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Infrared Spectra of Partially Deuterated Acetamide

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The infrared spectra of orthorhombic crystals of CH_3CONH_2, CD_3CONH_2, and their *N*-deuterated and partially *N*-deuterated samples have been recorded in the region between 4000 and 400 cm^{-1}. The bands due to the *trans*- and *cis*-NHD species have been assigned by comparing the spectra of various samples containing the NH_2, ND_2 and NHD species in different proportions. In the spectra of the 50% *N*-deuterated samples, the absorption bands near 1530 and 1360 cm^{-1} have been assigned to the amide II and III modes, respectively, of the *trans*-NHD species characteristic of the *trans* conformation of the –CONH– group, and those near 1480 and 1400 cm^{-1} to the NH in-plane deformation and the CN stretching modes, respectively, of the *cis*-NHD species. These assignments were confirmed by the normal coordinates analysis of eight isotopic species of acetamide based on the Urey-Bradley force field.

The hydrogen atoms in the amide group of acetamide are easily substituted by deuterium atoms by the exchange reaction with heavy water. If a mixture of water and heavy water is used in the exchange reaction, the resulting samples should contain the molecular species involving the NH_2, ND_2 and NHD groups. This report presents the assignment of infrared absorption frequencies of the NHD species of acetamide and *C*-deuterated acetamide obtained by this partial *N*-deuteration. As shown in Fig. 1, there are two geometrical isomers of the NHD species arising from the planarity of amide group. Molecular vibrations of these NHD species are of interest because of their structure involving the biochemically important –CONH– group. Our attention was drawn to this point first by observing a strong band near 1520 cm^{-1} in the infrared spectra of incompletely deuterated primary amides and noticing an analogy between this band and the amide II band of *trans*-*N*-monosubstituted amides.

It is well known that the conformation of the C=O and the NH bonds is an important factor determining the vibration modes and frequencies of the –CONH– group. The amide II and III frequencies arising from the coupling between the CN stretching and the NH in-plane deformation vibrations are observed only for the trans conformation.[1] Miyazawa has calculated the normal vibrations of the hypothetical *cis* form of *N*-methylacetamide using the Urey-Bradley force constants which reproduce the observed frequencies of the *trans* form, and has obtained almost pure CN stretching and the NH in-plane deformation vibrations instead of their coupled vibrations.[2] Since the *trans*- and *cis*-isomers of the NHD species in the present study have exactly the same force field with each other, they are expected to afford experimental evidences of the change of vibrational modes given rise to by the purely geometrical effect on the –CONH– group.

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

[2] T. Miyazawa, T. Shimanouchi and S. Mizushima, *ibid.*, **29**, 611 (1958).

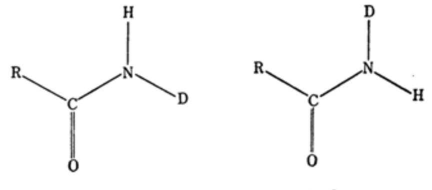
Experimental

Commercially available acetamide was purified by the crystallization from ether and ethanol solutions. *C*-Deuterated acetamide was prepared by the reaction between NH_3 gas and CD_3COCl, in ether at $-20°C$, and was purified by the same way as acetamide. For the preparation of CD_3COCl, commercially available CD_3COOD (Merk AG. Darmstadt) was treated with benzoyl chloride according to Bender's method.[3] These NH_2 compounds were converted into the corresponding ND_2 compounds by the exchange reaction with heavy water. The partially *N*-deuterated samples were prepared by using mixtures of water and heavy water in various proportions.

The infrared spectra were recorded on Koken DS 301 infrared spectrophotometer equipped with sodium chloride (4000—700 cm^{-1}) and potassium bromide (700—400 cm^{-1}) prisms. The measurement was made for the orthorhombic crystal obtained by the crystallization from molten liquid[4] between two potassium bromide plates or between two sodium chloride plates. The crystal form of the partially *N*-deuterated samples prepared in the same way was confirmed to be orthorhombic from the absorptions of the NH_2 species contained in the samples. The absorptions of the ND_2 species in the partially *N*-deuterated samples were then used to identify the crystal form of the almost completely *N*-deuterated samples. It was also found from the comparison of infrared spectra that the orthorhombic crystal was converted into the trigonal crystal on mulling with Nujol or hexachlorobutadiene.

Results and Discussion

A detailed assignment of the infrared absorption bands of acetamide, *C*-deuterated acetamide and their ND_2 species have been given by Suzuki on the basis of the normal coordinates analysis of the a′ vibrations.[5] Although the crystal spectra reported by Suzuki are those of the trigonal form, most of his assignments for the NH_2 and ND_2 species are applicable to the presently investigated orthorhombic form because the infrared absorptions of these two forms are not seriously different from each other.[6] The trigonal form is better than the orthorhombic one to prevent the sample from atmospheric water and to maintain the orginal concentration of the *N*-deuterated species, since the Nujol and hexachlorobutadiene mulls can be prepared more quickly than the crystal film. For investigating the spectral change around 1500 cm^{-1} on successive *N*-deuteration, however, the orthorhombic form was found to be more appropriate since it showed much sharper absorption bands in this region than the corresponding bands of the trigonal form. In Figs. 2—5, the infrared spectra of orthorhombic form of acetamide and *C*-deuterated acetamide obtained from a equimolar mixture of



trans-form *cis*-form

Fig. 1. Structurs of the NHD species.

