2$.**—This compound was prepared from DCOOD and urea by the following procedures. First, DCOOD was prepared by the thermal decomposition of anhidrous heavy oxalic acid $(COOD)_2$ which was obtained by the exchange reaction of $(COOH)_2$ and D_2O[14]. DCOOD was then mixed with urea and heated at about 150°C for 4 hr.[15] Ammonia, carbon dioxide and water produced by the reaction were pumped out in vacuum. From the residual, $DCONH_2$ was distilled out. It was treated with a small amount of aqueous solution of potassium hydroxide to neutralize the remaining free acid and distilled in vacuum again.

Replacement of the amide hydrogen by deuterium was accomplished by adding an excess of D_2O, evaporating the heavy water in vacuum, and repeating this procedure three times.

Infrared Spectra.—Infrared spectra were measured in the region from 3600 to 525 cm^{-1} with a Perkin-Elmer grating spectrometer model 112G equipped with a KBr foreprism[16], and in the region from 700 to 300 cm^{-1} with a Perkin-Elmer spectrometer model 21, equipped with a CsBr prism. All the measurements were made in the liquid state.

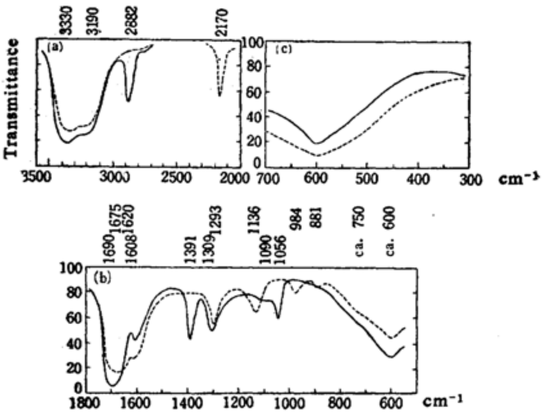

Fig. 1. Infrared spectra of $HCONH_2$ and $DCONH_2$.
(a) 3600～2000 cm^{-1} (b) 1800～525 cm^{-1}
(c) 700～300 cm^{-1};
—— $HCONH_2$ and ---- $DCONH_2$.

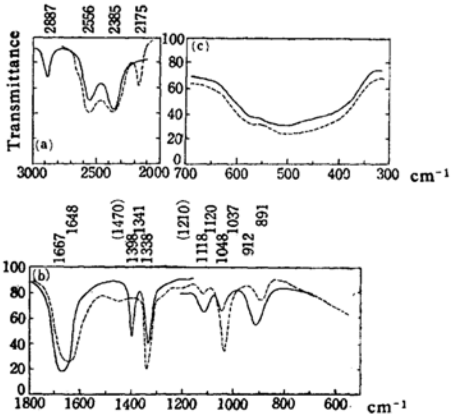

Fig. 2. Infrared spectra of $HCOND_2$ and $DCOND_2$.
(a) 3000～2000 cm^{-1} (b) 1800～525 cm^{-1}
(c) 700～300 cm^{-1};
—— $HCOND_2$ and ---- $DCOND_2$.

Infrared Spectra

Infrared spectra of $HCONH_2$ and $DCONH_2$ are shown in Figs. 1 (a)-(c), and those of $HCOND_2$ and $DCOND_2$ in Figs. 2 (a)-(c). As may be expected, the bands at 2882, 1391 and 1056 cm^{-1} of $HCONH_2$ which are assigned respectively to the CH stretching, CH in-plane and out-of-plane deformation vibrations, completely disappear on the *C*-deuteration, and new bands appear at 2170, 984 and 881 cm^{-1}. These are assigned to the CD stretching, CD in-plane and out-of-plane deformation vibrations respectively. Besides these, every band below 1700 cm^{-1} is more or less affected by the *C*-deuteration as well as by the *N*-deuteration. This fact suggests that, in almost every normal mode, the CH, NH_2, CD and/or ND_2 deformation motions more or less take place.

