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Infrared Spectra of Biuret-hydrate and Its Deuterated Compound

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The infrared spectra between 4000 and 33 cm^{-1} of biuret-hydrate and between 4000 and 250 cm^{-1} of its deuterated compound have been recorded. The vibrational assignments have been made by referring to the infrared spectra of the related compounds and the isotopic frequency shift. Normal coordinate analysis of the in-plane vibrations of biuret and biuret-d_5 as twelve-body problem has been carried out by using the molecular model of the planar *trans-cis* conformation. A simple Urey-Bradley force field has been employed and the force constants have been refined by the least squares method. The calculation of potential energy distributions has shown that the NH in-plane deformation and the CN stretching vibrations couple appreciably with each other and give the imide II and III bands at 1515 and 1365 cm^{-1}, respectively, just as in the case of diacetamide.

In the infrared spectra for the condensed phase, aliphatic imides[1] and monosubstituted amides[2] show the imide II band and the amide II band, respectively, in the region between 1550 and 1500 cm^{-1}. These bands are fairly strong and quite characteristic of the –CONH– group in which the C=O and the NH bonds take the *trans* conformation with each other.[3] It has been proved by the normal coordinate analysis of *N*-methylacetamide[4] and diacetamide[5] that both the amide II and the imide II bands arise from the coupling between the NH in-plane deformation and the CN stretching vibrations of the *trans* –CONH– group. According to the X-ray analysis, a molecule of biuret ($NH_2CONHCONH_2$) has the *trans-cis* –CONHCO– group[6] in the biuret-hydrate crystal. It is interesting to examine the infrared spectra of this crystal and to see if there exists the coupling analogous to the case of amides and imides.

Besides the hydrate crystal, biuret has also the anhydrate crystal. The infrared spectra of both crystals have been recorded in the region between 4000 and 650 cm^{-1} and several bands have already been assigned.[7-9] In the present paper, we report the infrared spectra of biuret-hydrate between 4000 and 33 cm^{-1} and the assignment of the fundamental frequencies of biuret given on the basis of the spectral change on deuteration and a comparison with related compounds such as urea,[10] diacetamide[5] and acylureas.[11] This paper includes also the normal coordinate analysis of the in-plane vibrations of biuret and biuret-d_5 in the *trans-cis* conformation.

Experimental

Commercially available biuret was purified several times by recrystallization from water and ethanol. The hydrate was prepared by crystallization from water.[12] Deuterated biuret-hydrate was prepared by the usual exchange reaction with heavy water, and was left in the atmosphere saturated with heavy water for three weeks in order to avoid the contamination of the anhydrate crystal in the sample.

The infrared spectra were recorded on a Koken DS 301 infrared spectrophotometer equipped with sodium chloride and potassium bromide prisms (4000—450 cm^{-1}), on a Perkin Elmer model 521 grating spectrophotometer (900—250 cm^{-1}) and on a Hitachi FIS-3 grating spectrophotometer (400—33 cm^{-1}). The samples were subjected to the measurement in the form of a solid dispersed in Nujol and hexachlorobutadiene (H.C.B.). The absorption frequencies are listed in Tables 1 and 2 together with the assignment.

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[1] T. Uno and K. Machida, This Bulletin, **34**, 551 (1961).

[2] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Methuen & Co., Ltd., London, John Wiley & Sons, Inc., New York (1958), p. 203.

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

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

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[11] T. Uno, K. Machida, K. Hanai and Y. Saito, This Bulletin, **42**, 619 (1969).

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Results and Discussion

The Region above 1800 cm^{-1}. Biuret-hydrate shows four bands at 3487, 3438, 3214 and 3010 cm^{-1}. These bands are obviously due to the stretching vibrations of the NH and the NH_2 group as well as of the crystal water, but it is rather difficult to assign them to the specific vibrations of individual groups. These bands are replaced by the bands at 2585, 2412, 2321 and 2272 cm^{-1} on deuteration.

