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## ADVERTISEMENT



## Characteristic Infrared Bands of Monosubstituted Amides

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Infrared spectra of various monosubstituted amides and the corresponding deuterated compounds have been measured in the gaseous, liquid, and crystalline states and in solutions. From the experimental results, the bands characteristic of the amide structure have been determined. Furthermore, from the comparison with the spectra of related substances and by the application of the product rule, the assignments of these characteristic bands have been made. The observed change of frequencies of these characteristic bands with change of state confirms this assignment.

#### INTRODUCTION

MANY papers have been published concerning the RCONHR'. Molecules in which R and R' are in the trans-position with respect to each other show two characteristic bands at 1650 cm<sup>-1</sup> (the amide I band) and 1550 cm<sup>-1</sup> (the amide II band) in the  $6\mu$  region, whereas those with R and R' in the cis-position show only one band at 1650 cm<sup>-1</sup>. The amide I band has been assigned to the C=O stretching frequency. However, the assignment of the amide II band of the trans-form has given rise to much controversy.1 Richards and Thompson<sup>2</sup> have observed the frequency change of this band with change of state, noticed that this is not observed in N,N-disubstituted amides, and assigned it to the N-H in-plane bending vibration. Randall et al.<sup>3</sup> have measured the frequency change of this band on deuteration, and assigned it to the stretching vibration of the C-N bond which has appreciable double bond character. Lenormant<sup>4</sup> has measured the infrared spectra of amides and their various derivatives and considered the amide II band to arise from the C=Ogroup of the tautomeric form. Fraser and Price<sup>5</sup> have pointed out that it is very probable for the C=Ostretching, C-N stretching, and N-H in-plane bending vibrations to have considerable interaction among each other, and have given new interpretation of the amide I, II, and 1270 cm<sup>-1</sup> band, the last of which reduces in intensity on deuteration. Letaw and Gropp<sup>6</sup> have observed the influence of various substituents on the frequency of the amide II band of N-butylacetamide and concluded that this band arises from the stretching vibration of the C-N bond.

In the longer wavelength region, Shimanouchi,

Kuratani, and Mizushima<sup>7</sup> have measured the polarized infrared spectra of diketopiperazine and assigned the 840 cm<sup>-1</sup> band to the N-H out-of-plane bending vibration. Sutherland has pointed out that the 1230, 1160, and 720 cm<sup>-1</sup> bands are characteristic to polypeptides.<sup>1</sup> Kessler and Sutherland<sup>8</sup> have measured the infrared dichroism and the frequency change on deuteration of the 720 cm<sup>-1</sup> band of monosubstituted amides, and assigned it to the N-H out-of-plane bending vibration.

The determination of the character of vibration of the peptide bond is necessary as a part of the program concerning the structure determination of polypeptides now going on in our laboratory.9 In view of the controversy referred to above as well as the incomplete assignment of the amide characteristic bands, we have measured the infrared spectra of a series of monosubstituted amides and their deuterated compounds and the change of the characteristic bands with change of state. Based on this measurement we have assigned the characteristic frequencies of the amide structure.

## EXPERIMENTAL

#### Diformylhydrazine

The sample was kindly given us by Professor I. Nitta, Osaka University. Melting point: 155°C.

#### Diacetylhydrazine

The sample was synthesized by heating a mixture of sodium acetate and hydrazine sulfate and treating with acetic anhydride.<sup>10</sup> It was purified by recrystallization from methanol solution. Melting point: 137°C.

#### N,N'-Dimethyloxamide

The sample was synthesized from dimethyl oxalate and methylamine, and was purified by recrystallization from aqueous solution.<sup>11</sup> Melting point: 215°C.

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<sup>&</sup>lt;sup>1</sup> G. B. B. M. Sutherland, Advances in Protein Chemistry. VII (Academic Press, Inc., New York, 1952). See also L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* (Methuen, and Com-pany, Ltd., London, 1954). <sup>2</sup> R. E. Richards and H. W. Thompson, J. Chem. Soc. 1947, 1949.

<sup>1248.</sup> 

<sup>&</sup>lt;sup>3</sup> Randall, Fowler, Fuson, and Dangle, Infrared Determination of Organic Structures (D. Van Nostrand Company, Inc., New York, 1949).

 <sup>&</sup>lt;sup>477,7</sup>
 <sup>4</sup> H. Lenormant, Ann. chim. 12, 459 (1950).
 <sup>6</sup> R. D. B. Fraser and W. C. Price, Nature 170, 490 (1952).
 <sup>6</sup> H. Letaw, Jr., and A. H. Gropp, J. Chem. Phys. 21, 1621 (1953).

<sup>&</sup>lt;sup>7</sup> Shimanouchi, Kuratani, and Mizushima, J. Chem. Phys. 19, 1479 (1951). See also R. Newman and R. M. Badger, ibid. 19, 1147 (1951).

<sup>&</sup>lt;sup>8</sup> H. K. Kessler and G. B. B. M. Sutherland, J. Chem. Phys. 21, 570 (1953).

<sup>&</sup>lt;sup>9</sup> For the summary of our previous work, see S. Mizushima, Structure of Molecules and Internal Rotation (Academic Press, Inc., New York, 1954), and also S. Mizushima, Advances in Protein Chemistry. IX (Academic Press, Inc., New York, 1954). <sup>10</sup> G. Pellizzari, Gazz. chim. Ital. **391**, 536 (1909).

<sup>&</sup>lt;sup>11</sup> O. Wallach and A. Boehringer, Ann. Chem. Justus Liebig 184, 51 (1877).

## Polyglycine

The sample was prepared<sup>12</sup> and supplied by Professor J. Noguchi, Kanazawa University.

## **N-Methylacetamide**

The sample was synthesized by the action of methylamine on methylacetate dissolved in methanol. It was purified by fractional distillation.

#### **N-Ethylacetamide**

The sample was prepared by the reaction of ethylamine and methylacetate. It was purified by fractional distillation.

#### **N-Methylformamide**

The sample was prepared by the action of methylamine on methylformate dissolved in methanol and was purified by fractional distillation.

Corresponding N-deuterated compounds have been prepared in sealed tubes in the presence of  $D_2O$ . The excess of  $D_2O$  was evaporated in vacuum, after the exchange reaction had been completed.

The measurements of infrared absorption have been made by the Baird infrared spectrophotometer. The



FIG. 1. Infrared spectra of diformylhydrazine (solid line) and of deuterated diformylhydrazine (broken line) in the crystalline state (hexachlorobutadiene paste).



FIG. 2. Infrared spectra of diformylhydrazine (solid line) and of deuterated diformylhydrazine (broken line) in the crystalline state (Nujol paste).

<sup>12</sup> J. Noguchi, J. Chem. Soc. Japan 74, 961 (1953); J. Noguchi and T. Hayakawa, J. Am. Chem. Soc. 76, 2846 (1954).



FIG. 3. Infrared spectra of some amides (solid line) and of their N-deuterated compounds (broken line).



FIG. 4. Infrared spectra of N,N'-dimethyloxamide (solid line) and of deuterated N,N'-dimethyloxamide (broken line) in the crystalline state (hexachlorobutadiene paste).

NaCl prism was used in the frequency region 3600 to  $700 \text{ cm}^{-1}$ , and the KBr prism in the region 800 to  $400 \text{ cm}^{-1}$ .

The sample of diformylhydrazine (Figs. 1, 2, and 3), diacetylhydrazine (Fig. 3), N,N'-dimethyloxamide (Figs. 3, 4, and 5), polyglycine (Fig. 6), and their N-deuterated compounds have been measured as pastes of hexachlorobutadiene in the region 3600 to  $1200 \text{ cm}^{-1}$ , and of Nujol in the region 1800 to 400 cm $^{-1}$ . N-methylacetamide has been measured in the gaseous state at 200°C (Fig. 7), in carbon tetrachloride and carbon disulfide solutions at room temperature (Figs. 8 and 9), in the liquid state at 40°C (Fig. 6), and in the crystalline state at 15°C and at -60°C (Figs. 10 and 11). The N-deuterated compound has been measured in the gaseous state (Fig. 7), in carbon tetrachloride solution (Figs. 8 and 9), and in the liquid state (Fig. 6). N-ethylacetamide and its deuterated compound have been measured in the liquid state at room temperature (Fig. 6). N-methylformamide has been measured in the gaseous state at 200°C (Fig. 12), in the liquid state at room temperature (Fig. 13), and in the crystalline state at  $-60^{\circ}$ C. The N-deuterated compound has been measured in the gaseous (Fig. 12) and liquid states (Fig. 13).