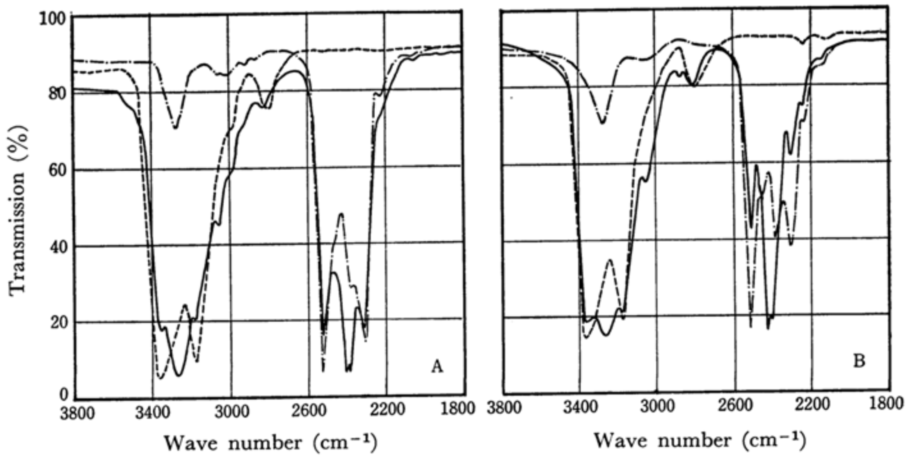


Fig. 2. Infrared spectra of acetamide (A) and *C*-deuterated acetamide (B) in the region between 4000 and 1800 cm^{-1}

--- shows the infrared spectra of the crystal from water,
—— from a equimolar mixture of water and heavy water, —·— from heavy water

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[3] M. L. Bender and M. S. Feng, *J. Am. Chem. Soc.*, **82**, 6319 (1960).

[4] W. C. Hamilton, *Acta Cryst.*, **18**, 866 (1965).

[5] I. Suzuki, This Bulletin, **35**, 1279 (1962).

[6] W. Kutzelnigg and R. Mecke, *Spectrochim. Acta*, **18**, 549 (1962).

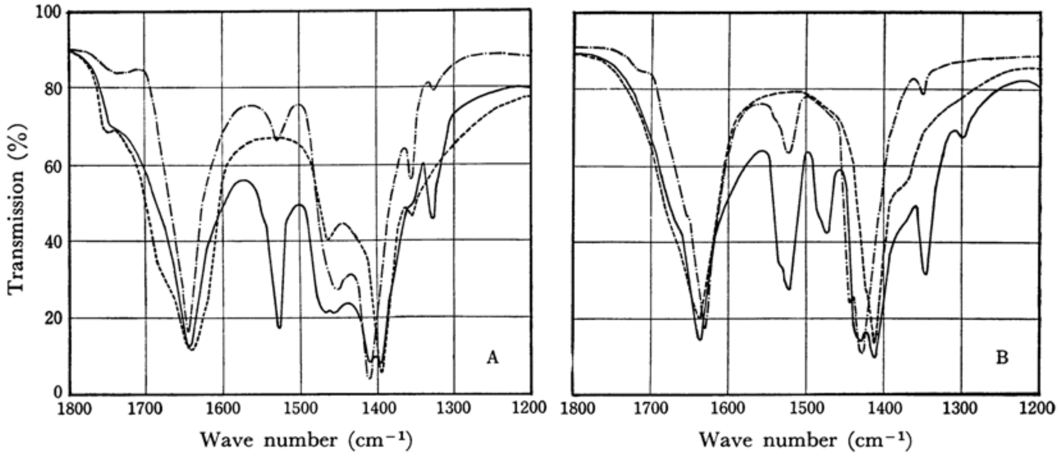

Fig. 3. Infrared spectra of acetamide (A) and *C*-deuterated acetamide (B) in the region between 1800 and 1200 cm^{-1}.

--- shows the infrared spectra of the crystal from water,

—— from a equimolar mixture of water and heavy water, —·— from heavy water

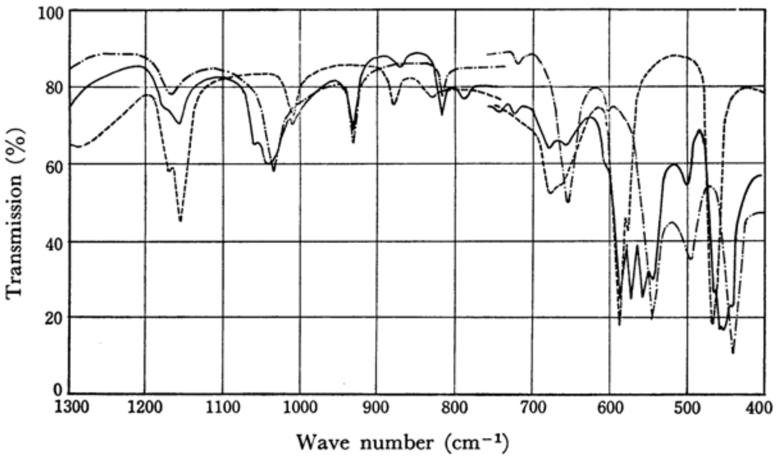

Fig. 4. Infrared spectra of acetamide in the region between 1300 and 400 cm^{-1}.