The Region between 1800 and 900 cm^{-1}. Figure 1 shows the infrared spectra between 1800 and 800 cm^{-1} of biuret-hydrate and its deuterated compound. The undeuterated compound shows only three bands between 1750 and 1550 cm^{-1}, although two C=O stretching and two NH_2 bending bands are expected in this region. On deuteration, the two bands at 1749 and 1718 cm^{-1} shift slightly to lower frequencies and the band at 1608 cm^{-1} disappears completely as seen in Fig. 1. It is obvious therefore that the former bands are due to the C=O stretching vibrations and the latter to the NH_2 bending vibrations. By referring to biuret-anhydrate which shows two peaks at 1620 and 1588 cm^{-1},[8,6] it is conceivable that the two NH_2 bending absorptions of hydrate crystal overlap to give one band at 1608 cm^{-1}. The corresponding ND_2 bending absorptions of deuterated biuret-hydrate were identified as the weak bands at 1168 and 1130 cm^{-1} from analogy with urea-d_4.[10] The band at 1130 cm^{-1} of biuret-hydrate may be assigned to the NH_2 rocking vibrations and the band at 915 cm^{-1} of deuterated biuret-hydrate to the ND_2 rocking vibrations. These frequencies are comparable to the corresponding frequencies of urea and urea-d_4.[10]

Takimoto assigned the bands of biuret-anhydrate at 1420, 1326 and 950 cm^{-1} to the CN stretching vibrations.[9] The bands of biuret-hydrate corresponding to these bands are observed at 1420, 1365 and 958 cm^{-1}. Among these bands, the bands at 1420 and 958 cm^{-1} hardly shift on deuteration as seen in Fig. 1, and are assigned undoubtedly to the CN stretching vibrations. The 1365 cm^{-1} band cannot be assigned to a simple CN stretching vibration since this band disappears on deuteration as seen in Fig. 1. Uno and Machida concluded in consequence of the normal coordinate analysis of diacetamide that the imide II and III bands arise from the coupling between the NH in-plane deformation and the CN stretching vibrations of the –CONHCO– group. Analogously the deuteration sensitive band at 1365 cm^{-1} of biuret-hydrate may be assigned to the imide III band arising from the coupling between the NH in-plane deformation and the CN stretching vibrations of the –CONHCO– group. To the imide II absorption of biuret-hydrate expected from this coupling, we assigned the weak band at 1515 cm^{-1} which disappears on deuteration. Such a weak imide II band has also been found around 1480 cm^{-1} for acylureas.[11] The 1096 cm^{-1} band is assigned to the remaining CN stretching vibration. For deuterated biuret-hydrate, the bands at 1462, 1435, 1273 and 935 cm^{-1} can be assigned to the four CN stretching vibrations. According to the normal coordinate analysis, however, the band at 1273 cm^{-1} is due to a complicated vibration concerned with the CN stretching, the ND in-plane deformation (imide III′) and the ND_2 rocking vibrations.

The Region between 900 and 33 cm^{-1}. Figure 2 shows the infrared spectra between 900 and 33 cm^{-1} of biuret-hydrate and between 900 and 250 cm^{-1} of deuterated biuret-hydrate. Referring to the C=O out-of-plane deformation frequency of urea (785 cm^{-1}) and urea-d_4 (776 cm^{-1}),[10] we assigned the bands at 801 and 765 cm^{-1}

