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Vibrational spectra of nucleic acid constituents—I
Planar vibrations of uracil

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Abstract—Laser-Raman spectra and i.r. spectra of polycrystalline uracil, N,N-dideutero uracil, C,C-dideutero uracil, and perdeutero uracil have been obtained. The i.r. absorption bands and Raman lines are assigned to fundamental modes by a comparison of the spectra of four isotopically substituted analogs. A normal coordinate calculation has been carried out for the planar modes. A 23 parameter valence force field is proposed which reproduces 83 observed frequencies with an average error of 0.76% (*ca.* 8 cm^{-1}). The planar modes are described in terms of potential energy distribution and Cartesian displacements.

INTRODUCTION

THE INFRARED [1, 2] and Raman [3] spectra of various nucleic acid constituents, including uracil, have been reported in some detail. Because of the high complexity and low symmetry of these molecules no detailed band assignments or normal coordinate calculations have been possible. Some recent developments have made attempts to carry out such calculations more feasible. A considerable body of empirical information on force constants and their transferability in moderately complex molecules has been developed over the past years [4–7]. Detailed relationships have been proposed between some bond lengths and corresponding bond stretching force constants [8, 9]. It has been possible to prepare deuterated analogs which substantially facilitate the determination of force constants and thus permit a better understanding of the vibrational motions giving rise to observed absorption bands and Raman shifts.

The present communication describes the Raman and i.r. spectra of uracil and three deuterated analogs. Band assignments are carried out on the basis of deuteration shifts and a normal coordinate analysis of the planar vibrations. Skeletal stretching force constants are evaluated with the help of bond length correlations [8–10]. A valence-type force field with five transferred and eighteen variable force constants was adjusted to obtain a least squares fit for 83 observed frequencies. The nature of the planar vibrations is discussed in terms of Cartesian displacements and the potential energy distribution.

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STRUCTURAL CONSIDERATIONS

Crystalline uracil belongs to the space group $C_{2h}^5 - P2_{1/a}$ with four molecules of C_s point symmetry per unit cell [11]. The four molecules are arranged into two hydrogen bonded dimers (site symmetry C_i) parallel to (001). There are two NH to C=O hydrogen bonds between the molecules of one dimer, and additional hydrogen bonds between the dimers. In principle, molecular a' and a'' modes split into A_g, B_u, A_u, and B_g crystal modes [12]. The *ungerade* modes are i.r. active, the *gerade* modes Raman active. Raman and i.r. frequencies do not coincide. Coupling between molecular modes within one dimer is expected to be stronger than coupling between dimers; coupling between modes associated with hydrogen bonding is expected to be stronger than intermolecular coupling between other modes. In practice, the splitting between the different branches of molecular modes is expected to be small [3]. In this communication, the vibrations are analyzed on the basis of molecular C_s symmetry and the modes are classified as in-plane (*ip*) and out-of-plane (*op*). The observed Raman lines belong to the crystal species A_g and B_g, the i.r. bands to B_u and A_u.

EXPERIMENTAL

Uracil was obtained from the Cyclo Chemical Corporation* and used after recrystallization from water. N,N-dideutero uracil was prepared by recrystallization of a small amount of uracil from D_2O. The process was repeated until no NH bands were observed in the i.r. spectrum of the product. Perdeutero uracil was prepared from perdeutero cyanoacetyl urea by catalytic reduction with deuterium. Details will be given elsewhere. C,C-dideutero uracil was prepared from the perdeutero compound by repeated recrystallization from H_2O. No isotopic impurities could be detected by i.r. methods in any of the deuterated uracil analogs.

Infrared spectra were obtained with a Beckman Model IR-7 spectrometer. Mineral oil (Nujol) mulls were used for most of the spectral region, halocarbon mulls for regions where Nujol absorbs (3200–2800 cm^{-1} and 1500–1300 cm^{-1}). Raman spectra were obtained at the University of Pittsburgh with a Spex Industries Ramalog system equipped with a Carson Laboratories Argon–Ion laser, and an attachment for solid polycrystalline microsamples. The Raman data were obtained with the Argon 4880 Å line as excitation.

Numerical computations were carried out on a Univac 1107 computer (Bluebell, Pa.) and an in-house IBM 1130 computer with previously used FORTRAN programs [10].