When $HCOND_2$ or $DCOND_2$ was exposed in the atomopheric air for a while, several weak bands appeared besides the absorption bands illustrated in Figs. 2 (a)-(c). These bands are supposed to be arising from *N*-monosubstituted amides, which were produced by the partial hydrogenation due to the atomospheric water vapour. The positions of these bands were also determined; 3300, 2460, 1470, 1212 and about 700 cm^{-1} for HCONHD (both cis and

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TABLE I. THE SYMMETRY COORDINATES

Symmetry coordinate		Vibrational mode	Abr.
S_1	$(\Delta r_{NHa}-\Delta r_{NHb})/\sqrt{2}$	NH_2 antisym. stretching	$\nu_a(NH_2)$
S_2	$(\Delta r_{NHa}+\Delta r_{NHb})/\sqrt{2}$	NH_2 symm. stretching	$\nu_s(NH_2)$
S_3	Δr_{CH}	CH stretching	$\nu(CH)$
S_4	Δr_{CO}	CO stretching	$\nu(CO)$
S_5	Δr_{CN}	CN stretching	$\nu(CN)$
S_6	$(2\Delta\alpha_{HNH}-\Delta\alpha_{CNHa}-\Delta\alpha_{CNHb})/\sqrt{6}$	NH_2 bending	$b(NH_2)$
S_7	$(\Delta\alpha_{NCH}-\Delta\alpha_{HCO})/\sqrt{2}$	CH deformation	$\delta(CH)$
S_8	$(\Delta\alpha_{CNHa}-\Delta\alpha_{CNHb})/\sqrt{2}$	NH_2 rocking	$r(NH_2)$
S_9	$(2\Delta\alpha_{OCN}-\Delta\alpha_{NCH}-\Delta\alpha_{HCO})/\sqrt{6}$	NCO deformation	$\delta(NCO)$
S_{10}	$(\Delta\alpha_{CNHa}+\Delta\alpha_{CNHb}+\Delta\alpha_{HNH})/\sqrt{3}$	redundant	—
S_{11}	$(\Delta\alpha_{NCH}+\Delta\alpha_{HCO}+\Delta\alpha_{OCN})/\sqrt{3}$	redundant	—

TABLE II. THE FINAL SET OF FORCE CONSTANTS (md/A)

K_{NH}	5.80	H_{HNH}	0.40	$F_{H\cdots H}$	0
K_{CH}	3.74	H_{HNC}	0.32	$F_{H\cdots C}$	0.46
K_{CO}	8.80	H_{HCN}	0.18	$F_{H\cdots N}$	0.70
K_{CN}	6.15	H_{HCO}	0.20	$F_{H\cdots O}$	0.92
$F'=-F/10$		H_{NCO}	0.34	$F_{O\cdots N}$	1.50

trans forms), and 3300, 2460, 1470, 1290, 1053 and about 700 cm^{-1} for DCONHD.

The values of the observed frequencies are given in the first column of Table III.

Calculation of Normal Vibrations

The calculation of normal vibrations was made by the method presented by Wilson[17], according to which the secular equation was set in the form $|\boldsymbol{GF}-\lambda\boldsymbol{E}|=0$, where $\boldsymbol{F}$ and $\boldsymbol{G}$ are the potential and reciprocal kinetic energy matrices respectively. It was assumed that the molecule has a planar configuration (C_s), the normal vibrations are classified into 9 in-plane (A′) and 3 out-of-plane (A″) vibrations. In the present paper, only the in-plane vibrations were treated. The structural parameters used in this calculation are as follows; the bond lengths of $r(NH)=1.04$, $r(CN)=1.30$, $r(CH)=1.07$ and $r(C=O)=1.225$ A[4,5], all the bond angles are assumed to be 120°. The symmetry coordinates $\boldsymbol{S}$ obtained from the internal coordinates $\boldsymbol{R}$ by a linear transformation;

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

are given in Table I.

Force Constants. — The potential function employed in the calculation is of the Urey-Bradley type[18];

$$2V=\sum K_i(\Delta r_i)^2+\sum H_{ij}r^0{}_i r^0{}_j(\Delta\alpha_{ij})^2$$
$$+\sum F_{ij}(\Delta q_{ij})^2+\text{linear terms}$$

where r_i and r_j are bond lengths with equilibrium values $r^0{}_i$ and $r^0{}_j$; α_{ij} are bond angles and q_{ij} distances betweeen nonbonded atoms. K, H and F are stretching, bending and repulsive force constants respectively.