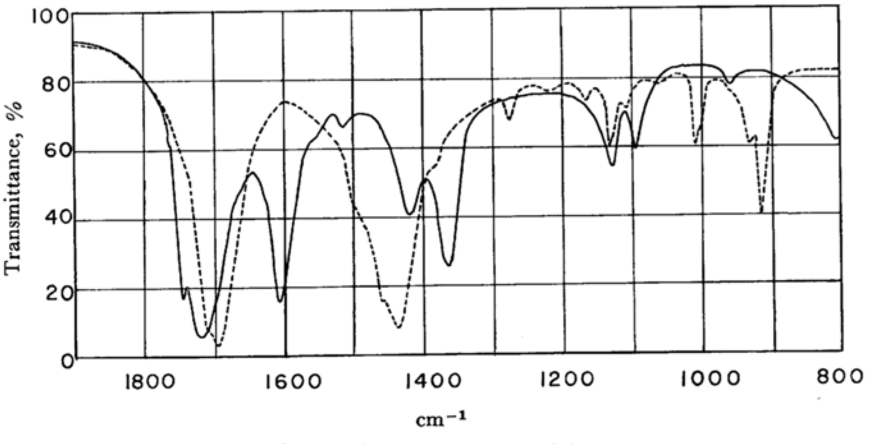

Fig. 1. Infrared spectra of biuret-hydrate (——) and its deuterated compound (----) in the region between 1900 and 800 cm^{-1}.

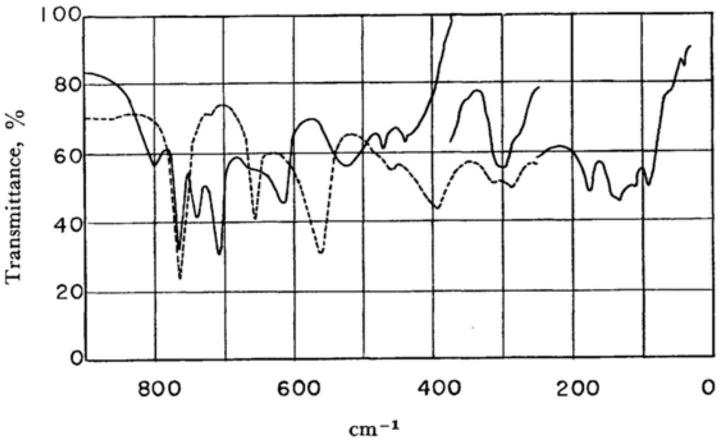

Fig. 2. Infrared spectra biuret-hydrate (——) and its deuterated compound (----) in the region between 900 and 33 cm^{-1}.

of biuret-hydrate and the band at 764 cm^{-1} of deuterated biuret-hydrate to the corresponding vibrations. The band at 712 cm^{-1} is assigned to the NH_2 wagging or the NH out-of-plane deformation (imide V) vibrations and the band at 520 cm^{-1} to the NH_2 torsional vibration from analogy with urea$^{10)}$ and diacetamide.$^{5)}$ The counterparts of these bands for deuterated biuret-hydrate are found at 558 and 392 cm^{-1}. Throughout this region the spectral change on deuteration is so complicated that the assignment of the bands due to the in-plane deformation vibrations is quite difficult. From the large separation between the in-plane NH and ND deformation and the in-plane skeletal deformation frequencies, it is expected at first sight that the shift of the latter frequencies on deuteration may not be appreciable. Normal coordinate analysis revealed, however, fairly big effects of the deuteration on the in-plane skeletal deformation frequencies. We assigned the bands at 741, 618, 471, 439 and 178 cm^{-1} for biuret-hydrate and the bands at 653, 558, 450 and 392 cm^{-1} for deuterated biuret-hydrate to the skeletal in-plane deformation vibrations by referring to the calculated frequencies.