--- shows the infrared spectra of the crystal from water,

—— from a equimolar mixture of water and heavy water, —·— from heavy water

water and heavy water are shown together with the spectra of the corresponding NH_2 and ND_2 species. We assumed that this mixture gave approximately rise to the deuteration of 50% of amide hydrogen atoms in the whole sample and the resulting crystal included the NHD species in the maximum concentration attainable. The absorption bands due to the NH_2 and ND_2 species appearing in the spectra of this 50% *N*-deuterated samples can be differentiated from those due to the NHD species by referring to the spectra of the NH_2 and ND_2 species. Observed frequencies and assignments are listed in Table 1.

4000—1800 cm^{-1}. The strong bands near 3300 and 2400 cm^{-1} observed for the 50% *N*-deuterated sample of acetamide are assigned to the NH and ND stretching vibrations, respectively, of the NHD compounds. The appearance of these NX (X=H or D) stretching frequencies between the symmetric and antisymmetric NX_2 stretching frequencies is to be expected from the removal of the vibrational coupling between two equivalent NX bonds. The ND stretching band consists of two peaks attributable to the *trans*- and *cis*-NHD species, but the NH stretching band does not show any splitting. A broad band near 2800 cm^{-1} observed for orthorhombic acetamide disappears on *N*-deuteration but does not disappear on *C*-deuteration.

1800—1200 cm^{-1}. In the region between 1700 and 1600 cm^{-1} where the C=O stretching and the NH_2 bending frequencies are expected, the orthorhombic crystal of acetamide shows a strong absorption band consisting of a peak at 1640 cm^{-1} and a

TABLE 1. OBSERVED FREQUENCIES AND ASSIGNMENTS FOR *N*-50% DEUTERATED SAMPLES

Acetamide		*C*-deuterated acetamide	
3380 m	NH$_2$ asym. stretching (NH$_2$)*	3380 m	NH$_2$ asym. stretching (NH$_2$)
3270 vs	NH stretching (*trans*- and *cis*-NHD)	3265 vs	NH stretching (*trans*- and *cis*-NHD)
3190 m	NH$_2$ sym. stretching	3190 m	NH$_2$ sym. stretching (NH$_2$)
3055 w	Combination or over-tone (*trans*- and *cis*-NHD)	3050 vw	Combination or over-tone (*trans*- and *cis*-NHD)
3000 vw	CH$_3$ asym. stretching	2810 w	Combination or over-tone (NH$_2$)
2930 vw	CH$_3$ sym. stretching	2527 vs	ND$_2$ asym. stretching (ND$_2$)
2815 w	Combination or over-tone (NH$_2$)	2420 vs	ND stretching (*cis*-NHD)
2530 vs	ND$_2$ asym. stretching (ND$_2$)	2400 sh	ND stretching (*trans*-NHD)
2417 vs	ND stretching (*cis*-NHD)	2320 s	ND$_2$ asym. stretching (ND$_2$)
2395 vs	ND stretching (*trans*-NHD)	2240 vw	CD$_3$ asym. stretching
2316 s	ND$_2$ sym. stretching (ND$_2$)	2120 vw	CD$_3$ sym. stretching
1652 vs	C=O stretching NH$_2$ bending (NH$_2$)	1634 vs	C=O stretching NH$_2$ bending (NH$_2$)
1530 vs	Amide II (*trans*-NHD)	1529 s	Amide II (*trans*-NHD)
1475 sh	NH deformation (*cis*-NHD)	1475 m	NH deformation (*cis*-NHD)
1460 mb	CH$_3$ deg. deformation	1421 vs	CN stretching (ND$_2$)
1411 vs	CN stretching (ND$_2$)	1410 vs	CN stretching (NH$_2$ and *cis*-NHD)
1398 vs	CN stretching (NH$_2$ and *cis*-NHD)	1348 s	Amide III (*trans*-NHD)
1358 sh	CH$_3$ sym. deformation	1187 vw	ND$_2$ bending (ND$_2$)
1327 m	Amide III (*trans*-NHD)	1152 w	NH$_2$ rocking (NH$_2$)
1175 sh	ND$_2$ bending (ND$_2$)	1088 sh	CD$_3$ sym. deformation (*cis*-NHD)
1154 wb	NH$_2$ rocking (NH$_2$)	1084 w	CD$_3$ sym. deformation (NH$_2$ and *trans*-NHD)
1060 sh	ND deformation (*trans*-NHD)	1070**	CD$_3$ sym. deformation (ND$_2$)
1045 mb	CH$_3$ rocking (*cis*-NHD)	1039 m	CD$_3$ deg. deformation ND deformation (*trans*-NHD)
1036 sh	CH$_3$ rocking (ND$_2$)	975 wb	ND deformation (*cis*-NHD)
1010 vw	CH$_3$ rocking (NH$_2$)	962 w	ND$_2$ rocking (ND$_2$)
933 m	ND deformation (*cis*-NHD) ND$_2$ rocking (ND$_2$)	831 sh	CC′ stretching (NH$_2$)
871 w	CC′ stretching (*cis*-NHD and NH$_2$)	828 vw	CC′ stretching (*cis*-NHD)
819 w	CC′ stretching (*trans*-NHD and ND$_2$)	812 w	CD$_3$ rocking
680 wb	out-of-plane (NH$_2$)	760 vw	CC′ stretching (ND$_2$ and *trans*-NHD)
655 wb	out-of-plane (ND$_2$)	670 wb	out-of-plane (NH$_2$)
586 s	NCO deformation (NH$_2$)	625 vwb	out-of-plane (ND$_2$)
568 s	NCO deformation (*cis*-NHD)	566 s	NCO deformation (NH$_2$)
556 s	NCO deformation (*trans*-NHD)	546 s	NCO deformation (*cis*-NHD)
548 sh	NCO deformation (ND$_2$)	538 s	NCO deformation (*trans*-NHD)
500 wb	out-of-plane (ND$_2$)	526 m	NCO deformation (ND$_2$)
466 sh	CC′ deformation (NH$_2$)	490 wb	out-of-plane (ND$_2$)
460 s	CC′ deformation (*trans*-NHD)		
455 s	CC′ deformation (*cis*-NHD)		
442 sh	CC′ deformation (ND$_2$)		

* Parenthesis shows type of amino-group in the molecular species related to the absorption indicated.