The values of the force constants were first transferred from diformylhydrazine, *N*-methylacetamide[19] and urea[20]. A refinement of the values of the force constants was made by the method developed by Miyazawa[21]. The final set of their values is given in Table II, and the calculated frequencies with these values are shown in the second column of Table III.

The calculated frequencies are in excellent agreement with the observed ones, the maximum deviation being 3.0% and the average deviation 1.3%. Therefore, the values of the force constants obtained in this calculation may be used for the normal vibration calculations of the molecules which are closely related with formamide[22].

***L* Matrix and Potential Energy Distribution.** —In order to clarify the nature of the observed frequencies precisely, it is desirable to calculate the relative amplitude of each symmetry coordinate in a given normal mode of vibration. The symmetry coordinates $\boldsymbol{S}$ are related linearly to the normal coordinates $\boldsymbol{Q}$ through the matrix expression;

$$\boldsymbol{S}=\boldsymbol{LQ}$$

The relative amplitude for each symmetry coordinate in a given normal vibration is given

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TABLE III. THE OBSERVED AND CALCULATED FREQUENCIES, AND POTENTIAL ENERGY DISTRIBUTIONS

		Frequency			P. E. D. $(F_{ii}L^2_{is}/\lambda_s)\times 100$								
		ν_{obs}	ν_{calc}	$\varDelta$	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
	ν_1	3330	3367	−1.1	100	0	0	0	0	0	0	0	0
	ν_2	3190	3268	−2.5	0	99	0	0	0	0	0	0	0
	ν_3	2882	2935	−1.8	0	0	102	0	0	0	0	0	0
	ν_4	1690	1681	+0.5	0	1	0	64	33	8	19	3	0
$HCONH_2$	ν_5	1608	1606	+0.1	0	0	0	11	3	85	3	1	1
	ν_6	1391	1398	−0.5	0	0	1	19	7	0	65	2	4
	ν_7	1309	1304	+0.4	0	0	0	1	57	6	13	13	9
	ν_8	1090	1103	−1.2	0	0	0	11	8	1	1	73	1
	ν_9	608	617	−1.5	0	0	1	0	0	0	0	8	90
	ν_1	2556	2494	+2.4	100	0	0	0	0	0	0	1	0
	ν_2	2385	2361	+1.0	0	98	0	0	2	1	0	0	0
	ν_3	2887	2936	−1.7	0	0	102	0	0	0	0	0	0
	ν_4	1667	1672	−0.3	0	0	0	73	29	1	22	2	0
$HCOND_2$	ν_5	1398	1400	−0.1	0	0	1	25	16	3	49	1	5
	ν_6	1338	1362	+1.8	0	2	0	1	43	22	30	1	3
	ν_7	1118	1098	+1.8	0	1	0	0	14	69	1	6	9
	ν_8	912	905	+0.8	0	0	0	6	4	4	0	66	13
	ν_9	570	554	+2.7	0	0	1	0	0	1	0	24	74
	ν_1	3330	3366	−1.1	100	0	0	0	0	0	0	0	0
	ν_2	3190	3266	−2.5	0	100	0	0	0	0	0	0	0
	ν_3	2170	2146	+1.1	0	0	103	2	1	0	0	0	1
	ν_4	1675	1669	+0.4	0	0	0	62	37	14	9	3	0
$DCONH_2$	ν_5	1620	1609	+1.2	0	1	0	18	1	80	2	1	1
	ν_6	1293	1313	−1.6	0	0	0	11	60	6	3	11	12
	ν_7	1136	1120	−1.4	0	0	0	13	2	0	8	71	2
	ν_8	984	998	−1.4	0	0	0	0	7	1	80	6	0
	ν_9	600	610	−1.5	0	0	0	0	0	0	1	8	90
	ν_1	2556	2498	+2.4	100	0	0	0	0	0	0	1	0
	ν_2	2383	2362	+0.9	0	98	0	0	2	1	0	0	0
	ν_3	2175	2146	+1.3	0	0	103	2	1	0	0	0	0
	ν_4	1648	1654	−0.4	0	0	0	78	32	1	11	2	0
$DCOND_2$	ν_5	1341	1366	−1.9	0	2	0	18	56	23	0	2	7
	ν_6	1120	1123	−0.3	0	1	0	2	8	63	19	1	6
	ν_7	1037	1006	+3.0	0	0	0	2	5	8	62	14	4
	ν_8	891	891	0	0	0	0	4	5	5	10	56	12
	ν_9	560	548	+2.4	0	0	0	0	0	0	1	24	76