Normal Coordinate Analysis

Since it is almost impossible to give a complete assignment of all fundamental frequencies of such a big molecule as biuret on the purely empirical basis, we have carried out the normal coordinate analysis according to Wilson's method.$^{13)}$ The **G** matrices were set up by using the *trans-cis* conformation and the structural parameters based on Hughes *et al.*'s X-ray study$^{6)}$ as shown in Fig. 3. The

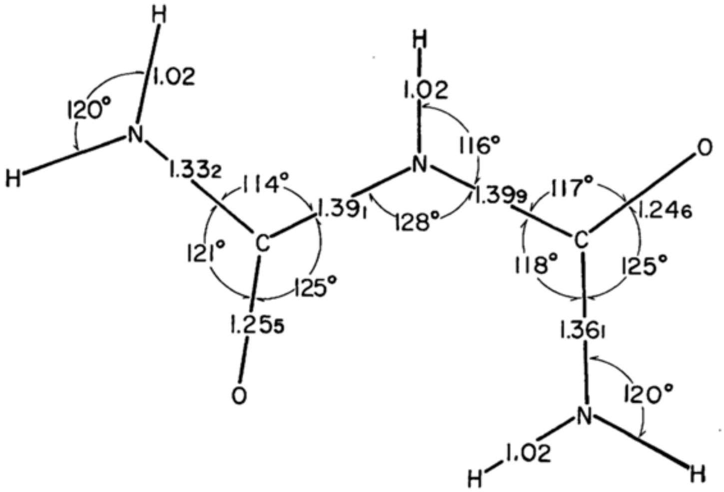

Fig. 3. Structural parameters.

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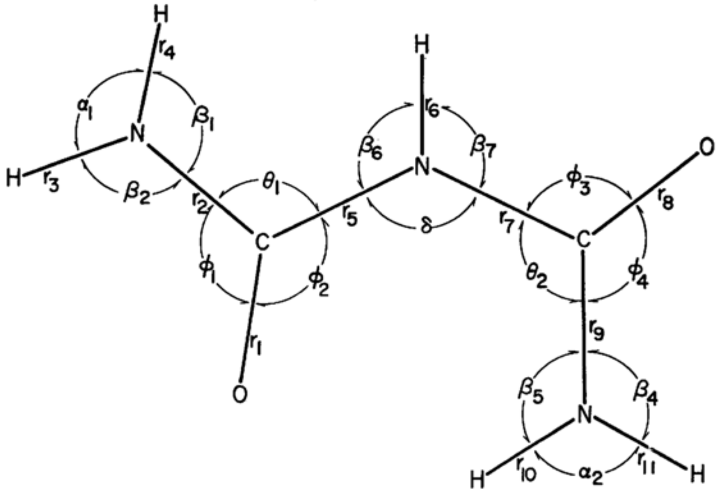

Fig. 4. Internal coordinates.

TABLE 1. INFRARED FREQUENCIES OF BIURET-HYDRATE

	Assignment
3487 s 3438 s 3214 sb 3010 m	NH$_2$ asym. and sym. stretching NH stretching OH stretching
1745 s	C=O stretching
1718 vs	C=O stretching
1608 s	NH$_2$ bending
1515 w	Imide II band
1420 m	CN stretching
1365 s	Imide III band
1130 m	NH$_2$ rocking
1096 m	CN stretching
958 w	CN stretching
801 w	C=O out-of-plane deformation
765 m	C=O out-of-plane deformation
741 m	skeletal in-plane deformation
712 m	NH$_2$ wagging or NH out-of-plane deformation
618 m	skeletal in-plane deformation
520 w	NH$_2$ torsion
471 w	skeletal in-plane deformation
439 w	skeletal in-plane deformation
300 mb	skeletal out-of-plane deformation
280 sh	skeletal out-of-plane deformation
178 w	skeletal in-plane deformation

TABLE 2. INFRARED FREQUENCIES OF DEUTERATED BIURET-HYDRATE

	Assignment
2585 s 2412 s 2321 s 2272 sh	ND$_2$ asym. and sym. stretching ND stretching OD stretching
1710 sh	C=O stretching
1695 vs	C=O stretching
1462 sh	CN stretching
1435 vs	CN stretching
1273 m	CN stretching
1168 vw 1130 w	ND$_2$ bending
1011 w	ND deformation and skeletal stretching
935 w	CN stretching
915 m	ND$_2$ rocking
764 m	C=O out-of-plane vibration
653 m	skeletal in-plane deformation
558 s	skeletal in-plane deformation ND$_2$ wagging or ND out-of-plane deformation
450 w	skeletal in-plane deformation
392 m	skeletal in-plane deformation ND$_2$ torsion
307 mb	skeletal out-of-plane deformation
280 mb	skeletal out-of-plane deformation