** Observed only in the spectra of CD_3COND_2.

shoulder at its high frequency side. Since the assignment of both the peak and the shoulder to fundamentals was found to be necessary from a slight high frequency shift of the apparent absorption maximum on 50% *N*-deuteration, we divided the whole absorption of acetamide into two Lorenz type components, and estimated the position of the unobserved peak of the high frequency component to be 1665 cm^{-1} (Fig. 3-A). Similarly, the high frequency component of the corresponding absorption of *C*-deuterated acetamide was estimated to be 1655 cm^{-1} (Fig. 3-B).

Each of 50% *N*-deuterated samples of acetamide and *C*-deuterated acetamide shows clearly two bands at 1530 and 1328 cm^{-1} attributable to the NHD species. From analogy in the conformation between the *trans*-NHD species and *trans*-*N*-monosubstituted amides, it is conceivable that the CN stretching and the NH in-plane deformation vibrations of the *trans*-NHD species couple appreciably with each other and give rise to the amide II and III bands at 1530 and 1327 cm^{-1},

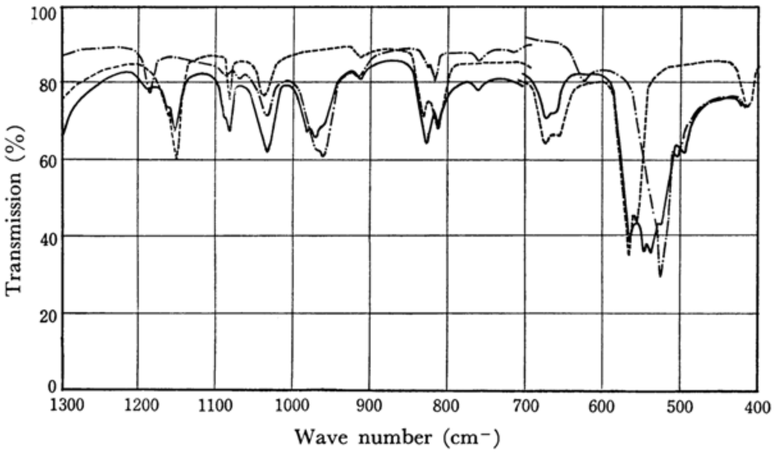

Fig. 5. Infrared spectra of *C*-deuterated acetamide in the region between 1300 and 400 cm^{-1}.
- - - shows the infrared spectra of the crystal from water,
—— from a equimolar mixture of water and heavy water, —·— from heavy water

respectively. The frequencies of these bands are comparable with the amide II and the amide III frequencies (1566 and 1301 cm^{-1}, respectively) of *N*-methylacetamide[2] crystal at +15°C. The absorption bands due to the *cis*-NHD species may be found from analogy to *cis*-*N*-monosubstituted amides, for which the coupling between the CN stretching and the NH in-plane deformation vibrations is not appreciable. Supposedly, the NH in-plane deformation frequencies of *cis*-CH_3CONHD and *cis*-CD_3CONHD are not far from the corresponding frequency of diketopiperazine crystal (b_u: 1443 cm^{-1}).[7] For each of 50% *N*-deuterated samples of acetamide and *C*-deuterated acetamide, we observed an absorption band near 1480 cm^{-1} assignable to the NH in-plane deformation vibration of *cis*-NHD species. The intensity change of this absorption on the progress of *N*-deuteration was not obvious for *cis*-CH_3CONHD because of the overlap of the CH_3 degenerate deformation band at 1453 cm^{-1}. It was recognized clearly, however, for *cis*-CD_3CONHD which did not show any interfering fundamental in this region.

1200—400 cm^{-1}. For both acetamide and *C*-deuterated acetamide, most of the bands observed between 1200 and 700 cm^{-1} for the 50% *N*-deuterated samples appear also in the spectra of either the NH_2 or ND_2 species. This result seems to contradict with the fact that the ND in-plane deformation (amide III′) mode of both *trans*- and *cis*-NHD species has an intrinsic frequency around 1000 cm^{-1} and is likely to couple with other modes having similar intrinsic frequencies. The normal coordinate analysis discussed in the following section ascertained, however, that the absorptions due to the NHD species overlap considerably with those due to the NH_2 or the ND_2 species.

As seen in Fig. 4, the NCO deformation band of acetamide at 586 cm^{-1} splits into four bands on 50% *N*-deuteration. This fact suggests that the NCO deformation frequencies of the NH_2, ND_2, *trans*-NHD and *cis*-NHD species are different from one another. The middle two bands observed at 568 and 556 cm^{-1} can be assigned to the NHD species. Similar splitting on 50% *N*-deuteration are observed for the NCO deformation band at 566 cm^{-1} of *C*-deuterated acetamide in Fig. 5 and for the CC′ deformation band at 466 cm^{-1} of acetamide in Fig. 4.

