

VIBRATIONAL SPECTRA, FORCE CONSTANTS AND MEAN AMPLITUDES OF VIBRATIONS OF UREA AND DEUTERATED UREA

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ABSTRACT

The vibrational spectra of urea and deuterated urea have been recorded. Using a most general potential function, the force constants and the mean amplitudes of vibration have been calculated.

INTRODUCTION

INFRA-RED studies of urea ($\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NH}_2$) have been carried out by Keller,¹ Waldron and Badger,² Stewart,³ Spinner⁴ and Yamaguchi *et al.*,⁵ Anantha-krishnan,⁶ Kohlauch and Pongratz,⁷ and Otvos and Edsell⁸ have recorded the Raman spectra. The work of Otvos and Edsell includes data on urea- d_4 in D_2O . Kellner⁹ has carried out a normal co-ordinate treatment of urea using a simple valence force field. Yamaguchi *et al.* have obtained the infra-red spectra of urea and urea- d_4 in the region $500\text{--}1700\text{ cm.}^{-1}$ They have calculated the normal modes of vibration using the Urey-Bradley type of potential function.

In the present investigation the infra-red spectra of urea and deuterated urea have been recorded in the region from $400\text{--}4000\text{ cm.}^{-1}$ The fundamental modes have been assigned. A normal co-ordinate treatment was carried out considering the molecule as a four-body problem with C_{2v} symmetry and using a general quadratic potential function. The mean amplitudes of stretching vibrations have also been evaluated.

EXPERIMENTAL

Deuterated urea was prepared by repeated recrystallization from D_2O and removing water under vacuum. In spite of a number of exchanges it was not possible to get a completely deuterated sample. A number of frequencies corresponding to partially deuterated species were also observed.

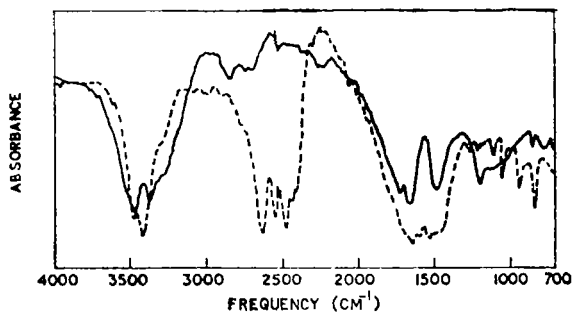


FIG. 1. Infra-red spectra of Urea (—) and deuterated urea (---) in KBr pellet.

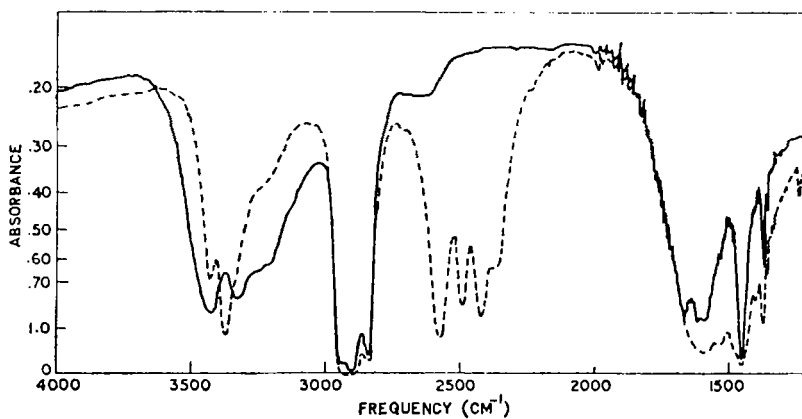


FIG. 2

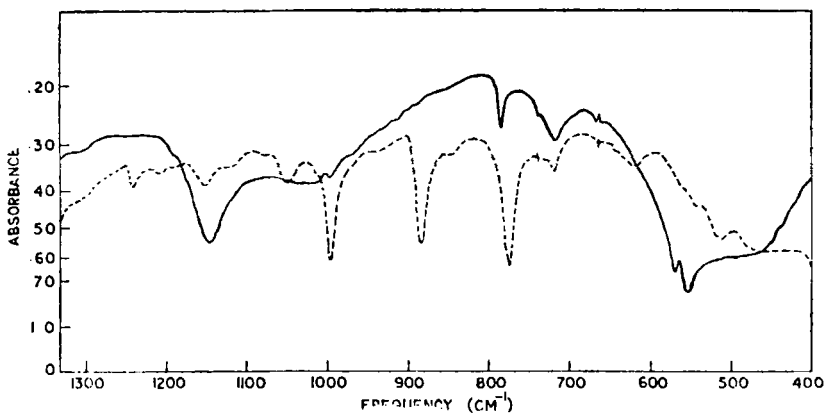


FIG. 3

FIGS. 2-3. Infra-red spectra of urea (—) and deuterated urea (---) in nujol mull.