ASSIGNMENTS

The Raman spectra of crystalline uracil and three deuterated analogs are presented in Fig. 1, the i.r. spectra in Fig. 2. Assignments and calculated frequencies (see below) for the planar modes are summarized in Tables 1–4, tentative assignments

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* Mention of commercial items is for your convenience and does not constitute an endorsement of this over similar products by the U.S. Department of Agriculture.

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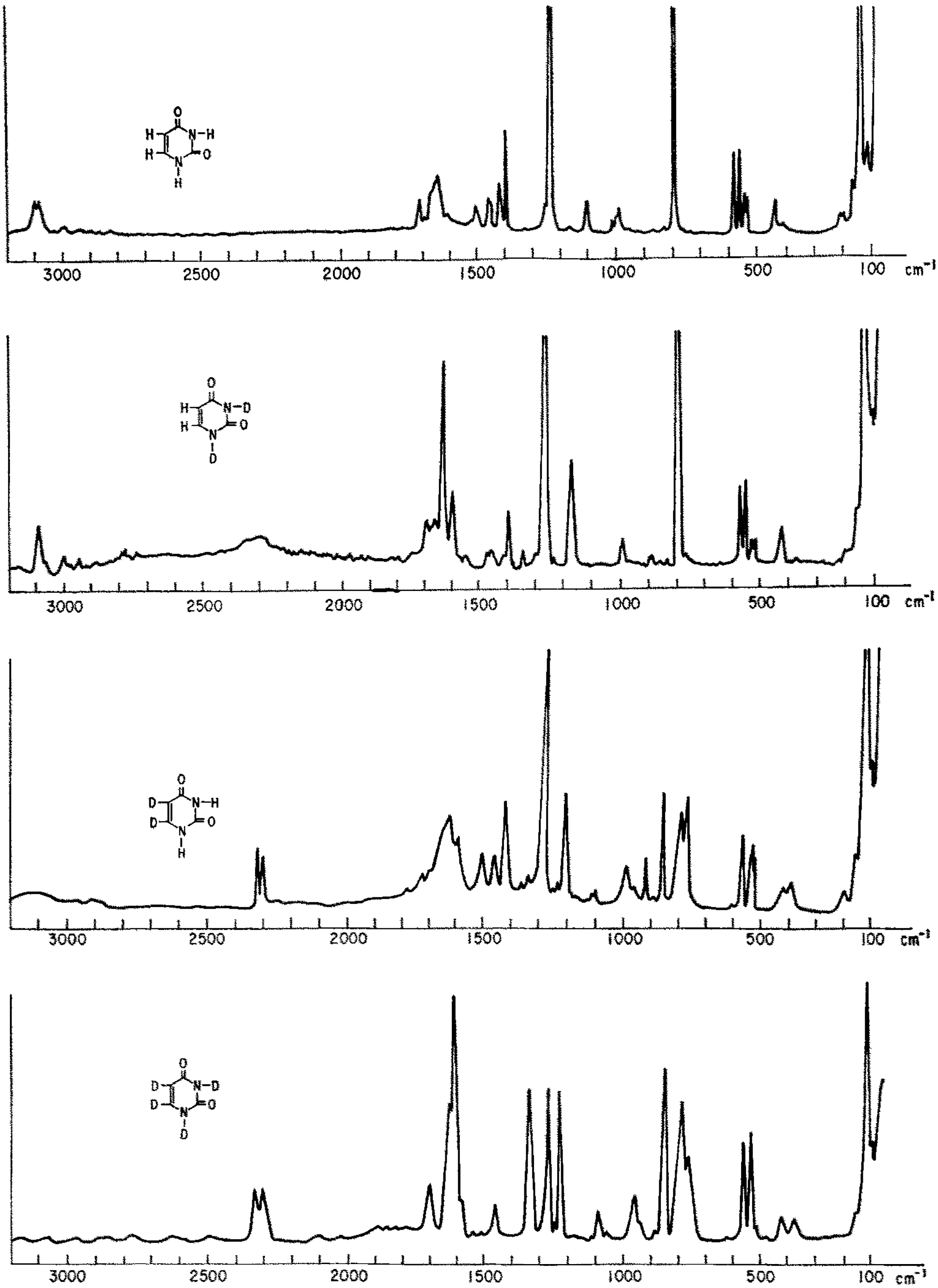

Fig. 1. Raman spectra of polycrystalline uracil, N,N-dideutero uracil, C,C-dideutero uracil, and perdeutero uracil.