Normal Coordinate Analysis

On assigning the infrared absorption bands of CH_3CONHD and CD_3CONHD from analogy with *N*-monosubstituted amides, we assumed that the vibrational modes of the –CONH– group were not much affected by the change in the *N*-substituent atom from carbon to deuterium. In order to verify this assumption, we carried out the normal coordinate analysis of the eight isotopic species of acetamide formed by the combination of the CH_3 and CD_3 groups with the NH_2, *trans*-NHD, *cis*-NHD and ND_2 groups. The ***G*** matrices were set up by using the structural parameters based

TABLE 2. STRUCTURAL PARAMETER

Bond length, Å		Angle	
R(C=O)	1.260	∠CCN	117.2°
R(C-N)	1.334	∠CCO	119.6°
R(C-C′)	1.505	∠NCO	123.2°
R(N-H)	1.02	∠CCH, ∠HCH	109°28′
R(C-H)	1.08	∠CNH, ∠HNH	120.0°

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[7] K. Fukushima, Y. Ideguchi and T. Miyazawa, This Bulletin, **37**, 349 (1964).

TABLE 3. SYMMETRY COORDINATES FOR ACETAMIDE

Symmetry coordinate	Description of mode	Abbr.
$S_1 = \Delta r_6$	CN stretching	νCN
$S_2 = \Delta r_2$	CC′ stretching	νCC′
$S_3 = \Delta r_1$	C=O stretching	νC=O
$S_4 = \{2\Delta\phi_{78}-(1+\sqrt{3})\Delta\phi_{68}+(\sqrt{3}-1)\Delta\phi_{67}\}/2\sqrt{3}$	*trans*-NH deformation	δ_t-NH
$S_5 = \{2\Delta\phi_{78}-(1+\sqrt{3})\Delta\phi_{67}+(\sqrt{3}-1)\Delta\phi_{68}\}/2\sqrt{3}$	*cis*-NH deformation	δ_c-NH
$S_6 = (2\Delta\phi_{16}-\Delta\phi_{12}-\Delta\phi_{26})/\sqrt{6}$	NCO deformation	δNCO
$S_7 = (\Delta\phi_{26}-\Delta\phi_{12})/\sqrt{2}$	CC′ deformation	δCC′
$S_8 = (2\Delta\phi_{34}-\Delta\phi_{35}-\phi_{45})/\sqrt{6}$	CH_3 degenerate deformation	$\delta_d CH_3$
$S_9 = (\Delta\phi_{23}+\Delta\phi_{24}+\Delta\phi_{25}-\Delta\phi_{34}-\Delta\phi_{35}-\Delta\phi_{45})/\sqrt{6}$	CH_3 symmetric deformation	$\delta_s CH_3$
$S_{10} = (2\Delta\phi_{25}-\Delta\phi_{23}-\Delta\phi_{24})/\sqrt{6}$	CH_3 rocking	ρCH_3
$S_{11} = \Delta r_7$	*trans*-NH stretching	ν_t-NH
$S_{12} = \Delta r_8$	*cis*-NH stretching	ν_c-NH
$S_{13} = (2\Delta r_5-\Delta r_3-\Delta r_4)/\sqrt{6}$	CH_3 antisymmetric stretching	$\nu_a CH_3$
$S_{14} = (\Delta r_3+\Delta r_4+\Delta r_5)/\sqrt{3}$	CH_3 symmetric stretching	$\nu_s CH_3$

TABLE 4. PRODUCT RULE AND SUM RULE

Product rule	Obs.	Calcd.	Sum rule	
$\Pi\nu_{i\ NH_2}/\Pi\nu_{i\ ND_2}$*	3.77	3.71	$\sum\nu^2_{i\ NH_2}+\sum\nu'^2_{i\ ND_2}$	8.65×10^7
$\Pi\nu_{i\ cis}/\Pi\nu_{i\ trans}$	1.00	1.00	$\sum\nu^2_{i\ trans}+\sum\nu'^2_{i\ cis}$	8.60×10^7
$\Pi\nu'_{i\ NH_2}/\Pi\nu'_{i\ ND_2}$	3.73	3.73	$\sum\nu^2_{i\ cis}+\sum\nu'^2_{i\ trans}$	8.60×10^7
$\Pi\nu'_{i\ cis}/\Pi\nu'_{i\ trans}$	1.03	1.00	$\sum\nu^2_{i\ ND_2}+\sum\nu'^2_{i\ NH_2}$	8.65×10^7

$\nu_{i\ NH_2}$: infrared absorption frequency of CH_3CONH_2, $\nu_{i\ cis}$: *cis*-CH_3CONHD, $\nu_{i\ trans}$: *trans*-CH_3CONHD, $\nu_{i\ ND_2}$: CH_3COND_2, $\nu'_{i\ NH_2}$: CD_3CONH_2, $\nu'_{i\ cis}$: *cis*-CD_3CONHD, $\nu'_{i\ trans}$: *trans*-CD_3CONHD, $\nu'_{i\ ND_2}$: CD_3COND_2

TABLE 5. FORCE CONSTANTS (md/Å)