$\varDelta=[\nu_{obs}-\nu_{calc}/\nu_{obs}]\times 100$

by the corresponding element of the $\boldsymbol{L}$ matrix. The elements of the $\boldsymbol{L}$ matrix computed for each species of formamide are given in Table IV. (The $\boldsymbol{L}$ matrix is normalized to $\boldsymbol{G}$; $\boldsymbol{LL'}=\boldsymbol{G}$[23])

It has been shown that the ratios of the potential energy distribution (P. E. D.) among the symmetry coordinates (S_i) for a given normal coordinate (Q_s) can approximately be expressed as $F_{ii}L^2_{is}/\lambda_s$,[24] where F_{ii} is a diagonal element of the $\boldsymbol{F}$ matrix, λ_s is sth frequency parameter. These are also computed and the results are shown in Table III.

Numerical Computations.—All the numerical computations were carried out with a parametron computor PC 1, which was designed and constructed by Professor H. Takahashi and his collaborators in the Department of Physics, Faculty of Science, University of Tokyo. The routines used in the computations have been programmed by Shimanouchi, Takeda and the present writer. The details will be published elsewhere[23].

The Nature of the Observed Bands

Based on the calculated values of vibrational amplitudes and potential energy distributions

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TABLE IV. THE ELEMENTS OF THE L MATRICES

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	
Q_1	1.048	−0.001	−0.013	0.002	0.000	0.001	−0.051	0.128	0.076	
Q_2	0.001	1.012	−0.028	−0.002	−0.049	−0.196	−0.009	−0.001	−0.005	
Q_3	0.013	0.028	1.035	−0.031	−0.031	0.010	−0.031	0.075	0.114	
Q_4	0.003	0.007	−0.001	−0.316	0.254	0.530	−0.724	0.297	0.079	
Q_5	−0.002	0.053	−0.017	0.126	0.069	1.606	0.284	−0.158	−0.090	$HCONH_2$
Q_6	0.008	0.007	0.043	−0.142	−0.094	0.094	1.106	0.185	0.208	
Q_7	−0.004	−0.015	−0.018	0.033	0.258	−0.359	0.466	−0.453	−0.288	
Q_8	0.014	−0.002	−0.015	0.087	0.081	−0.097	0.129	0.914	0.105	
Q_9	−0.009	0.001	0.017	0.004	0.010	−0.028	−0.037	−0.170	0.427	
Q_1	0.776	−0.007	0.013	−0.002	0.001	0.004	−0.088	0.204	0.115	
Q_2	0.008	0.726	0.022	−0.001	−0.090	−0.250	−0.008	0.004	0.009	
Q_3	−0.010	−0.014	1.035	−0.031	−0.028	0.016	−0.029	0.067	0.112	
Q_4	0.007	−0.014	−0.003	0.336	−0.237	−0.149	0.770	−0.238	−0.082	
Q_5	0.008	−0.019	0.048	−0.165	−0.146	−0.272	0.959	0.148	0.239	$HCOND_2$
Q_6	0.009	0.052	−0.013	0.039	0.234	0.699	0.725	−0.156	−0.170	
Q_7	−0.006	0.035	0.011	−0.011	−0.106	0.992	−0.122	0.249	0.237	
Q_8	−0.003	−0.002	−0.003	0.053	0.046	−0.205	0.060	0.708	0.237	
Q_9	−0.011	0.001	0.015	−0.001	0.008	−0.044	−0.036	−0.261	0.347	
Q_1	1.048	−0.003	−0.003	0.001	0.000	0.001	−0.047	0.128	0.077	
Q_2	0.004	1.012	−0.006	−0.002	−0.050	−0.196	−0.007	0.000	−0.003	
Q_3	0.005	0.008	0.770	−0.064	−0.047	0.018	−0.035	0.145	0.184	
Q_4	0.004	0.012	−0.028	−0.310	0.266	0.680	−0.486	0.274	0.065	
Q_5	−0.003	0.052	0.003	0.162	0.038	1.553	0.198	−0.176	−0.091	$DCONH_2$
Q_6	0.006	0.017	−0.004	−0.101	−0.268	0.351	0.228	0.423	0.328	
Q_7	0.013	−0.001	−0.024	0.095	0.043	−0.053	−0.316	0.912	0.107	
Q_8	0.006	−0.001	0.009	0.003	0.067	−0.087	0.876	0.239	0.051	
Q_9	−0.009	0.001	0.011	0.003	0.009	−0.026	−0.056	−0.166	0.423	
Q_1	0.777	−0.004	−0.006	−0.001	0.001	0.004	−0.073	0.202	0.112	
Q_2	0.004	0.726	−0.028	0.003	−0.088	−0.251	0.004	−0.004	−0.001	
Q_3	0.006	0.027	0.760	−0.064	−0.051	−0.002	−0.033	0.126	0.183	
Q_4	0.004	−0.017	0.023	0.344	−0.245	−0.165	0.525	−0.231	−0.077	
Q_5	0.001	0.052	−0.001	0.135	0.268	0.711	−0.104	−0.194	−0.261	$DCOND_2$
Q_6	0.001	0.038	0.004	−0.041	−0.081	0.965	0.478	0.124	0.202	
Q_7	0.009	−0.007	0.018	−0.035	0.056	−0.307	0.773	−0.371	−0.143	
Q_8	−0.002	−0.002	−0.004	0.043	0.052	−0.226	0.282	0.643	0.226	
Q_9	−0.010	0.001	0.011	−0.001	0.007	−0.042	−0.056	−0.257	0.347	