NH$_2$ and the NH stretching vibrations were separated from the other vibrations.[13,14] A description of the internal coordinates is shown in Fig. 4 and the internal symmetry coordinates were constructed as shown in Table 3. A simple Urey-Bradley force field was employed, and the fifteen force constants shown as the set A of Table 4 were used first. In a trial calculation we transferred the bending constant H(CNC) and the repulsion constant F(CNC) from diacetamide[5] and the other force constants from urea,[15] but the calculated frequencies were

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[14] E. B. Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations," McGrow Hill, New York (1955), p. 74.

[15] A. Yamaguchi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **78**, 1319 (1957); A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **10**, 1319 (1957).

TABLE 3. INTERNAL SYMMETRY COORDINATES

Symmetry coordinates	Description of modes	Abbr.
$S_1 = \Delta r_1$	C=O stretching	νC=O
$S_2 = \Delta r_8$	C=O stretching	νC=O
$S_3 = \Delta r_2$	CN stretching	νCN
$S_4 = \Delta r_5$	CN stretching	νCN
$S_5 = \Delta r_7$	CN stretching	νCN
$S_6 = \Delta r_9$	CN stretching	νCN
$S_7 = (2\Delta\alpha_1 - \Delta\beta_1 - \Delta\beta_2)/\sqrt{6}$	NH_2 bending	βNH_2
$S_8 = (\Delta\beta_1 - \Delta\beta_2)/\sqrt{2}$	NH_2 rocking	ρNH_2
$S_9 = (2\Delta\alpha_1 - \Delta\beta_4 - \Delta\beta_5)/\sqrt{6}$	NH_2 bending	βNH_2
$S_{10} = (\Delta\beta_4 - \Delta\beta_5)/\sqrt{2}$	NH_2 rocking	ρNH_2
$S_{11} = (2\Delta\delta - \Delta\beta_6 - \Delta\beta_7)/\sqrt{6}$	CNC deformation	δCNC
$S_{12} = (\Delta\beta_7 - \Delta\beta_6)/\sqrt{2}$	NH deformation	δNH
$S_{13} = (2\Delta\theta_1 - \Delta\phi_1 - \Delta\phi_2)/\sqrt{6}$	NCN deformation	δNCN
$S_{14} = (\Delta\phi_2 - \Delta\phi_1)/\sqrt{2}$	CO deformation	δCO
$S_{15} = (2\Delta\theta_2 - \Delta\phi_3 - \Delta\phi_4)/\sqrt{6}$	NCN deformation	δNCN
$S_{16} = (\Delta\phi_4 - \Delta\phi_3)/\sqrt{2}$	CO deformation	δCO

TABLE 4. FORCE CONSTANTS

Set A		Set B		Dispersion
$K(CO)$	7.83	$K(CO)_T$	8.00_0	0.41
		$K(CO)_C$	8.05_6	0.32
$K(CN)_U$	6.07	$K(CN)_{UT}$	6.04_7	0.19
		$K(CN)_{UC}$	5.49_5	0.33
$K(CN)_I$	3.56	$K(CN)_I$	3.73_6	0.18
$H(HNH)$	0.35	$H(HNH)$	0.35_1	0.00
$H(CNH)_I$	0.26	$H(CNH)_I$	0.19_0	0.01
$H(CNH)_U$	0.42	$H(CNH)_U$	0.42_3	0.00
$H(NCN)$	0.63	$H(NCN)$	0.77_6	0.07
$H(CNC)$	0.50*	$H(CNC)$	0.13_5	0.04
$H(NCO)$	0.27	$H(NCO)$	0.22_8	0.01
$F(HNH)$	0.0*	$F(HNH)$	0.0*	—
$F(CNH)_I$	0.61	$F(CNH)_I$	0.83_8	0.07
$F(CNH)_U$	0.22	$F(CNH)_U$	0.16_8	0.02
$F(NCN)$	0.89	$F(NCN)$	0.77_7	0.09
$F(CNC)$	0.54	$F(CNC)$	0.98_5	0.28
$F(NCO)$	1.28	$F(NCO)$	1.34_3	0.03