Force constant (md/Å)		Dispersion	Force constant (md/Å)		Dispersion
K(CN)	5.52_5	0.034	H(HCC)	0.37_9	0.001
K(CO)	7.43_8	0.028	F(HNH)	0.0 (assumed)	—
K(CC)	3.18_7	0.029	F(HNC)	0.37_6	0.003
K(CH)	4.61_7	0.000	F(NCO)	1.22_8	0.021
K(NH)	5.72_8	0.001	F(CCN)	0.13_7	0.016
H(HNH)	0.37_5	0.000	F(CCO)	0.56_3	0.023
H(HNC)	0.40_6	0.000	F(HCH)	0.06_9	0.000
H(NCO)	0.52_1	0.005	F(HCC)	0.36_2	0.001
H(CCN)	0.62_5	0.006	κ	-0.11_8 md Å	0.000
H(CCO)	0.24_7	0.009	P(NH-NH)	-0.14_9	0.000
H(HCH)	0.40_1	0.000			

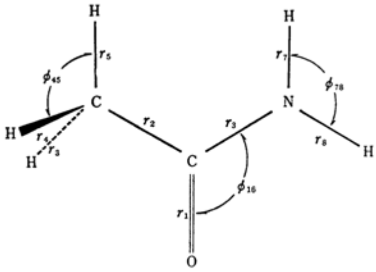

Fig. 6. Molecular structure and internal coordinates of acetamide.

on Hamilton's X ray study[4] as shown in Table 2. The description of the internal coordinates is shown in Fig. 6, and the internal symmetry coordinates are listed in Table 3. A simple Urey-Bradley force field was employed first but an interaction constant between the two NH stretching coordinates in the NH_2 group, P(NH–NH), was introduced after several trial calculations. The stretch-stretch interaction constant of this type was first introduced for methyl group[8] and water[9] as a supplementary

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[8] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta,* **18**, 513 (1962).

[9] K. Kuchizu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2460 (1962).

TABLE 6. FUNDAMENTAL FREQUENCIES AND MAIN POTENTIAL ENERGY DISTRIBUTIONS FOR CH_3CONH_2 AND CD_3CONH_2

	CH_3CONH_2						CD_3CONH_2				
	Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.		Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.
ν_1	3380	3375	0.2	$S_{11}(49)$, $S_{12}(49)$	ν_aNH_2	ν'_1	3380	3375	0.2	$S_{11}(49)$, $S_{12}(49)$	ν_aNH_2
ν_2	3190	3190	0.0	$S_{11}(51)$, $S_{12}(51)$	ν_sNH_2	ν'_2	3190	3190	0.0	$S_{11}(51)$, $S_{12}(51)$	ν_sNH_2
ν_3	3000	3005	0.2	$S_{13}(100)$	ν_aCH_3	ν'_3	2240	2234	0.3	$S_{13}(100)$	ν_aCD_3
ν_4	2636	2636	0.0	$S_{14}(100)$	ν_sCH_3	ν'_4	2120	2109	0.5	$S_{14}(99)$	ν_sCD_3
ν_5	1665	1670	0.3	$S_3(38)$, $S_4(33)$	$\nu C{=}O$	ν'_5	1655	1660	0.3	$S_3(29)$, $S_4(46)$	$\nu C{=}O$
ν_6	1640	1627	0.8	$S_5(60)$, $S_4(24)$	βNH_2	ν'_6	1639	1620	1.1	$S_5(51)$, $S_3(37)$	βNH_2
ν_7	1470	1471	0.0	$S_8(44)$, $S_{10}(16)$	δ_dCH_3	ν'_7	1413	1414	0.1	$S_1(46)$, $S_2(27)$	νCN
ν_8	1398	1400	0.1	$S_1(32)$, $S_2(22)$	νCN	ν'_8	1152	1151	0.1	$S_5(31)$, $S_4(22)$	ρNH_2
ν_9	1358	1361	0.2	$S_9(83)$	δ_sCH_3	ν'_9	1084	1078	0.7	$S_9(74)$	δ_sCD_3
ν_{10}	1154	1146	0.7	$S_5(32)$, $S_4(21)$	ρNH_2	ν'_{10}	1041	1036	0.5	$S_8(71)$, $S_{10}(17)$	δ_dCD_3
ν_{11}	1010	1018	0.8	$S_{10}(70)$, $S_8(30)$	ρCH_3	ν'_{11}	831	839	1.0	$S_2(20)$, $S_{10}(15)$	$\nu CC'$
ν_{12}	878	879	0.1	$S_2(43)$, $S_1(20)$	$\nu CC'$	ν'_{12}	813	806	0.8	$S_{10}(53)$, $S_8(20)$	ρCD_3
ν_{13}	586	582	0.7	$S_6(76)$, $S_2(17)$	δNCO	ν'_{13}	566	556	1.8	$S_6(67)$, $S_2(20)$	δNCO
ν_{14}	466	465	0.2	$S_7(87)$	$\delta CC'$	ν'_{14}	420	422	0.5	$S_7(80)$	$\delta CC'$