shown in Tables III and IV, the nature of the observed bands will be discussed.

The Bands above 2000 cm^{-1}.—The 3330, 3190 and 2882 cm^{-1} bands of $HCONH_2$ are undoubtedly assigned respectively to the NH_2 antisymmetric, NH_2 symmetric stretching and the CH stretching vibrations. As may be seen from Table III, each of the normal vibrations corresponding to these frequencies takes place along one of these symmetry coordinates, and practically no other vibrations are coupled with it. The bands at 3330, 3190 and 2170 cm^{-1} of $DCONH_2$ are likewise shown to be almost pure NH_2 antisymmetric, NH_2 symmetric stretching and CD stretching vibrations respectively. In a similar way, each of the three high frequencies of $HCOND_2$ and $DCOND_2$ is assigned to almost pure ND_2 antisymmetric, ND_2 symmetric, CH or CD stretching vibration.

The calculated frequencies of these NH_2, ND_2, CH and CD stretching vibrations are in agreement with the observed ones with the maximum deviation of 2.5%. In detail, however, there are systematic deviations found between the calculated and observed frequencies. Namely, the frequency difference $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$ is always negative for the NH_2 and CH stretching vibrations and always positive for the ND_2 and CD stretching vibrations. This may be interpreted as due to the anharmonicity in the internal potential in which the hydrogen or deuterium atoms are placed, which is neglected in the present calculation.

The Band at 1690 cm^{-1}.—To this band there are considerable contributions of both the ν(C=O) and ν(CN) vibrations. The energy associated with the ν(C=O) vibration is 50% of the total and that associated with the ν(CN) is 25%, while the amplitude ratio of the ν(CN) to the ν(C=O) is computed to be -0.73. Therefore, this band may well be called "N–C=O antisymmetric vibration" rather than "C=O stretching vibration". In addition, the contribution of the δ(CH) motion to this band is not negligible as it is in the case of *N*-methylformamide[22] and diformylhydrazine[19].

This band at 1690 cm^{-1} shifts towards lower frequency both on *N*-deuteration and *C*-deuteration the amount of shift being 23 and 15 cm^{-1} respectively. For $DCOND_2$, it is found at 1648 cm^{-1}. On the *C*-deuteration the contribution of the δ(CH) vibration is removed, and on the *N*-deuteration the interaction from the b(NH_2) vibration is removed. This may be the cause of the shifts of the band in question. The way of coupling of the ν(C=O) and ν(CN) vibrations in this normal mode seems to be unaffected by any deuteration.

The Band at 1608 cm^{-1}.—The band at 1608 cm^{-1} of $HCONH_2$ corresponds to almost pure b(NH_2) vibration. This band is not sensitive to the *C*-deuteration and is found at 1620 cm^{-1} in $DCONH_2$. The band corresponding to the b(ND_2) vibration is found at 1118 cm^{-1} in $HCOND_2$. The position of the band is hardly affected by *C*-deuteration, but its intensity becomes weaker.