* assumed

so deviated from the observed ones that we could not enter the refinement process. Then we took the values of the $K(CN)_I$, $H(CNH)_I$, $H(CNC)$, $F(CNH)_I$ and $F(CNC)$ from diacetamide[5] (the subscript I specifies the force constant concerned with the –CONHCO– group) and the other force constants from urea.[15] In the first step of the force constant refinement, only the frequencies higher than 900 cm^{-1} of biuret and deuterated biuret were taken into account, and the values of the stretching constants and the bending constants concerned with hydrogen atoms were adjusted several times by referring to the Jacobian matrix elements and were further refined by the least squares method. After this refinement the absorption frequencies below 900 cm^{-1} were assigned to the vibrational modes by referring to the calculated frequencies. This assignment was checked by the product rule[16] by assuming that the two unobserved frequencies of deuterated biuret were the same as the calculated frequencies. The observed product ratio (7.21) agrees well with the theoretical ratio (7.06) obtained from calculated frequencies. In the next step, we fixed the values of the repulsion constant $F(HNH)$ and the bending constant $H(CNC)$ to zero and 0.50, respectively, since they showed large dispersions, and refined all the other force constants to obtain a converged set (see the set A in Table 4). The value of the stretching constant $K(CN)_I$ obtained in this step is smaller than that of the CN stretching constant for the $-CONH_2$ groups, $K(CN)_U$. This result is comparable with the case of bis(biuret) copper(II) chloride[17] and is consistent with the expectation from the difference in the CN bond lengths between the –CONHCO– and the $-CONH_2$ groups. Since the two $-CONH_2$ groups are not equivalent to each other in the *trans-cis* conformation of biuret, it seems too crude to fix the two constants appearing pairwise for the two $-CONH_2$ groups to the same value. On the other hand, the increase in the number of independent force constants is not favorable to obtain any converged set of force constants uniquely. Accordingly, in the final step of the force constant refinement, we tried to refine only the stretching constants for the C=O and the CN bonds of each $-CONH_2$ group independently. Their values were initially taken from the set A, and the sixteen force constants except the repulsion constant $F(NHH)$ were refined by the least squares method to obtain a converged set. The force constants used in the final calculation are shown as the set B of Table 4

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17) B. B. Kedzia, P. X. Armendarez and K. Nakamoto, *J. Inorg. & Nuclear Chem.*, **30**, 849 (1968).

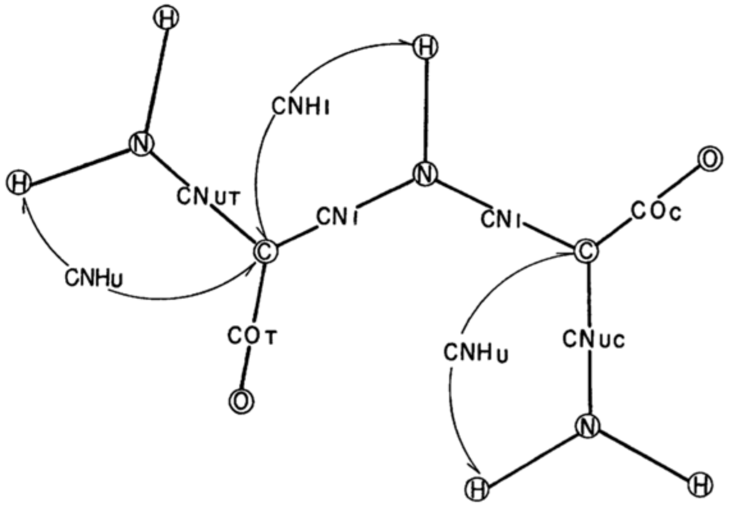

Fig. 5. The bonds and angles specified by the subscripted notation for the force constants.