$\Delta=(|\nu_{\text{obsd.}}-\nu_{\text{calcd.}}|/\nu_{\text{obsd.}})\times 100$

TABLE 7. FUNDAMENTAL FREQUENCIES AND MAIN POTENTIAL ENERGY DISTRIBUTIONS FOR *trans*-CH_3CONHD AND CD_3CONHD

	trans-CH_3CONHD						*trans*-CD_3CONHD				
	Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.		Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.
ν_1	3270	3293	0.7	$S_{11}(99)$	ν_t-NH	ν'_1	3265	3293	0.9	$S_{11}(99)$	ν_t-NH
ν_2	3000	3005	0.2	$S_{13}(100)$	ν_aCH_3	ν'_2	2424	2397	1.0	$S_{12}(98)$	ν_c-ND
ν_3	2926	2936	0.3	$S_{14}(100)$	ν_sCH_3	ν'_3	2240	2234	0.3	$S_{13}(100)$	ν_aCD_3
ν_4	2395	2397	0.1	$S_{12}(98)$	ν_c-ND	ν'_4	2120	2109	0.5	$S_{14}(100)$	ν_sCD_3
ν_5	1652	1652	0.0	$S_3(59)$, $S_1(17)$	$\nu C{=}O$	ν'_5	1628	1633	0.3	$S_3(67)$, $S_1(17)$	$\nu C{=}O$
ν_6	1530	1534	0.2	$S_5(57)$, $S_1(23)$	Amide II	ν'_6	1529	1531	0.1	$S_5(67)$, $S_1(17)$	Amide II
ν_7	1453	1451	0.1	$S_8(60)$, $S_{10}(14)$	δ_dCH_3	ν'_7	1348	1334	1.0	$S_1(26)$, $S_5(16)$	Amide III
ν_8	1359	1375	1.2	$S_9(88)$	δ_sCH_3						
ν_9	1327	1316	0.8	$S_1(27)$, $S_5(13)$	Amide III	ν'_8	1084	1077	0.6	$S_9(66)$	δ_sCD_3
						ν'_9	1039	1048	0.9	$S_4(30)$, $S_8(18)$	δ_c-ND
ν_{10}	1060	1051	0.8	$S_4(36)$, $S_3(26)$	δ_c-ND	ν'_{10}	1039	1032	0.7	$S_8(53)$, $S_{10}(12)$	δ_dCD_3
ν_{11}	1010	1017	0.7	$S_{10}(70)$, $S_8(30)$	ρCH_3	ν'_{11}	812	819	0.8	$S_{10}(60)$, $S_8(23)$	ρCD_3
ν_{12}	819	818	0.1	$S_2(45)$, $S_4(22)$	$\nu CC'$	ν'_{12}	760	767	0.9	$S_2(29)$, $S_4(18)$	$\nu CC'$
ν_{13}	556	559	0.5	$S_6(75)$, $S_2(11)$	δNCO	ν'_{13}	538	539	0.2	$S_6(70)$, $S_2(15)$	δNCO
ν_{14}	460	460	0.0	$S_7(85)$	$\delta CC'$	ν'_{14}	—	416	—	$S_7(78)$, $S_{10}(11)$	$\delta CC'$

$\Delta=(|\nu_{\text{obsd.}}-\nu_{\text{calcd.}}|/\nu_{\text{obsd.}})\times 100$

constant in the Urey-Bradley force field. In the present calculation, this force constant was preferred to the repulsion constant F(HNH) in fitting the NH_2 asym. and sym. stretching frequencies simultaneously. The force constants other than K(NH) and K(CH) were initially taken from Suzuki's work.[5] At the first step of the force constant refinement, only the frequencies of the NH_2 and ND_2 species and the frequencies higher than 1200 cm^{-1} of the NHD species were taken into account, and the values of K(NH), K(CH), K(CO), K(CN) and K(CC) were adjusted by referring to the Jacobian matrix elements. The stretching constants as well as the bending and repulsion constants concerned with hydrogen atoms were refined next by the least squares method for these frequencies. After this refinement, the absorption frequencies below 1200 cm^{-1} attributable to the NHD species were assigned to the vibrational modes of either the *trans* or *cis* species by referring to the calculated frequencies. This assignment was checked by the product rule and independently by the sum rule for isotopic molecules,[10] by as-

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[10] J. C. Decius and E. B. Wilson, *J. Chem. Phys.*, **19**, 1409 (1951).

TABLE 8. FUNDAMENTAL FREQUENCIES AND MAIN POTENTIAL ENERGY DISTRIBUTIONS FOR *cis*-CH_3CONHD AND CD_3CONHD

	cis-CH_3CONHD						*cis*-CD_3CONHD				
	Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.		Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.
ν_1	3270	3291	0.7	$S_{12}(99)$	ν_c-NH	ν'_1	3265	3292	0.8	$S_{12}(99)$	ν_c-NH
ν_2	3000	3005	0.2	$S_{13}(100)$	ν_aCH_3	ν'_2	2420	2400	0.8	$S_{11}(97)$	ν_t-ND
ν_3	2926	2935	0.3	$S_{14}(100)$	ν_sCH_3	ν'_3	2240	2234	0.3	$S_{13}(100)$	ν_aCD_3
ν_4	2417	2400	0.7	$S_{11}(97)$	ν_t-ND	ν'_4	2120	2109	0.5	$S_{14}(100)$	ν_sCD_3
ν_5	1652	1659	0.4	$S_3(53)$, $S_1(20)$	$\nu C{=}O$	ν'_5	1636	1644	0.5	$S_3(57)$, $S_2(20)$	$\nu C{=}O$
ν_6	1475	1480	0.4	$S_4(51)$, $S_8(25)$	δ_c-NH	ν'_6	1475	1469	0.4	$S_4(53)$, $S_5(34)$	δ_c-NH
ν_7	1453	1460	0.5	$S_8(19)$, $S_5(20)$	δ_dCH_3	ν'_7	1413	1414	0.1	$S_1(45)$, $S_2(27)$	νCN
ν_8	1398	1399	0.1	$S_1(29)$, $S_8(19)$	νCN	ν'_8	1088	1083	0.5	$S_9(81)$	δ_sCD_3
ν_9	1359	1360	0.1	$S_9(84)$	δ_sCH_3	ν'_9	1039	1036	0.3	$S_8(70)$	δ_dCD_3
ν_{10}	1045	1025	1.9	$S_{10}(61)$, $S_8(26)$	ρCH_3	ν'_{10}	975	966	0.9	$S_5(53)$, $S_3(18)$	δ_t-ND
ν_{11}	933	952	2.0	$S_5(55)$, $S_{10}(10)$	δ_t-ND	ν'_{11}	828	828	0.0	$S_2(27)$, $S_9(15)$	$\nu CC'$
ν_{12}	871	875	0.5	$S_2(46)$, $S_1(19)$	$\nu CC'$	ν'_{12}	812	802	1.1	$S_{10}(59)$, $S_8(21)$	ρCD_3
ν_{13}	568	570	0.4	$S_6(75)$	δNCO	ν'_{13}	546	545	0.2	$S_6(68)$, $S_2(17)$	δNCO
ν_{14}	455	449	1.4	$S_7(82)$	$\delta CC'$	ν'_{14}	—	409	—	$S_7(77)$	$\delta CC'$