#### DIFORMYLHYDRAZINE

The molecule of diformylhydrazine, HCONH -NHCHO, in the crystalline state has been shown



FIG. 5. Infrared spectra of N,N'-dimethyloxamide (solid line) and of deuterated  $N_i N'$ -dimethyloxamide (broken line) in the crystalline state (Nujol paste).



FIG. 6. Infrared spectra of some amides (solid line) and of their N-deuterated compounds (broken line).

by Tomiie, Gu, and Nitta<sup>13</sup> to have the planar transform  $(C_{2h})$  and, therefore, the interpretation of the infrared absorption should be the simplest of the molecules studied in this research.

Of the twenty-four normal vibrations, the eight inplane vibrations  $(B_u)$  and four out-of-plane vibrations  $(A_u)$  are active in the infrared (see Table I). Of these  $\nu$ (C-H) and  $\delta$ (C-H) can be assigned easily by comparison with absorption bands observed for HCONH<sub>2</sub> (2880, 1393 cm<sup>-1</sup>) and HCOND<sub>2</sub> (2880, 1397 cm<sup>-1</sup>).<sup>14</sup>

TABLE I. Infrared frequencies of (H-CONH-)2 and (H-COND-)2.

-	Mode	(HCONH)2	(H-COND -)2	Wave number ratio
B <sub>u</sub>	$ \begin{array}{c} \nu(\mathrm{N-H}), \nu(\mathrm{N-D}) \\ \nu(\mathrm{C-H}) \\ \nu(\mathrm{C=O}) \\ \nu(\mathrm{C-N}) \\ \delta(\mathrm{N-H}), \delta(\mathrm{N-D}) \\ \delta(\mathrm{C-H}) \\ \delta(\mathrm{O=C-N}) \end{array} $	$\begin{matrix} 3100\\ 2900\\ 1610(I)\\ 1480(II)\\ 1229(III)\\ 1368\\ 753(IV) \end{matrix}$	2250 2920 {1605(I) 1338(II') 985(III') 1389 751(IV)	$\begin{array}{c} 1.378 \\ 0.993 \\ 1.003 \\ 1.106 \\ 1.248 \\ 0.985 \\ 1.003 \end{array}$
Au	$\pi (N-H) \pi (C-H) \tau (C-N) \tau (N-N)$	770(V)	540(V')	1.43

<sup>\*</sup>  $\nu$ ; stretching,  $\delta$ : bending in-plane,  $\pi$ : bending out-of-plane,  $\tau$ : torsion.

Therefore, the remaining bands at 1610, 1480, and 1229  $cm^{-1}$  of  $(HCONH-)_2$  must be concerned with the vibrations of the parts of the molecule containing the C=O, C-N, and N-H bonds. The corresponding bands of the N-deuterated compound were observed at 1605, 1338, and 985 cm<sup>-1</sup>.

The 770 cm<sup>-1</sup> band of  $(HCONH-)_2$  is not much different in frequency from the 840 cm<sup>-1</sup> band of diketopiperazine and 720 cm<sup>-1</sup> band of N-methylformamide arising from  $\pi(N-H)$ ,<sup>7,8</sup> and shifts, on deuteration, to 540 cm<sup>-1</sup> which is close to the  $\pi$ (N-D) frequencies of diketopiperazine- $d_2$  (652 cm<sup>-1</sup>) and of N-methylformamide-d (530 cm<sup>-1</sup>). Therefore the 770 and 540 cm<sup>-1</sup> bands can be assigned to  $\pi(N-H)$  and  $\pi$ (N-D), respectively.

The 753 cm<sup>-1</sup> band of  $(HCONH-)_2$  and the 751 cm<sup>-1</sup> band of  $(HCOND-)_2$  are also found in  $HCONHCH_3$ (771 cm<sup>-1</sup>), HCOOCH<sub>3</sub> (768 cm<sup>-1</sup>), and in HCOOC<sub>2</sub>H<sub>5</sub>  $(775 \text{ cm}^{-1})$ , respectively, and can be assigned to one of the skeletal bending vibrations. The contribution of  $\delta(O=C-N)$  will be greater than that of  $\delta(C-N-N)$ in this higher skeletal bending vibration, because the  $\delta(O=C-N)$  frequency of HCONH<sub>2</sub> (600 cm<sup>-1</sup>)<sup>14</sup> is



FIG. 7. Infrared spectra of N-methylacetamide (solid line) and of deuterated N-methylacetamide (broken line) in the gaseous state at 200°C.

higher than the  $\delta(C-N-N)$  frequency of CH<sub>3</sub>NHNH<sub>2</sub> (443 cm<sup>-1</sup>).<sup>15</sup>

In order to check the assignment described above, the product rule is applied.<sup>16</sup> As the vibrations  $\nu$ (N-H) and  $\nu(C-H)$  can be separated from other in-plane vibrations, we may apply the rule to the product of these two frequencies. The ratio of the products of observed frequencies of the two isotopic molecules is found to be 1.37, which is exactly the value to be expected from the isotopic relation [Appendix I, Eqs. (2) and (3)]. The ratio of the product for the four remaining in-plane frequencies is  $(1610 \times 1480 \times 1229 \times 1368)/(1605 \times 1338)$  $\times$ 985 $\times$ 1389)=1.37. This is also in good agreement with the value 1.36 calculated from the isotopic relation [Appendix I, Eqs. (2) and (4)].

<sup>&</sup>lt;sup>13</sup> Tomiie, Gu, and Nitta, Presented at the Meeting of Structural Chemistry of the Chemical Society of Japan (1952). <sup>14</sup> J. C. Evans, J. Chem. Phys. 22, 1228 (1954); T. Miyazawa,

J. Chem. Soc. Japan 76, 821 (1955).

 <sup>&</sup>lt;sup>15</sup> Axford, Janz, and Russell, J. Chem. Phys. 19, 704 (1951).
 <sup>16</sup> (a) E. Teller, cited by C. K. Ingold *et al.* J. Chem. Soc. 1936, 971; (b) O. Redlich, Z. physik. Chem. B28, 371 (1935); (c) E. B. Wilson, Jr., J. Chem. Phys. 9, 76 (1941).

The ratio of the  $\pi(N-H)$  and the  $\pi(N-D)$  frequencies has been found to be 1.43 (Table I). If we assume that the three other out-of-plane frequencies hardly change on deuteration, the ratio of the products of the out-of-plane frequencies of the two isotopic molecules will be close to 1.43, which is in good agreement with the value 1.40 calculated from the kinetic energy matrices for the out-of-plane vibrations [Appendix I, Eq. (5)].

#### CHARACTERISTIC FREQUENCIES IN CONDENSED PHASES

Let us now discuss the vibration bands of monosubstituted amides in general. The results of our measurements made in condensed phases may be summarized as follows (see Tables II, IV, and V):

(1) The 1650  $cm^{-1}$  band (the amide I band) does not change in frequency and in intensity on deuteration. However, the frequency of this band changes with the change of state of aggregation.

(2) The 1550  $cm^{-1}$  band (the amide II band) disappears on deuteration. The frequency changes considerably with the change of state.



FIG. 8. Infrared spectra of N-methylacetamide (solid line) and of deuterated N-methylacetamide (broken line) in carbon tetrachloride solution (1.5%).

(3) For each of the monosubstituted amides studied, a strong absorption band is observed in the region 1200 to 1300 cm<sup>-1</sup>. It also disappears on deuteration. This can be concluded to arise from the structure - CONHand corresponds to the 1229 cm<sup>-1</sup> band of diformylhydrazine. The frequency also changes considerably with the change of state. Hereafter let us call this the amide III band.