The infra-red spectra were obtained with a Perkin-Elmer model 221 spectrophotometer in the region 700–4000 cm^{-1} and also on a Perkin-Elmer model 331 grating spectrophotometer in the region 400–4000 cm^{-1} . The solid samples were in the form of KBr pellets; the mull technique was also employed. The data for urea and deuterated urea, along with the assignments, are given in Table I. The spectra are shown in Figs. 1–3.

TABLE I
Vibrational frequency data for urea and deuterated urea (in cm^{-1})

Urea		Deuterated urea		Assignment
Mull	KBr pellet	Mull	KBr pellet	
3435 vs	3450 vs	—	—	NH ₂ asy. stretch
...	...	—	3390 vs	NHD stretch
3335 vs	3350 vs	—	...	NH ₂ sy. stretch
3260 sh	3260 sh	Combination
...	...	2585 vs	2590 vs	ND ₂ asy. stretch
...	...	2500 vs	2500 vs	NHD stretch
...	...	2430 vs	2440 vs	ND ₂ sy. stretch
..	...	2375 sh	2410 shb	combination
1675 vs	1678 vs	1675 vs	1675 vs	C = O stretch
1610 vs	1600 vs	—	—	NH ₂ in-plane bend
1460 s	1460 vs	1500 } vsb 1460 }	1500 } vsb 1460 }	N–C–N asy. stretch
...	—	1247 w	—	ND ₂ in-plane bend
...	—	1212 w	...	NHD in-plane bend
1150 s	1145 s	—	—	NH ₂ rock
...	...	1055 m	1050 w	NHD rock
1010 w	1000 w	1005 m	995 m	N–C–N sy. stretch
...	...	890 m	895 m	ND ₂ rock
790 m	785 m	778 m	775 m	CONN out-of-plane bend
720 w	710 m	...	720 m	NH ₂ wagging
575 w	..	550 w	..	N–C–N in-plane rock
560 w	..	520 w	...	N–C–N bend

w—weak, m—medium, s—strong, vs—very strong, b—broad, sh—shoulder.

Normal Co-ordinate Treatment

The well-known Wilson's^{9a} F-G matrix method and the theory of small vibrations developed by Morino *et al.*,¹² and Cyvin¹¹ are used to evaluate the force constants and the mean square amplitudes. The mean square amplitude of a normal vibration is given by

$$\langle Q_k^2 \rangle = \left(\frac{h}{8\pi^2 \nu_k} \right) \coth \left(\frac{h \nu_k}{2kT} \right) \quad (1)$$

where h is Planck's constant, k is Boltzmann's constant, T the absolute temperature and ν_k is the frequency of the k -th normal vibration. The mean square amplitude of a vibration for a given interatomic displacement r_i is given by

$$r_i^2 = \sum_k C_{ik}^2 Q_k^2$$

or in matrix notation

$$r = C Q \quad (2)$$

The evaluation of C involves the following transformations. The internal displacement co-ordinates are related to the symmetry co-ordination by the transformation

$$R = U r \quad (3)$$

The symmetry co-ordinates R are related to the normal co-ordinates Q by the transformation

$$R = L Q \quad (4)$$

Thus the transformation from internal displacement co-ordinates to normal co-ordinates is given by

$$\begin{aligned} r &= (U' L) Q \\ &= C Q \end{aligned}$$

Hence

$$C = U' L \quad (5)$$

where U' is the transpose of U .

The elements of the L matrix in (5) are determined by solving a set of homogeneous linear equations given by

$$(GF - \lambda_k E) L_k = 0 \quad (6)$$

where L is the k -th column of the L matrix, F the potential energy matrix involving the force constants, G is the inverse kinetic energy matrix involving the structural parameters and E is the unitary matrix.