$\Delta = (|\nu_{\text{obsd.}} - \nu_{\text{calcd.}}|/\nu_{\text{obsd.}}) \times 100$

TABLE 9. FUNDAMENTAL FREQUENCIES AND MAIN POTENTIAL ENERGY DISTRIBUTIONS FOR CH_3COND_2 AND CD_3COND_2

	CH_3COND_2						CD_3COND_2				
	Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.		Obsd	Calcd	Δ(%)	P.E.D. (%)	Abbr.
ν_1	3000	3005	0.2	$S_{13}(100)$	ν_aCH_3	ν'_1	2527	2506	0.8	$S_{11}(49)$, $S_{12}(48)$	ν_aND_2
ν_2	2926	2936	0.3	$S_{14}(100)$	ν_sCH_3	ν'_2	2320	2307	0.6	$S_{11}(49)$, $S_{12}(51)$	ν_sND_2
ν_3	2530	2506	1.0	$S_{11}(49)$, $S_{12}(48)$	ν_aND_2	ν'_3	2240	2234	0.3	$S_{13}(100)$	ν_aCH_3
ν_4	2316	2307	0.4	$S_{11}(49)$, $S_{12}(51)$	ν_sND_2	ν'_4	2120	2109	0.5	$S_{14}(99)$	ν_sCH_3
ν_5	1644	1645	0.1	$S_3(59)$, $S_1(20)$	$\nu C{=}O$	ν'_5	1628	1625	0.2	$S_3(68)$, $S_1(21)$	$\nu C{=}O$
ν_6	1453	1462	0.6	$S_8(47)$, $S_{10}(14)$	δ_dCH_3	ν'_6	1431	1422	0.6	$S_1(50)$, $S_2(30)$	νCN
ν_7	1411	1413	0.1	$S_1(42)$, $S_2(23)$	νCN	ν'_7	1187	1198	0.9	$S_4(57)$, $S_5(33)$	βND_2
ν_8	1359	1363	0.3	$S_9(90)$	δ_sCH_3	ν'_8	1070	1068	0.2	$S_9(77)$	δ_sCD_3
ν_9	1185	1190	1.3	$S_4(61)$, $S_5(32)$	βND_2	ν'_9	1039	1034	0.5	$S_8(69)$, $S_{10}(15)$	δ_dCD_3
ν_{10}	1036	1021	1.5	$S_{10}(63)$, $S_8(27)$	ρCH_3	ν'_{10}	962	954	0.8	$S_5(40)$, $S_3(21)$	ρND_2
ν_{11}	933	943	1.0	$S_5(43)$, $S_1(13)$	ρND_2	ν'_{11}	817	808	1.1	$S_{10}(62)$, $S_8(23)$	ρCD_3
ν_{12}	817	816	0.1	$S_2(46)$, $S_3(22)$	$\nu CC'$	ν'_{12}	760	766	0.8	$S_2(31)$, $S_4(18)$	$\nu CC'$
ν_{13}	548	551	0.5	$S_6(73)$	δNCO	ν'_{13}	526	531	0.9	$S_6(69)$, $S_2(13)$	δNCO
ν_{14}	442	444	0.4	$S_7(79)$	$\delta CC'$	ν'_{14}	—	404	—	$S_7(75)$	$\delta CC'$

$\Delta = (|\nu_{\text{obsd.}} - \nu_{\text{calcd.}}|/\nu_{\text{obsd.}}) \times 100$

suming the unobserved CC′ deformation frequencies for CD_3COND_2 and *trans*- and *cis*-CD_3CONHD to be the same as the calculated frequencies. The theoretical product rule ratios were obtained from the calculated frequencies. Both the product rule and the sum rule are well satisfied by the assigned frequencies as seen in Table 4. Then at the final step, we added the interaction constant P(NH–NH) with the initial value of zero, fixed the repulsion constant F(HNH) to zero, and refined all other force constants simultaneously to obtain a converged set. The force constants used in the final calculation are shown in Table 5 together with their dispersions. Tables 6—9 show the frequencies calculated from these force constants, the corresponding observed frequencies and the potential energy distributions. The agreement between the calculated and the observed frequencies are quite excellent throughout all isotopic species. It is seen from Table 7 that the coupling between the NH in-plane deformation and the CN stretching vibrations takes place only for the *trans*-NHD species just as shown by the calculation for *N*-methylacetamide.[1)]

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