(4) In N-deuterated compounds, in place of the amide II and III bands, two bands are observed at 1450 cm<sup>-1</sup> and 950 cm<sup>-1</sup>, respectively, and their frequencies change considerably with the change of state. Hereafter, we shall call these the amide II' and the amide III' bands. These correspond to the 1338 cm<sup>-1</sup> and the 985 cm<sup>-1</sup> bands of  $(\text{HCOND}-)_2$ .

(5) A strong band assigned to a skeletal vibration, is observed at *ca* 620 cm<sup>-1</sup> for molecules which have the structure  $-CH_2CONH-$ , and at *ca* 760 cm<sup>-1</sup> for molecules which have the structure HCONH- and -NHCO-CONH-. The frequency and the intensity



FIG. 9. Infrared spectra of N-methylacetamide (solid line) and of deuterated N-methylacetamide (broken line) in carbon tetrachloride solution (6.5%).



FIG. 10. Infrared spectra of N-methylacetamide in the crystalline state at  $-60^{\circ}$ C.

hardly change on deuteration. The change of the state of aggregation hardly affects the frequency value. Let us call it the amide IV band.

(6) The absorption arising from  $\pi(N-H)$  of diketopiperazine has been observed at 840 cm<sup>-1</sup>. The corresponding absorption of the monosubstituted amides in the *trans*-form is observed at 700-750 cm<sup>-1</sup>. It disappears on deuteration and its frequency changes considerably with the change of state. Let us call it the amide V band.

(7) The  $\pi(N-D)$  band of diketopiperazine- $d_2$  is observed at 652 cm<sup>-1</sup>. The corresponding band of the N-deuterated monosubstituted amide is observed in the region 510 to 570 cm<sup>-1</sup>. We shall call it the amide V' band.

FIG. 11. Infrared spectra of N-methylacetamide in the crystalline state (capillary film) at  $-60^{\circ}$ C (solid line) and  $+15^{\circ}$ C (broken line).





FIG. 12. Infrared spectra of N-methylformamide (solid lines) and of deuterated N-methylformamide (broken line) in the gaseous state at 200°C.



FIG. 13. Infrared spectra of N-methylformamide (solid line) and of deuterated N-methylformamide (broken line) in the liquid state (3/100 mm).

(8) Another characteristic absorption band is observed at ca 600 cm<sup>-1</sup> for molecules which have the structure



such as polyglycine, N-methylacetamide, and N-ethylacetamide. This band also disappears on deuteration. We shall call this the amide VI band. Its frequency changes with the change of state in the same sense as the amide V band (Table IV). The amide VI band is also observed in diacetylhydrazine and in N,N'-dimethyloxamide at somewhat lower frequency.

(9) The band corresponding to the amide VI band is observed at 588 cm<sup>-1</sup> for diacetylhydrazine- $d_2$  and at 531 cm<sup>-1</sup> for N,N'-dimethyloxamide- $d_2$ . In the case of deuterated N-methylacetamide and N-ethylacetamide, however, no corresponding band is observed. Product rule consideration which is given in later part of this paper shows that this band is overlapped by the amide IV band.

(10) The amide I, III, and IV frequencies can also be observed in the Raman effect as lines with strong or medium intensity, whereas the amide II, V, and VI frequencies appear as weak lines.<sup>9,17</sup> Sometimes the

amide II frequency cannot be observed in the Raman effect, but it is observed distinctly in the Raman spectra of HCONHCH<sub>3</sub> and CH<sub>3</sub>CONHC<sub>2</sub>H<sub>5</sub> (see Appendix II).

### TYPES OF CHARACTERISTIC VIBRATIONS

The molecule of a monosubstituted amide RCONHR' has nine in-plane vibrations and three out-of-plane vibrations. In the following we shall discuss the types of these vibrations.

From the comparison with the spectrum of  $(HCONH-)_2$ , the amide I, II, and III bands are found to be related to  $\nu$ (C=O),  $\nu$ (C-N), and  $\delta$ (N-H), but not in a simple manner. This is readily seen from the values of these frequencies. The contribution of  $\nu$  (C=O) is greatest to the amide I band, whereas the contribution of  $\delta(N-H)$  is very small, since the amide I band hardly changes in frequency on deuteration. However, there will be considerable contribution of  $\nu(C-N)$  to this band, since the C-N bond acquires partial doublebond character<sup>17,18</sup> and its bond frequency is not much different from that of  $\nu(C=O)$ . There is a similar situation in HCONH<sub>2</sub>, where the modes of the skeletal normal vibrations can be calculated as shown in Appendix III. In that case the ratio of the contribution of  $\nu(C=O)$  to that of  $\nu(C-N)$ , which is expressed in terms of the elements of the L-matrix, is +1.0 to -0.7

TABLE II. Characteristic infrared frequencies of molecules of the type RCONHR' and RCONDR'.

	I	11	ш	IV	v	VI
CH <sub>3</sub> CONHCH <sub>3</sub> (vapor)	1718	1487	1247			
(dil. nonpolar soln.)	1700	1500	1260	627	648	585
(liquid)	1653	1567	1299	627	725	600
$(crystal, +15^{\circ}C)$	1653	1566	1301	628	745	606
(crystal, $-60^{\circ}$ C)	1635	1583	1312	629	<b>79</b> 0	615
CH3CONHCH2CH3 (liquid	d) 1655	1565	1295	619	710	602
( CH CONH )	∫1690	∫1555	∫1235	670	705	600
$(-CH_2CONH-)_n$	\1630	1535	1275	020	705	000
HCONHCH <sub>3</sub> (vapor)	1727	1490	1200			
(liquid)	1672	1545	1244	771	720	• • •
(crystal)	1672	1575	1269	767	800	•••
$(HCONH-)_2$ (crystal)	1610	1480	1229	753	770	
$(CH_3CONH-)_2$ (crystal)	1597	1506	1260	629	640	556
$(-CONHCH_3)_2$ (crystal)	1658	1532	1239	760	775	537
	I	II'	III'	IV	V'	VI'
CH <sub>3</sub> CONDCH <sub>3</sub> (vapor)	1715	1385	920			
(liquid)	1642	1475	960	627	510	(627)
CH3CONDCH2CH3 (liquid	d) 1640	1473	960	619	525	(619)
$(-CH_2COND-)_n$	∫1690	1475	950			
	1630					
HCONDCH <sub>3</sub> (vapor)	1727	1372				
(liquid)	1667	1435	983	763	530	• • •
$(HUOND - )_2$ (crystal)	1605	1338	985	751	545	
$(CH_3CUND-)_2$ (crystal)	1595	1413	(947)	029	430	388 521
(-CONDCH <sub>3</sub> ) <sub>2</sub> (crystal)	1050	1445	935	703	507	551

<sup>18</sup> P. Vaughan and J. Donohue, Acta Cryst. 5, 530 (1952). See also other references cited in reference 1.

<sup>&</sup>lt;sup>17</sup> Mizushima, Shimanouchi, Nagakura, Kuratani, Tsuboi, Baba, and Fujioka, J. Am. Chem. Soc. **72**, 3490 (1950).

in the 1688 cm<sup>-1</sup> band ( $\nu_a$ ) and +0.5 to +1.0 in the 1310 cm<sup>-1</sup> band  $(\nu_s)$ . The amide I band of the monosubstituted amide is also considered to be the  $\nu_a$  band,

in which the C=O and C-N bonds stretch and contract with the phase difference of 180°, since the frequency and its shift on deuteration are almost the same as those of the  $\nu_a$  band of HCONH<sub>2</sub>.

The determination of types of vibration corresponding to the amide II, III, II', and III' bands can be made most clearly in the case of diformylhydrazine, since in the infrared active vibration  $(B_u)$  of this molecule there is no interference caused by  $\nu(C-R)$ and  $\nu(N-R')$ . The diagonal elements of the kinetic energy matrices show that on deuteration  $\nu_s$  frequency will be reduced by a factor of 1.01 and  $\delta(N-H)$  frequency by a factor of 1.36.\* None of the amide II and III bands shows this reduction. However, the ratio  $v_{\rm II}v_{\rm III}/v_{\rm II}, v_{\rm III'}$  is found to be 1.38 which is close to the value  $1.37 = 1.01 \times 1.36$ . This means that in the II and III bands the contribution of  $\nu_s$  and  $\delta(N-H)$  should be taken account of simultaneously.