The percentage potential energy distribution among the various symmetry co-ordinates for a given mode of vibration is given by¹² $(F_{ij}L_{ia}L_{ja}/\lambda_a) \times 100$. The diagonal elements which are much greater than the cross terms are given in Table (V).

If we treat NH_2 as a single mass point the molecule will have C_{2v} symmetry with the distribution $(3A_1 + 2B_1 + B_2)$. The symmetry co-ordinates for the A type are:

$$R_1 = \Delta D$$

$$R_2 = \frac{1}{\sqrt{2}} (\Delta d_1 + \Delta d_2)$$

$$R_3 = \frac{1}{\sqrt{6}} (2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2)$$

$$R_* = \frac{1}{\sqrt{3}} (\Delta\alpha + \Delta\beta_1 + \Delta\beta_2) \equiv 0 \dots\dots\dots \text{Redundant}$$

The symmetry coordinates for the B_1 type are:

$$R_4 = \frac{1}{\sqrt{2}} (\Delta d_1 - \Delta d_2)$$

$$R_5 = \frac{1}{\sqrt{2}} (\Delta\beta_1 - \Delta\beta_2)$$

The symmetry co-ordinate for the B_2 type is:

$$R_6 = \Delta\gamma$$

The various bond lengths and angles are shown in Fig. (4); $\Delta\gamma$ is the change in the angle between the plane NCN and the bond $C=O$.

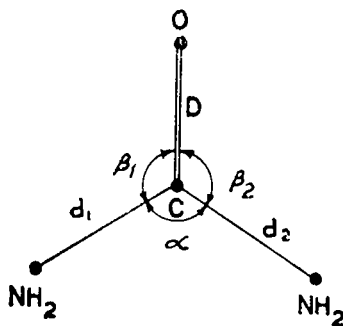


FIG. 4

The coefficients of the general quadratic potential function are given below.

	ΔD	Δd_1	Δd_2	$\Delta \alpha$	$\Delta \beta_1$	$\Delta \beta_2$
ΔD	f_D	f_D^d	f_D^d	f_D^α	f_D^β	f_D^β
Δd_1		f_d	f_d^d	f_d^α	f_d^β	$f'_d \alpha^\beta$
Δd_2			f_d	f_d^α	$f'_d \beta$	f_d^β
$\Delta \alpha$				f_α	f_α^β	f_α^β
$\Delta \beta_1$					f_β	J_β^β
$\Delta \beta_2$						f_β

where the various constants have the usual¹³ meaning; the primed constants represent interactions between a bond and angle not containing that bond.

The F-matrix formed by the coefficients of the potential function and the coefficients contained in the symmetry co-ordinates is given below.

$$\begin{vmatrix} F_{11} & F_{12} & F_{13} \\ & F_{22} & F_{23} \\ & & F_{33} \end{vmatrix} = \begin{vmatrix} J_d & \sqrt{2}f_D^d & \frac{\sqrt{2}}{3}(J_D^\alpha - f_D^\beta) \\ & f_d + f_d^d & \frac{1}{\sqrt{3}}(2f_d^\alpha - f_d^\beta - f'_d \alpha^\beta) \\ & & \frac{1}{3}(2f_\alpha + f_\beta + f_\beta^\beta - 4f_\alpha^\beta) \end{vmatrix} \text{ for } A_1 \text{ type}$$

The F-matrices for the B₁ and B₂ types are:

$$\begin{vmatrix} F_{44} & F_{45} \\ & F_{55} \end{vmatrix} = \begin{vmatrix} f_d - f_d^d & f_d^\beta - f'_d \alpha^\beta \\ & f_\beta - f_\beta^\beta \end{vmatrix} \text{ for } B_1 \text{ type}$$

$$F_{66} = J_\gamma$$

The elements of the G-matrices were evaluated with the help of the Decius¹⁴ Tables. The structural parameters are C = O = 1.26 Å, C - N = 1.34 Å. All the angles are taken as 120°.