TABLE 5. FUNDAMENTAL FREQUENCIES AND MAIN POTENTIAL ENERGY DISTRIBUTIONS FOR BIURET

	Obsd	Calcd	Δ(%)	P. E. D. (%)	Abbr.
ν_1	1745	1743	0.1	$S_1(53)$, $S_3(17)$, $S_{12}(16)$, $S_{13}(15)$	νC=O
ν_2	1718	1722	0.3	$S_2(56)$, $S_6(21)$, $S_{15}(15)$	νC=O
ν_3	1608	1611	0.2	$S_7(68)$, $S_3(11)$, $S_9(10)$	βNH_2
ν_4	1608	1604	0.1	$S_9(70)$	βNH_2
ν_5	1515	1522	0.4	$S_{12}(71)$, $S_4(13)$	Imide II
ν_6	1420	1419	0.1	$S_5(35)$, $S_4(30)$, $S_3(17)$, $S_6(15)$	νCN
ν_7	1365	1368	0.3	$S_3(29)$, $S_5(20)$, $S_6(20)$, $S_{12}(10)$	Imide III
ν_8	1130	1133	0.3	$S_8(40)$, $S_{10}(33)$, $S_1(10)$	ρNH_2
ν_9	1130	1125	0.5	$S_{10}(36)$, $S_8(31)$, $S_2(13)$	ρNH_2
ν_{10}	1096	1097	0.1	$S_4(20)$, $S_3(15)$, $S_1(14)$	νCN
ν_{11}	958	964	0.4	$S_6(25)$, $S_5(18)$, $S_{13}(10)_5$	νCN
ν_{12}	741	732	0.9	$S_{14}(25)$, $S_{15}(24)$, $S_{11}(10)$	skel.
ν_{13}	618	617	0.1	$S_{16}(46)$, $S_{14}(22)$, $S_{13}(21)$	skel.
ν_{14}	471	471	0.0	$S_{15}(37)$, $S_{14}(28)$, $S_{13}(12)$	skel.
ν_{15}	439	427	2.7	$S_{16}(30)$, $S_{13}(29)$	skel.
ν_{16}	178	172	4.4	$S_{11}(73)$, $S_{15}(12)$	skel.

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

together with their dispersions. The bonds and angles specified by the subscripted notation for the force constants are indicated in Fig. 5. Tables 5 and 6 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 is excellent throughout both isotopic species.

It is seen from Table 5 that the coupling of the NH in-plane deformation vibration with the CN stretching vibrations does occur for the imide II and III frequencies empirically assigned, although it is not so appreciable as in the case of diacetamide.5) As seen in Tables 5 and 6, the skeletal in-plane deformation vibrations couple appreciably with one another for the frequencies below 700 cm^{-1}, and it is difficult to assign each fundamental frequency to the vibration of a particular group. The vibrational mode of 1011 cm^{-1} band of deuterated biuret is quite complicated by the mixing of the C=O stretching, the CN stretching, the ND in-plane deformation, the ND_2 bending and the CNC deformation vibrations as seen in Table 6. This situation may be comparable with the cases for the 1035 cm^{-1} band of diacetamide-d_1 contributed by the skeletal stretching and deformation vibrations5) and for the 1005 cm^{-1} band of urea-d_4 contributed by the C=O stretching and the ND_2 bending vibrations.15) As seen in Table 4, the values of the stretching constant $K(\mathrm{CO})_{\mathrm{T}}$ and $K(\mathrm{CO})_{\mathrm{C}}$ obtained in the final calculation are not