On the assumption that the force constants of the diformylhydrazine molecule are nearly the same as the corresponding constants of the formamide molecule and that there is no interaction between the  $\nu_s$  and  $\delta(N-H)$ or  $\delta(N-D)$  vibrations, Miyazawa has estimated  $\nu_s$ ,  $\delta(N-H)$  and  $\delta(N-D)$  as 1340, 1350, and 1000 cm<sup>-1</sup>, respectively.<sup>19</sup> As the observed frequencies of the II' and III' bands are close to the estimated values, the II' band can be considered to correspond to the almost pure  $\nu_s$  and the III' band to the almost pure  $\delta(N-D)$ . This assignment is compatible with the fact that such a frequency is observed not only in monosubstituted amides in the trans-form but also in those in the cisform, such as  $\delta$ -valerolactam-d (983 cm<sup>-1</sup>),  $\epsilon$ -caprolactam-d (953 cm<sup>-1</sup>), and diketopiperazine- $d_2$  (970 cm<sup>-1</sup>). However, in the II and III bands with frequencies 1480 and 1229 cm<sup>-1</sup> the deviations from the predicted values are very large, and accordingly it is concluded that in both of them the contribution of both  $\nu_s$ and  $\delta(N-H)$  are considerable.

In the case of monosubstituted amides in general, there are additional contributions of  $\nu(C-R)$  and  $\nu(N-R')$  to the amide II and III bands, and therefore, the experimental value of  $\nu_{II}\nu_{III}/\nu_{III}/\nu_{III}$  does not agree so well with the theoretical value 1.37 as in the case of diformylhydrazine. However, we may consider that both  $\nu_s$  and  $\delta(N-H)$  considerably contribute to the II and III bands whereas  $\nu_s$  essentially contributes to the II' band and  $\delta(N-D)$  to the III' band. In conclusion, the experimental result referred to above confirms the suggestion given by Fraser and Price as to the assignments of the amide I, II, III, and II' bands. The present assignment of the III' band, however, is different from theirs which seems improbable from the product rule consideration.

A question has often arisen as to why the amide II band has not been observed in disubstituted amides, RCONR'R". This is probably due to the fact that in the case of disubstituted amides the identification of the characteristic frequency  $v_s$  becomes difficult for the following reason. As explained above there is strong coupling between  $\nu_s$  and  $\delta(N-H)$  so that the II band of monosubstituted amides is shifted to higher frequency and can be identified as an amide characteristic band. On the other hand in the case of disubstituted amides, with no N-H bond, the  $\nu_s$  band appears near the region of C-H deformation frequencies, and accordingly becomes difficult to be identified. For  $CH_3CON(CH_3)_2$ , however, this band is identified, since it appears at 1497 cm<sup>-1</sup>, sufficiently separated from the CH deformation frequency.<sup>‡</sup>

Another problem which has often been discussed is that the II band has not been observed in monosubstituted amides in the *cis*-form. It is considered that in the *cis*-form the coupling between  $\nu_s$  and  $\delta(N-H)$  is small and the  $\nu_s$  band lies in the region of the CH deformation frequencies.<sup>20</sup> Actually for diketopiperazine we observed an  $\nu_s$  band at 1440 cm<sup>-1</sup> in place of the amide II band of polyglycine. In the case of the transform the coupling between these two vibrations is strong and accordingly the amide II band is shifted to higher frequencies sufficiently above the CH deformation frequencies, and can easily be identified as one of the characteristic amide frequencies.

Let us now discuss the nature of the amide IV band. According to our previous Raman and infrared measurements, molecules containing the C=O group show a strong absorption band or a strong Raman line in the region 450 to 750 cm<sup>-1,21,22</sup> This band has been shown by the normal vibration calculation to correspond to the skeletal deformation vibration in which the C=Obond plays an important role.23 This assignment of the amide IV band is quite reasonable as shown below: (a) This is the only band in the region 800 to 600  $\rm cm^{-1}$ which is fairly strong and does not change on deuteration. (b) This band has been observed as a strong

<sup>\*</sup> See Appendix I. The diagonal elements in this case should be modified according to the approximate separation of high and low frequencies. [See reference 16(c).]

<sup>&</sup>lt;sup>19</sup> T. Miyazawa, J. Chem. Soc. Japan **76**, 341 (1955). <sup>†</sup> The value of  $\langle v_{II}/\nu_{II} \rangle \times \langle v_{III}/\nu_{III} \rangle$  is 1.44 for CH<sub>3</sub>CONHCH<sub>3</sub>, 1.43 for CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>3</sub>, 1.38 for  $(-CH_2CONH-)_n$ , 1.36 for HCONHCH<sub>3</sub>, 1.42 for  $(CH_3CONH-)_2$ , and 1.41 for  $(-CONHCH_3)_2$ .

<sup>&</sup>lt;sup>‡</sup> The  $\nu_s$  band is identified at 1406 cm<sup>-1</sup> for CH<sub>3</sub>CONH<sub>2</sub> and 1475 cm<sup>-1</sup> for CH<sub>3</sub>CONDCH<sub>3</sub>. The value of 1497 cm<sup>-1</sup> for the  $\nu_s$  frequency of CH<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub> is reasonable, since it is expected that the substitution of the second methyl group shifts the  $\nu_a$  higher than that of CH<sub>3</sub>CONDCH<sub>3</sub>.

<sup>&</sup>lt;sup>20</sup> See also R. M. Badger and A. D. E. Pullin, J. Chem. Phys. 22, 1142 (1954).

<sup>&</sup>lt;sup>21</sup> Nakagawa, Ichishima, Kuratani, Miyazawa, Shimanouchi, and Mizushima, J. Chem. Phys. **20**, 1720 (1952); Mizushima, Shimanouchi, Miyazawa, Ichishima, Kuratani, Nakagawa, and Shido, J. Chem. Phys. 21, 815 (1953).

<sup>&</sup>lt;sup>22</sup> T. Miyazawa, J. Chem. Soc. Japan 74, 743 (1953), 75, 86, 540 (1954)

<sup>&</sup>lt;sup>23</sup> I. Nakagawa, J. Chem. Soc. Japan **74**, 243 (1953); T. Miyazawa, *ibid.* **75**, 303 (1954).

Raman line for CH<sub>3</sub>CONHCH<sub>3</sub>,<sup>9,17</sup> CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>3</sub>, and HCONHCH<sub>3</sub> (see Appendix II). (c) The corresponding frequency has been observed for CH3COOCH3 (639 cm<sup>-1</sup>), CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub> (632 cm<sup>-1</sup>), HCOOCH<sub>3</sub> (768 cm<sup>-1</sup>), and (-COOCH<sub>3</sub>)<sub>2</sub> (780 cm<sup>-1</sup>),<sup>22</sup> which have skeletal structures similar, respectively, to CH<sub>3</sub>CONHCH<sub>3</sub>, CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>3</sub>, HCONHCH<sub>3</sub>, and  $(-CONHCH_3)_2$ . (d) Molecules having the structure  $-CH_2CONH-$  show this band at 620 cm<sup>-1</sup>, which is different in position from the corresponding band at 760 cm<sup>-1</sup> for molecules having the structure HCONH-. This is just what would be expected for the skeletal bending vibration.§

The amide V or the V' band is undoubtedly assigned to the vibration in which the contribution of the  $\pi(N-H)$  or  $\pi(N-D)$  is greatest, since the observed frequency ratio|| is not much different from the value (1.33) calculated from the kinetic energy matrices (Appendix IV). The discrepancy is, however, significant and the coupling with other out-of-plane vibrations should be taken into account.