The Band at 1391 cm^{-1}.—The band at 1391 cm^{-1} of $HCONH_2$ can be assigned to the δ(CH) vibration. However, contributions of both the ν(CN) and ν(C=O) vibrations are not negligible. In the normal vibration, the C–N and C=O bonds stretch and contract in phase with an amplitude ratio of $+0.66$. This band is not sensitive to *N*-deuteration and is found at 1398 cm^{-1} in $HCOND_2$. The band at 984 cm^{-1} in $DCONH_2$ corresponds to almost pure δ(CD) vibration. It shifts towards higher frequency on *N*-deuteration by 53 cm^{-1}. As is seen from Tables III and IV the shift can be explained as due to the interaction between δ(CD) and r(ND_2) vibrations.

The Band at 1309 cm^{-1}.—This band is mainly due to the ν(CN) vibration, although there are energetically small contributions of δ(CH) and r(NH_2) vibrations. The contribution of the ν(C=O) motion is shown to be quite negligible by the present calculation, in contradiction to some previous authors' expectation[12,13]. On *N*-deuteration the band moves to higher frequency by 29 cm^{-1}. The nature of the normal mode corresponding to this band is more complex. Here, the contributions of the δ(CH) and b(ND_2) vibrations are as important as the ν(CN) vibration.

It is noted that the contribution of the ν(C=O) vibration increases on *C*-deuteration, while that of the δ(CH) becomes negligible. In the corresponding normal vibration at 1341 cm^{-1} of $DCOND_2$ the energy associated with the ν(C=O) vibration is 16% of the total.

The Bands at 1090 and ca. 600 cm^{-1}.—The band which occurs at about 1090 cm^{-1} in $HCONH_2$ can be assigned to the r(NH_2) vibration, although there is a small contribution of the ν(C=O) vibration. On *C*-deuteration it shifts towards higher frequency by about 40 cm^{-1}. The broad band at about 600 cm^{-1} of $HCONH_2$ corresponds to almost pure δ(NCO) vibration. (It is overlapped with another broad band arising from the NH_2 wagging vibration.) The band is insensitive to *C*-deuteration. In *N*-deuterated formamides, an interaction between the r(ND_2) and δ(NCO) vibrations takes place, and this gives rise to two obserbed bands at 912 and about 570 cm^{-1} in $HCOND_2$ and those at 891 and about 560 cm^{-1} in $DCOND_2$. In addition, there is a small contribution of the δ(CD) vibration to the band at 891 cm^{-1} of $DCOND_2$.

The Out-of-plane Vibrations—Of three out-of-plane vibrations, two can easily be identified. They are the CH out-of-plane deformation and NH_2 wagging vibrations; π(CH) and w(NH_2).

Of $HCONH_2$, the π(CH) vibration is assigned to a band at 1056 cm^{-1}. On *N*-deuteration it is a little shifted, while on *C*-deuteration it disappears as is expected from the assignment. The band at 881 cm^{-1} in $DCONH_2$ can be assigned to the π(CD) vibration, although its intensity is comparatively weak. In $DCOND_2$ it is probably overlapped by the r(ND_2) band at 891 cm^{-1} and cannot be distinguished. The above assignment is consistent with the result given by a study on the infrared spectra of $DCONHCH_3$ and $DCONDCH_3$[22]. Both of them show a band at 864 cm^{-1}, the intensity of which is as weak as that of the 881 cm^{-1} band of $DCONH_2$.

A broad band found at about 750 cm^{-1} in both $HCONH_2$ and $DCONH_2$ is assigned to the w(NH_2) vibration. On *N*-deuteration it moves to lower frequency up to about 450 cm^{-1}.

Another out-of-plane vibration, the NH_2 twisting or torsional vibration, is expected to occur at a lower frequency than 300 cm^{-1}. The Raman line found at 200 cm^{-1} of $HCONH_2$[9] may be assigned to this vibration.

Thus, a complete assignment has been made of the infrared absorption bands of the four isotopic species of formamide observed in the 3600~300 cm^{-1} region. The present assignment for $HCONH_2$ and $HCOND_2$ is in comformity with that proposed by Miyazawa[13] except for a few minor points, but considerably different from others' assignments.

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