The force constants used for evaluating the F-matrix are:

$$F_D = 10.200 \text{ md/Å.}, f_D^d = 1.500 \text{ md/rad.}, f_d = 1.500 \text{ md/rad.}^2$$

$$F_d = 6.350 \text{ md/Å.}, f_d^d = 1.150 \text{ md/rad.}, f_\beta = 1.300 \text{ md/rad.}^2$$

$$f_\gamma = 2.697 \text{ md/rad.}^2$$

TABLE II

Observed and calculated values of the fundamentals of urea and deuterated urea (cm.^{-1})

Type	Urea		<i>d</i> urea	
	Observed	Calculated	Observed	Calculated
A ₁	560	559	520	532
	1010	1021	1005	980
	1675	1663	1675	1660
B ₁	575	577	550	558
	1460	1440	(1460- 1500)	1422
B ₂	790	790	789	789

TABLE III

L-matrix elements for urea and deuterated *u*

	Q ₁	Q ₂	Q ₃	Q ₄	Q ₅	Q ₆
R ₁	1.28870 (1.29210)	-0.25997 (-0.24944)	-0.14885 (-0.13724)	0	0	0
R ₂	-0.69704 (-0.68226)	-0.85031 (-0.81148)	0.20219 (0.20506)	0	0	0
R ₃	1.46181 (1.44643)	0.48085 (0.53156)	1.17917 (1.11542)	0	0	0
R ₄	0	0	0	-1.46305 (-1.43500)	0.33014 (0.32652)	0
R ₅	0	0	0	1.64523 (1.66497)	1.17432 (1.12568)	0
R ₆	0	0	0	0	0	1.27900 (1.27710)

Values for deuterated urea are given in parenthesis.

TABLE IV
Mean amplitudes of vibration for urea and deuterated urea (A)

Type	Urea		<i>d</i> urea	
	T=0° K.	T=298° K.	T=0° K.	T=298° K.
C=O	0.03936	0.03949	0.03936	0.03951
C—N	0.04392	0.04432	0.04327	0.04372

TABLE V
(0/0) Potential energy distribution among symmetry co-ordinates

	Q ₁	Q ₂	Q ₃	Q ₄	Q ₅	Q ₆
S ₁	86.71 (87.33)	9.38 (9.30)	10.2 (9.6)	0	0	0
S ₂	18.6 (17.9)	73.8 (72.6)	18.45 (20.97)	0	0	0
S ₄	0	0	0	76.0 (74.8)	24.0 (25.2)	0
S ₅	0	0	0	24.0 (25.2)	76.0 (74.8)	0
S ₆	0	0	0	0	0	70.5 (70.5)

Values in parentheses refer to deuterated urea.

The rest of the constants are zeros. The frequencies are compared in Table II for both urea and deuterated urea. The values of the L matrices, mean amplitudes and the potential energy distribution are given in Tables III, IV and V respectively.

Assignments

When NH₂ is considered as a single mass unit, the urea molecule has C_{2v} symmetry with the fundamental frequencies distributed as (3A₁ + 2B₁ + B₂). All are active in Raman and infra-red.

The three A_1 vibrations are the C = O stretching, the symmetric NCN stretching and the NCN in-plane bending mode. The C = O stretching mode is observed in the infra-red spectrum at 1675 cm.^{-1} . The symmetric NCN stretching is assigned to a band at 1010 cm.^{-1} in the infra-red spectra. This corresponds to an intense line in the Raman spectrum at 1015 cm.^{-1} . The third is the NCN in-plane bending mode at 560 cm.^{-1} . The two B_1 vibrations are the NCN asymmetric stretching mode at 1460 cm.^{-1} and the in-plane rocking mode at 575 cm.^{-1} . The B_2 vibration is the out-of-plane CONN bending mode observed at 789 cm.^{-1} . The corresponding frequencies for *d* urea and the calculated values are shown in Table II. It is seen that the asymmetric stretching frequency shifts towards higher frequency on deuteration. But the exact position is difficult to locate. This is because in the spectrum of the deuterated species a broad band is observed extending from 1460 cm.^{-1} to 1500 cm.^{-1} due to the presence of a number of frequencies belonging to the groups NH_2 , ND_2 and NDH . This is similar to the effect observed in oxamide¹⁵ and is attributed to the different amount of coupling between NCN stretching and ND_2 in-plane bending as compared to the coupling between NCN asymmetric stretching and ND_2 in-plane bending modes.

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