The molecule R"CH<sub>2</sub>CONHR' has another out-ofplane vibration  $\pi(C=O)$  in which the carbon atom of C=O moves up and down from the plane of C, O, and N atoms. This vibration is expected to appear at around 600 cm<sup>-1</sup>, since the  $\pi(C=O)$  band of the acetate ion CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> is observed at 615 cm<sup>-1.24</sup> The assignment of the amide VI band to this vibration is reasonable for the following reasons: (a) This band is observed for molecules having the structure -CH2CONH- and is not observed for molecules having the structure HCONH-.(b) The corresponding frequency is observed for CH<sub>3</sub>COOCH<sub>3</sub> (607 cm<sup>-1</sup>) and CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub> (607 cm<sup>-1</sup>). These are observed as a strong band in the infrared absorption and a weak line in the Raman effect, just as in the case of the amide VI band for CH<sub>3</sub>CONHCH<sub>3</sub> and CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>3</sub>. These ester bands are also to be assigned to the out-of-plane vibration of the CH<sub>3</sub>COO- skeletal framework. (c) The two Raman lines of CH<sub>3</sub>CONHCH<sub>3</sub> (289 and 435 cm<sup>-1</sup>) and those of CH<sub>3</sub>COOCH<sub>3</sub> (305 and 434 cm<sup>-1</sup>) can be assigned to the two remaining skeletal in-plane bending vibrations and there is no other band which could be assigned to  $\pi(C=O)$  vibration.

If the coupling between  $\pi(N-H)$  and  $\pi(C=O)$  is taken into consideration, the discrepancy referred to above can be explained straightforwardly. The observed ratio of the product of frequencies  $\nu_V \nu_{VI} / \nu_{V'} \nu_{VI'}$ of diacetylhydrazine and of N-methylacetamide is quite reasonable as shown in Appendix IV, although in the latter case the amide VI band is assumed to be overlapped by the IV band. These results mean that both  $\pi(N-H)$  and  $\pi(C=O)$  contribute to the amide V and the VI bands and that the contribution of  $\pi(N-H)$  is greater in the former vibration and that of  $\pi(C=O)$ is greater in the latter vibration. The frequency change of the characteristic bands on deuteration and on the change of state, which is to be discussed later, is reasonably interpreted on this basis.

## ASSIGNMENT OF OTHER BANDS

As explained above all the bands characteristic of amide structure can be assigned quite satisfactorily. Evidently as shown in Figs. 1, 2, 4, 5, 7-10, 12, and 13 there are absorption bands other than these which can be assigned as follows.

In the region 1500 to 900  $\text{cm}^{-1}$ , the bands arising from the skeletal vibrations related to  $\nu(C-CH_3)$  and  $\nu(CH_3-N)$  and those arising from the CH and CH<sub>3</sub> deformation vibrations are expected. The frequencies of skeletal vibrations depend largely on the structure of the skeleton, whereas those of the hydrogen deformation vibrations remain practically constant. The result of the assignment is shown in Table III. This assignment has been made on the basis of the normal vibration calculations made for many substances as well as the consideration of the observed Raman and infrared spectra of substances closely related to monosubstituted amide, e.g., RCONH<sub>2</sub>, RCOOCH<sub>3</sub>, etc.

TABLE III. Assignment of frequencies other than the amide characteristic frequencies.

(a) Bend	ling frequencies	of the CH group.	
	in-plane	out-of-plane	
$(H-CONH-)_2$	1368		
$(H - COND - )_2$	1389		
H−CONH−CH <sub>3</sub>	1385	1015	
$H-COND-CH_3$	1383	1020	
(b) Bending frequence	ies of the CH₃ g	roup attached to t	the nitrogen.
	sym. bending	asym, bending	rocking
$(-CONH-CH_3)_2$	1404	1462	1157
$(-COND-CH_3)_2$	1402	1465	1161
H-CONH-CH <sub>3</sub>	1414	1453	1149
H-COND-CH <sub>3</sub>	1406	overlapped	1156
CH <sub>3</sub> -CONH-CH <sub>3</sub>	1413	1445	1159
$CH_3 - COND - CH_3$	1401	1442	1179
(c) Bending frequencies of	of the CH3 grou	p attached to the	carbonyl group.
	sym. bending	asym. bending	rocking
$\overline{(CH_3 - CONH - )_2}$	1368	1437	1017
$(CH_3 - COND - )_2$	1366	overlapped	1025
CH <sub>3</sub> -CONH-CH <sub>3</sub>	1373	1413	1040, 987
CH <sub>3</sub> -COND-CH <sub>3</sub>	1375	1401	1041, 996
()	d) Skeletal stret	ching frequencies	
$(CH_3 - CONH - )_2$	921		
$(CH_3 - COND - )_2$	947		
$(-CONH-CH_3)_2$	986		
$(-COND - CH_3)_2$	1001		
H-CONH-CH <sub>3</sub>	958		
$H-COND-CH_3$	940		
CH3-CONH-CH3	1096, 881		
CH <sub>3</sub> -COND-CH <sub>3</sub>	1121 870		

<sup>§</sup> Empirically it is found that the higher skeletal bending fre-§ Empirically it is found that the higher skeletal bending frequency  $(B_u)$  of molecules of the type  $(-COR)_2$  is close to that of molecules of the type HCOR:  $(-COCH_3)_2$ , 540, HCOCH3, 510;  $(-CONH_2)_2$ , 640, HCONH2, 600;  $(-COOCH_3)_2$ , 780, HCOCH3, 768 cm<sup>-1</sup>. This is just the case for  $(-CONHCH_3)_2$  (760 cm<sup>-1</sup>),  $(-CONDCH_3)_2$  (763 cm<sup>-1</sup>), and HCONHCH3 (771 cm<sup>-1</sup>). || The value of  $\nu_V/\nu_{V'}$  is 1.42 for CH<sub>3</sub>CONHCH3, 1.35 for CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>3</sub>, 1.36 for HCONHCH3, 1.40 for (HCONH-)<sub>2</sub>, 1.49 for (CH<sub>3</sub>CONH-)<sub>2</sub>, and 1.37 for  $(-CONHCH_3)_2$ . <sup>24</sup> L. H. Jones and E. McLaren, J. Chem. Phys. 22, 1796 (1954).

#### CHANGE OF CHARACTERISTIC ABSORPTION WITH CHANGE OF STATE

It has been pointed out<sup>2</sup> that in the case of amides there are significant alterations in the spectra according to the state of aggregation in which the substance is measured. Changes in the spectra were often very useful for assigning the observed bands and for determining the molecular structure especially in the case of the study on the rotational isomers of dihalogenoethanes.<sup>9</sup> The method was applied to the present problem and the results are shown in Figs. 6-13 and in Tables II, IV, and V. In the present case little change is observed in the number of vibration bands, but almost all the amide bands change their positions considerably. These changes can be explained as due to the change in hydrogen bonding and in the electronic state of the amide structure (i.e., change in contributions of various structures).

The amide I vibration, in which the contribution of  $\nu(C=O)$  is great, decreases in frequency and the II' vibration, in which the contribution of  $\nu(C-N)$  is great, increases in frequency on passing along the series vapor, dilute nonpolar solution, liquid and crystal. This is explained from the fact that the contribution of the polar resonance structure



increases on passing along these series.

It is interesting to compare the change of the I band of N-methylacetamide with those of other molecules with similar structure. The difference in frequency observed between gaseous and liquid states is  $24 \text{ cm}^{-1}$ for CH<sub>3</sub>COCH<sub>3</sub><sup>25</sup> and 40 cm<sup>-1</sup> for CH<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub> (observed by us). These figures are compared with 65 cm<sup>-1</sup> for CH<sub>3</sub>CONHCH<sub>3</sub> as shown in Table IV.

In the gaseous state, the amide I band of N-methylacetamide was observed at 1718 cm<sup>-1</sup>, which is considerably lower than the C=O stretching frequency of CH<sub>3</sub>COOCH<sub>3</sub> at 1775 cm<sup>-1</sup> (vapor). The amide II' band was observed at 1385 cm<sup>-1</sup>, which is higher than the C-N stretching frequency 1054 cm<sup>-1</sup> of methyl-

TABLE IV. Changes of characteristic frequencies of N-methylacetamide with change of state.<sup>a</sup>

	$\Delta \nu_{I}$	$\Delta \nu_{II}$	$\Delta \nu_{III}$	$\Delta \nu_{IV}$	$\Delta \nu_{V}$	$\Delta \nu_{IV}$
Vapor→dil. nonpolar soln. Dil. nonpolar soln.→liquid Liquid→crystal (+15°C) Crystal (+15°C)→crystal (-60°C)	-18 -47 0 -18	+13 +67 -1 +17	$^{+13}_{+39}_{+2}_{+11}$	$0\\+1\\+1$	$^{+77}_{+20}_{+45}$	$^{+15}_{+6}_{+9}$

<sup>a</sup> In the crystalline state, we have made two observations, one above the transition point and the other below it. The transition point was found at 10°C according to the private communication from Dr. Post, Dr. Holtzberg, and Dr. Fankuchen, Polytechnic Institute of Brooklyn.