TABLE 6. FUNDAMENTAL FREQUENCIES AND MAIN POTENTIAL ENERGY DISTRIBUTIONS FOR DEUTERATED BIURET

	Obsd	Calcd	Δ(%)	P. E. D. (%)	Abbr.
ν_1'	1710	1713	0.2	$S_1(52)$, $S_2(17)$, $S_3(15)$, $S_{13}(13)$	νC=O
ν_2'	1695	1692	0.2	$S_2(56)$, $S_1(18)$, $S_6(14)$, $S_{15}(12)$	νC=O
ν_3'	1462	1462	0.0	$S_3(51)$, $S_4(45)$, $S_{14}(13)$	νCN
ν_4'	1435	1431	0.3	$S_6(50)$, $S_5(45)$, $S_{16}(14)$, $S_9(11)$	νCN
ν_5'	1273	1270	0.3	$S_4(19)$, $S_5(14)$, $S_{12}(28)$, $S_7(20)$	$\nu CN+\delta ND+\beta ND_2$
ν_6'	1168	1181	1.4	$S_9(56)$, $S_5(12)$	βND_2
ν_7'	1130	1112	1.8	$S_7(39)$, $S_{13}(35)$	$\beta ND_2+\delta ND$
ν_8'	1011	1007	0.4	$S_1(19)$, $S_7(15)$, $S_{12}(9)$, $S_{13}(7)$	$\nu C{=}O+\beta ND_2+\delta ND$
ν_9'	935	937	0.2	$S_8(19)$, $S_6(15)$, $S_{10}(14)$, $S_9(13)$	$\nu CN+\rho ND_2$
ν_{10}'	915	909	0.6	$S_{10}(45)$	ρND_2
ν_{11}'	—	853	—	$S_8(39)$, $S_6(14)$	ρND_2
ν_{12}'	653	664	1.9	$S_{14}(25)$, $S_{10}(18)$, $S_{15}(12)$	skel.
ν_{13}'	558	560	0.4	$S_{16}(50)$, $S_{13}(15)$, $S_{14}(13)$, $S_8(11)$	skel.
ν_{14}'	450	451	0.2	$S_{14}(34)$, $S_{15}(32)$	skel.
ν_{15}'	392	397	1.1	$S_{13}(39)$, $S_{16}(19)$	skel.
ν_{16}'	—	163	—	$S_{11}(72)$, $S_{15}(14)$	skel.

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

much different from each other, reflecting rather small difference between the two C=O bond lengths. These values correspond nearly to the average of the K(CO)'s for urea (6.49) and diacetamide (9.80). The values of the stretching constants for the CN bonds increase in the order $\mathrm{CN_I}<\mathrm{CN_{UC}}<\mathrm{CN_{UT}}$ as expected from the difference in the bond lengths. The $K(\mathrm{CN})_\mathrm{I}$ is similar to the $K(\mathrm{CN})_\mathrm{I}$ of diacetamide,[5] and the $K(\mathrm{CN})_\mathrm{UC}$ to the K(CN) of urea(5.24) and close to the K(CN) of acetamide(5.53).[18,19] The $K(\mathrm{CN})_\mathrm{UT}$ is close to that of *N*-methylformamide(6.15).[20] The values of H(NCN), F(NCN) and F(NCO) are comparable with those of urea. These results may be taken as indicating an excellent transferability of the Urey-Bradley force constants throughout a variety of urea and amide derivatives.

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[18] T. Uno, K. Machida and Y. Saito, This Bulletin, **42**, 897 (1969).

[19] I. Suzuki, *ibid.*, **35**, 1279 (1962).

[20] I. Suzuki, *ibid.*, **35**, 540 (1962).