<sup>25</sup> Hartwell, Richards, and Thompson, J. Chem. Soc. 1948, 1436.

TABLE V. Changes of characteristic frequencies of N-methylformamide with change of state.

	$\Delta \nu_I$	$\Delta \nu_{11}$	$\Delta \nu_{III}$	$\Delta \nu_{\rm IV}$	$\Delta \nu_{\rm V}$
Vapor→liquid Liquid→crystal	-55 0	+55 +30	$^{+44}_{+25}$	4	+80

amine. These two facts tell us that the contribution of the polar structure is considerable even in the gaseous state. This is in good agreement with the result of the ultraviolet absorption measurement.<sup>17</sup>

The amide III' band, in which  $\delta(N-D)$  plays the most important role, increases in frequency on condensation. This fact is explained by the increase of the in-plane bending constant of N-D bond which is caused by the formation of hydrogen bond in the liquid state.

The II and the III bands, to which both  $\nu_s$  and  $\delta(N-H)$  make contributions, are shifted to higher frequencies as shown in Table IV.

The facts that the I, II, and III bands of N-methylacetamide do not change in frequency on solidification, whereas there is a change in frequency of  $10-20 \text{ cm}^{-1}$ on crossing the transition point, tell us that intermolecular association in the liquid state is similar to that in the crystal above the transition point, but is different from that below the transition point.

The IV band can be assigned to a skeletal vibration in which C=O plays an important role. The frequency of this band hardly changes on hydrogen bond formation.

The frequency change observed between dilute nonpolar solution and the liquid state is greatest for the V band, which arises mainly from  $\pi(N-H)$ . Such a change will be expected if we see that in the liquid state both the hydrogen bond formation and the contribution of the polar structure becomes much more pronounced as compared with those in nonpolar solution. The  $\pi(N-H)$  will be increased in frequency by the greater contribution of the polar electronic state as well as by the stronger hydrogen bond formation. These two effects, both resulting in the frequency shift in the same sense, will explain the fact observed for the V band.

The frequency change of the amide VI band is not so great but in the same sense as the amide V band. This shows that the contribution of  $\pi(N-H)$  is smaller than that of  $\pi(C=O)$  but not negligible.

The measurements similar to those made for  $CH_3CONHCH_3$  have been carried out for N-methylformamide (Tables II and V). The results can be explained in the same way as in the case of N-methylacetamide.

In conclusion the experimental results described above concerning the change of frequency with change of state give additional evidence of the correctness of the assignments made here for the amide characteristic bands.

#### APPENDIX I

The kinetic energy matrix for the  $B_u$  vibrations of the planar molecules  $(C_{2h})$  of the type



is derived according to Wilson's method.<sup>16c</sup> The internal symmetry coordinates used are:

 $S_{1} = (\Delta r_{01} - \Delta r_{56})/\sqrt{2}$   $S_{2} = (\Delta r_{02} - \Delta r_{57})/\sqrt{2}$   $S_{3} = (\Delta r_{23} - \Delta r_{78})/\sqrt{2}$   $S_{4} = (\Delta r_{24} - \Delta r_{79})/\sqrt{2}$   $S_{5} = (2\Delta \alpha_{205} - \Delta \alpha_{102} - \Delta \alpha_{501} - 2\Delta \alpha_{750} \qquad (1)$   $+\Delta \alpha_{657} + \Delta \alpha_{056})/2\sqrt{3}$   $S_{6} = (\Delta \alpha_{102} - \Delta \alpha_{501} - \Delta \alpha_{657} + \Delta \alpha_{056})/2$   $S_{7} = (2\Delta \alpha_{320} - \Delta \alpha_{423} - \Delta \alpha_{024} - 2\Delta \alpha_{875} + \Delta \alpha_{978} + \Delta \alpha_{579})/2\sqrt{3}$   $S_{8} = (\Delta \alpha_{423} - \Delta \alpha_{024} - \Delta \alpha_{978} + \Delta \alpha_{579})/2.$ 

The elements of the kinetic energy matrix for the  $B_u$  vibrations are:

$$g_{11} = \mu_{01}$$

$$g_{12} = \mu_{102}$$

$$g_{13} = 0$$

$$g_{14} = 0$$

$$g_{15} = -\sqrt{3} x_{201}/\sqrt{2}$$

$$g_{16} = x_{201}/\sqrt{2}$$

$$g_{17} = \sqrt{3} x_{201}/\sqrt{2}$$

$$g_{22} = \mu_{02}$$

$$g_{23} = \mu_{024}$$

$$g_{25} = 0$$

$$g_{26} = -\sqrt{2} x_{102}$$

$$g_{27} = -\sqrt{3} x_{320}/\sqrt{2}$$

$$g_{38} = (x_{320} - 2x_{420})/\sqrt{2}$$

$$g_{33} = \mu_{23}$$

$$g_{34} = \mu_{423}$$

$$g_{35} = -\sqrt{3} x_{023}/\sqrt{2}$$

$$g_{36} = x_{023}/\sqrt{2}$$

$$g_{38} = (x_{023} - 2x_{423})/\sqrt{2}$$

$$g_{44} = \mu_{24}$$

$$g_{45} = \sqrt{3} x_{023}/\sqrt{2}$$

$$g_{46} = -x_{023}/\sqrt{2}$$

$$g_{48} = (x_{024} + x_{324})/\sqrt{2}$$

$$g_{56} = \sqrt{3} (-z_{02} + 2y_{102})/2$$

$$g_{56} = \sqrt{3} (-z_{02} - y_{320} + 2y_{024})/2$$

$$g_{58} = \sqrt{3} (-z_{02} - y_{320} + 2y_{024})/2$$

$$\begin{array}{l} g_{67} = \sqrt{3} \left( z_{02} - y_{320} - 2y_{102} \right) / 2 \\ g_{68} = \left( z_{02} + y_{320} - 2y_{102} - 2y_{024} \right) / 2 \\ g_{77} = 3 \left( z_{02} + z_{23} - 2y_{320} \right) / 2 \\ g_{78} = \sqrt{3} \left( z_{02} - z_{23} - 2y_{024} + 2y_{423} \right) / 2 \\ g_{88} = \left( 4z_{24} + z_{02} + z_{23} - 4y_{423} - 4y_{024} + 2y_{320} \right) / 2 \end{array}$$

where

 $\mu_i$ : the reciprocal of atomic mass  $m_i$ 

 $r_{ij}$ : the bond length

 $\tau_{ij}$ : the reciprocal of  $r_{ij}$ 

 $\alpha_{ijk}$ : the angle between the bond ij and jk ( $\alpha_{ijk}$  is positive if it is traced from ji to jk in the counter-clockwise direction.)

$$\mu_{ij} = \mu_i + \mu_j$$
  

$$\mu_{ijk} = \mu_j \cos\alpha_{ijk}$$
  

$$x_{ijk} = \mu_j \tau_{ij} \sin\alpha_{ijk}$$
  

$$y_{ijk} = \mu_j \tau_{ij} \tau_{jk} \cos a_{ijk}$$
  

$$z_{ij} = \mu_{ij} \tau_{ij}^2.$$

The elements of the kinetic energy matrix are calculated of diformylhydrazine and its deuterated compound,



Bond lengths and bond angles assumed are as follows: r(N-H) = 1.00, r(C-N) = 1.32, r(C=O) = 1.21, r(C-H) = 1.07 A,  $\alpha(C-N-N) = 116^{\circ}$ ,  $\alpha(H-N-C)$  $= 122^{\circ}$ ,  $\alpha(N-N-H) = 122^{\circ}$ ,  $\alpha(O=C-N) = 124^{\circ}$ ,  $\alpha(H-C=O) = 118^{\circ}$ , and  $\alpha(N-C-H) = 118^{\circ}$ .

For the calculations of the product rule the Wilson's method is applied and the following equations are used which are derived from the approximate separation of high and low frequencies.<sup>16c</sup>

$$\frac{\nu(N-H)\nu(C-H)}{\nu'(N-D)\nu'(C-H)} = \begin{vmatrix} g_{11} & g_{14} \\ g_{14} & g_{44} \end{vmatrix}^{\frac{1}{2}} / \begin{vmatrix} g_{11}' & g_{14} \\ g_{14} & g_{44} \end{vmatrix}^{\frac{1}{2}}$$
(3)

$$\frac{\nu_{\mathrm{I}}\nu_{\mathrm{II}}\nu_{\mathrm{III}}\delta(\mathrm{C}-\mathrm{H})}{\nu_{\mathrm{I}},\nu_{\mathrm{III}}\delta'(\mathrm{C}-\mathrm{H})} = \frac{|G(1,2,3,4,6,8)|^{\frac{1}{2}}}{|G'(1,2,3,4,6,8)|^{\frac{1}{2}}} \cdot \frac{\begin{vmatrix} g_{11}' & g_{14} \\ g_{14} & g_{44} \end{vmatrix}^{\frac{1}{2}}}{\begin{vmatrix} g_{11} & g_{14} \\ g_{14} & g_{44} \end{vmatrix}^{\frac{1}{2}}} \quad (4)$$

where G(1,2,3,4,6,8) is the sixth-order *G*-matrix with  $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$ ,  $S_6$ , and  $S_8$  as the coordinates and the letter with prime means the values for the corresponding deuterated molecule.

The kinetic energy matrix for the  $A_u$  vibrations is derived according to the Wilson's method. The internal

(2)

$$S_{1} = (-\theta_{14} + \theta_{13} + \theta_{54} - \theta_{53} + \theta_{69} - \theta_{68} - \theta_{09} - \theta_{08})/2\sqrt{2}$$

$$S_{2} = (\Omega_{0} + \Omega_{2} - \theta_{13} + \theta_{54} - \Omega_{5} - \Omega_{7} + \theta_{68} - \theta_{09})/2\sqrt{2}$$

$$S_{3} = (\Omega_{0} - \Omega_{2} + \theta_{14} - \theta_{53} - \Omega_{5} + \Omega_{7} - \theta_{69} + \theta_{08})/2\sqrt{2}$$

$$S_{4} = (-\theta_{26} + \theta_{27} + \theta_{16} - \theta_{17})/2$$

where all the valence angles are assumed to be  $120^{\circ}$ ,  $\theta_{il}$  means  $\sin \alpha_{ijk} \sin \alpha_{jkl}$  times the dihedral angle between the plane of atoms *i*, *j*, and *k* and that of atoms *j*, *k*, and *l* (as to the sign of  $\theta_{il}$ , see J. C. Decius, J. Chem. Phys. 16, 1025 (1948)), and  $\Omega_i$  means ( $\tau_{ij} \sin \alpha_{kil}$  $+ \tau_{ik} \sin \alpha_{lij} + \tau_{il} \sin \alpha_{jik}$ ) times the distance between the central atom *i* and the plane of atoms *j*, *k*, and *l* which surround the atom *i*. The elements of the kinetic energy matrix are:

$$g_{11} = 3\{\mu_0 \tau_{01}^2 + \mu_1 \tau_{01}^2 + \mu_2 (\tau_{23} - \tau_{24})^2 + \mu_3 \tau_{23}^2 + \mu_4 \tau_{24}^2\}/4$$

$$g_{12} = 3\{-\mu_0 \tau_{01}^2 - \mu_1 \tau_{01}^2 - \mu_2 (\tau_{23}^2 - \tau_{24}^2) - \mu_3 \tau_{23}^2 + \mu_4 \tau_{24}^2\}/4$$

$$g_{13} = 3\{-\mu_0 \tau_{01} (\tau_{01} + 2\tau_{02}) - \mu_1 \tau_{01}^2 + \mu_2 (\tau_{23} - \tau_{24}) + (\tau_{23} - \tau_{24})$$

$$g_{22} = 3\{\mu_0 \tau_{01}^2 + \mu_1 \tau_{01}^2 + \mu_2 (\tau_{23} + \tau_{24})^2 + \mu_3 \tau_{23}^2 + \mu_4 \tau_{24}^2\}/4 \quad (5)$$

$$g_{23} = 3\{\mu_0 \tau_{01} (\tau_{01} + 2\tau_{02}) + \mu_1 \tau_{01}^2 - \mu_2 (\tau_{23} + \tau_{24}) + \chi(2\tau_{02} + \tau_{23} + \tau_{24}) - \mu_3 \tau_{23}^2 - \mu_4 \tau_{24}^2\}/4 \quad (5)$$

$$g_{24} = 3\{\mu_0 \tau_{01} (\tau_{01} - \tau_{02}) + \mu_1 \tau_{01}^2 + \mu_2 \tau_{02} (\tau_{23} + \tau_{24})\}/2\sqrt{2}$$

$$g_{24} = 3\{\mu_0 (\tau_{02} + 2\tau_{02})^2 + \mu_1 \tau_{02}^2 + \mu_2 \tau_{02} (\tau_{23} + \tau_{24})\}/2\sqrt{2}$$

$$g_{33} = 3\{\mu_0(\tau_{01} + 2\tau_{02}) + \mu_1\tau_{01} + \mu_2(2\tau_{02} + \tau_{23} + \tau_{24})^2 + \mu_3\tau_{23}^2 + \mu_4\tau_{24}^2\}/4$$
  

$$g_{34} = 3\{\mu_0(\tau_{01} + 2\tau_{02})(\tau_{01} - \tau_{02}) + \mu_1\tau_{01}^2 - \mu_2\tau_{02}(2\tau_{02} + \tau_{23} + \tau_{24})\}/2\sqrt{2}$$
  

$$g_{44} = 3\{\mu_0(\tau_{01} - \tau_{02})^2 + \mu_1\tau_{01}^2 + \mu_2\tau_{02}^2\}/2.$$

The Wilson's method is used for the calculation of the product rule.

#### APPENDIX II

The Raman frequencies (cm<sup>-1</sup>) of liquid N-methylformamide measured by T. Sugita and the authors are: 1730(1), 1680(1b), 1652(5), 1545(3b), 1443(3b), 1410(3), 1382(8), 1323(2), 1250(8), 1150(5), 1037(3), 1015(3), 964(10), 912(0), 765(5), 662(5), 556(2), 372(4), 295(3), 224(1).

The Raman frequencies of liquid N-ethylacetamide measured by T. Arakawa and the authors are: 1648(7b), 1550(1), 1440(8b), 1349(2), 1295(8b), 1151(7b), 1113(2), 1072(7), 1002(3), 936(7b), 888(7b), 857(4), 821(1), 777(4), 709(1), 617(7b), 560(3), 510(1), 458(4b), 379(7b), 320(1), 295(1), 230(1).

#### APPENDIX III

The formamide molecule is treated as a three-body problem,  $O-CH-NH_2$ . If the potential energy of the Urey-Bradley type is assumed, four force constants, K(O-CH),  $K(CH-NH_2)$ ,  $H(O-CH-NH_2)$ , and

Set	K(O-CH)	$K(CH - NH_2)$	$H(O - CH - NH_2)$	$F(ONH_2)$
I	10.40	8.15	0.562	0.750
II	10.47	8.04	0.471	1.000
III	10.53	7.92	0.386	1.250
IV	10.59	7.79	0.305	1.500

 $F(O \cdots NH_2)$  are necessary for the calculation of three skeletal frequencies, where K is the stretching, H is the bending, and F is the repulsive force constant.<sup>26</sup>

Four sets of force constants, which give the frequencies in agreement with the observed ones (1688, 1310, and 600 cm<sup>-1</sup>),<sup>14</sup> are shown in Table VI, the value of  $F(O \cdots NH_2)$  being assumed to be 0.75, 1.00, 1.25, or  $1.50 \times 10^5$  dynes/cm.

The elements of *L*-matrix which is defined by

$$\begin{vmatrix} \Delta r (\mathrm{O-CH}) \\ \Delta r (\mathrm{CH-NH}_2) \\ \Delta \alpha (\mathrm{O-CH-NH}_2) \end{vmatrix} = L \begin{cases} Q_{1688} \\ Q_{1310} \\ Q_{600} \end{cases}$$

is shown in Table VII, where r is the bond distance,  $\alpha$  is the bond angle, and Q is the normal coordinate the wave number of which is given as a suffix.

TABLE VII. L-matrices for formamide.

Force constant I	Force constant II
$\begin{pmatrix} -0.34 & +0.15 & +0.01 \\ -0.24 & +0.29 & +0.02 \\ -0.05 & -0.25 & +0.39 \end{pmatrix}$	$\begin{pmatrix} +0.34 & +0.14 & +0.01 \\ -0.23 & +0.29 & +0.01 \\ -0.06 & -0.24 & +0.40 \end{pmatrix}$
Force constant III	Force constant IV
	r orec conordine r r

The ratios of the amplitude of r(O-CH) to that of  $r(CH-NH_2)$  for the vibrations  $Q_{1688}$  and  $Q_{1310}$  is practically independent on the four sets of force constants.

#### APPENDIX IV

The kinetic energy matrix for the out-of-plane vibrations (A'') is derived for molecules of the type:



The symmetry coordinates used are:

 $S_{1} = (-\theta_{35} + \theta_{36} + \theta_{25} - \theta_{26})/2$   $S_{2} = (\Omega_{1} + \Omega_{4} - \theta_{36} + \theta_{25})/2$  $S_{3} = (\Omega_{1} - \Omega_{4} + \theta_{35} - \theta_{26})/2$ 

<sup>26</sup> T. Shimanouchi, J. Chem. Phys. 17, 245, 734, 848 (1949).

and the elements of the kinetic energy matrix are:

 $g_{11} = 3 \left[ \mu_1 (\tau_{12} - \tau_{13})^2 + \mu_2 \tau_{12}^2 + \mu_3 \tau_{13}^2 + \mu_4 (\tau_{45} - \tau_{46})^2 \right]$  $+\mu_{5}\tau_{45}^{2}+\mu_{6}\tau_{46}^{2}]/4$  $g_{12} = 3 \left[ \mu_1 (\tau_{12}^2 - \tau_{13}^2) + \mu_2 \tau_{12}^2 - \mu_3 \tau_{13}^2 + \mu_4 (\tau_{45}^2 - \tau_{46}^2) \right]$  $+\mu_5\tau_{45}^2-\mu_6\tau_{46}^2/4$  $g_{13} = 3 \left[ \mu_1 (\tau_{12} - \tau_{13}) (\tau_{12} + \tau_{13} + 2\tau_{14}) + \mu_2 \tau_{12}^2 - \mu_3 \tau_{13}^2 \right]$  $-\mu_4(\tau_{45}-\tau_{46})(\tau_{45}+\tau_{46}+2\tau_{14})-\mu_5\tau_{45}^2+\mu_6\tau_{46}^2]/4$  $g_{22} = 3 \left[ \mu_1 (\tau_{12} + \tau_{13})^2 + \mu_2 \tau_{12}^2 + \mu_3 \tau_{13}^2 + \mu_4 (\tau_{45} + \tau_{46})^2 \right]$  $+\mu_5\tau_{45}^2+\mu_6\tau_{46}^2]/4$  $g_{23} = 3 \left[ \mu_1 (\tau_{12} + \tau_{13}) (\tau_{12} + \tau_{13} + 2\tau_{14}) + \mu_2 \tau_{12}^2 + \mu_3 \tau_{13}^2 \right]$  $-\mu_4(\tau_{45}+\tau_{46})(\tau_{45}+\tau_{46}+2\tau_{14})-\mu_5\tau_{45}^2-\mu_6\tau_{46}^2/4$  $g_{33} = 3 \left[ \mu_1 (\tau_{12} + \tau_{13} + 2\tau_{14})^2 + \mu_2 \tau_{12}^2 + \mu_3 \tau_{13}^2 \right]$  $+\mu_4(\tau_{45}+\tau_{46}+2\tau_{14})^2+\mu_5\tau_{45}^2+\mu_6\tau_{46}^2]/4.$ 

In the case of CH<sub>3</sub>CONHCH<sub>3</sub> and CH<sub>3</sub>CONDCH<sub>3</sub>, the methyl group is treated as a point mass and the bond lengths of C=O,  $C-CH_3$ , C-N, N-H, and

N-CH<sub>3</sub> are assumed as 1.21, 1.54, 1.34, 1.00, and 1.47 A, respectively. The ratio of the square root of the determinant of the G-matrix for CH<sub>3</sub>CONHCH<sub>3</sub> to that for  $CH_3CONDCH_3$  is 1.36. If it is assumed that the amide VI' band is overlapped by the amide IV band and that the C-N torsional frequency hardly changes on deuteration, the observed ratio becomes  $1.36 = (725 \times 600) / (510 \times 627)$  which is in agreement with the theoretical value.

In the case of N,N'-dimethyloxamide and of diacetylhydrazine, the G-matrix given in Appendix I, Eq. (5)is used. The methyl group is treated as a point mass and the torsional frequency is assumed not to change on deuteration. In the former case, the observed ratio is  $1.38 = \nu_V \nu_{VI} / \nu_{V'} \nu_{VI'}$ , and the theoretical one is 1.40. In the latter case, the observed ratio is 1.41, and the theoretical one is 1.40.

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## Derivation of the WLF Equation for the Mobility of Molecules in Molten Glasses

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A previous theory for the mobility of molecules in glasses near the glass temperature has been extended in an effort to deduce the semiempirical relation proposed by Williams, Landel, and Ferry. By focusing attention upon the free volume, one is able to derive their relation in a straightforward fashion subject to approximations valid near the glass temperature. The interpretation of the constants which WLF proposed for their relation is shown to be correct.

WILLIAMS, Landel, and Ferry have recently discovered an amazing correlating relation which describes the temperature dependence of the molecular relaxation times in glass forming substances.<sup>1</sup> They have found that if one takes the ratio of the relaxation time of the substance at a temperature T to that observed at the glass temperature  $T_g$ , then this ratio  $a_T$  is given by  $\log(a_T) = -17.4(T-T_g)/$  $(52+T-T_g)$ . This relation was found to apply to all well-studied glass forming substances in the range where  $T - T_g \lesssim 100^{\circ}$ C. It is quite startling that so simple a relation should describe the behavior of such dissimilar substances as glucose, boron trioxide, and polystyrene, as well as many others. One cannot escape the fact that there appears to be something very fundamental about this semiempirical relation.

The WLF relation was examined with respect to existing theories of glasses by its discoverers. Although the theoretical relations now known do not contradict the WLF relation, they give very little insight into why it is true. Indeed, the most insight into the meaning of the relation was obtained from a comparison with

another semiempirical relation, that of Doolittle.<sup>2</sup> The chief difficulty with the existing theories of glasses is the fact that they do not reduce so as to contain easily estimated parameters. WLF have shown this quite clearly for a theory of Dienes<sup>3</sup> and also for a portion of a theory proposed by the present author.<sup>4</sup>

In this paper we shall use the general method of our previous theory<sup>4</sup> to derive the WLF relation. It will be recalled that the basic idea behind our approach was to recognize that molecules or polymer segments cannot move as individuals in a substance which is near its glass temperature. On the contrary, when one segment moves or jumps, several others will have to cooperate with it in order to allow such a movement. We shall refer to this cooperating group of molecules or segments as a "unit." In our previous paper,<sup>4</sup> we calculated the behavior of such a system in two ways: first, with respect to energy considerations, and second, with respect to volume considerations. Both of these approaches appear to fit available experimental data if

<sup>2</sup> A. K. Doolittle, J. Appl. Phys. 22, 1471 (1951); 23, 236 (1952). <sup>3</sup> G. J. Dienes, J. Appl. Phys. 24, 779 (1953). <sup>4</sup> F. Bueche, J. Chem. Phys. 21, 1850 (1953).

<sup>&</sup>lt;sup>1</sup> Williams, Landel, and Ferry, J. Am. Chem. Soc. 77, 3701 (1955).