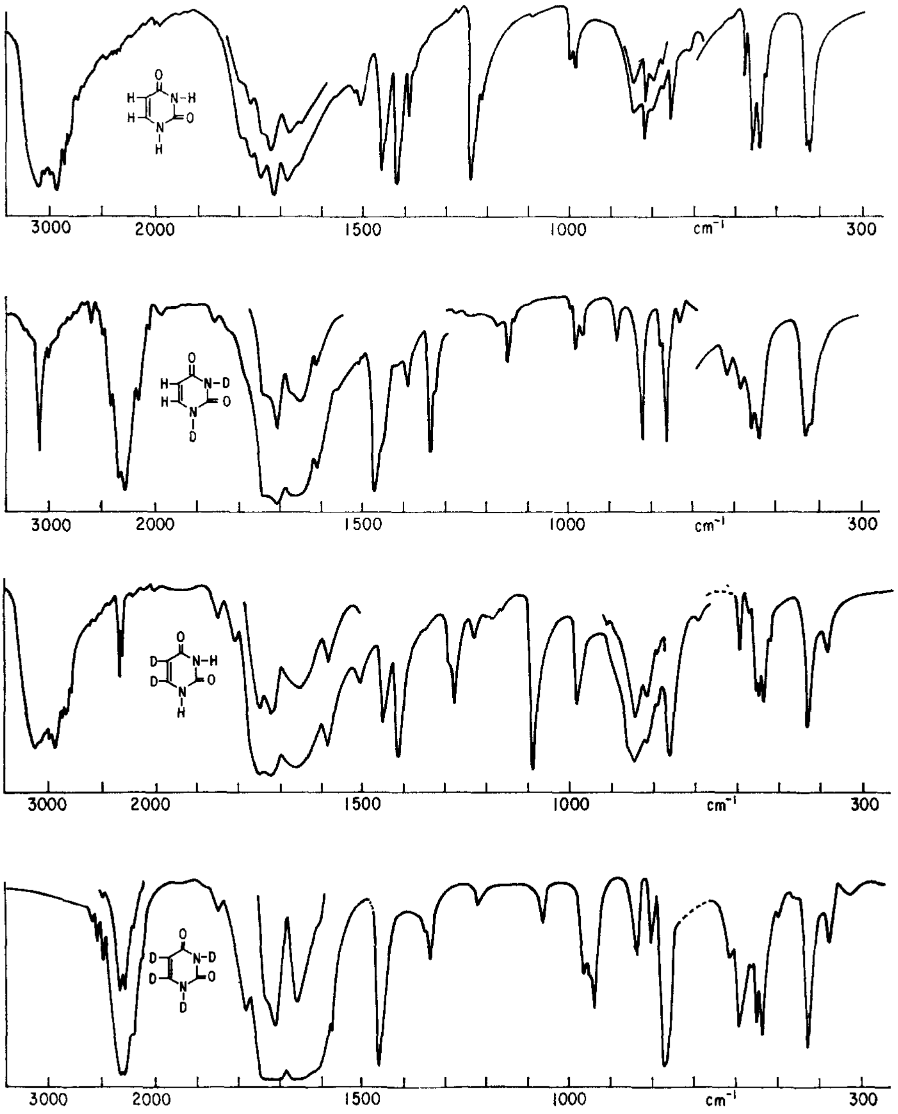

Fig. 2. Infrared spectra of polycrystalline uracil, N,N-dideutero uracil, C,C-dideutero uracil, and perdeutero uracil.

for some out-of-plane modes in Table 5. Different regions of the spectra and qualitative arguments regarding the proposed assignments are discussed below.

3300–2000 *cm*$^{-1}$. CH, CD, NH, ND *stretching modes*

CH and CD stretching modes are clean in all Raman spectra and in the i.r. spectra of N,N-dideutero and C,C-dideutero uracil (no overlapping with NH or ND). The two CH stretching modes of the N,N-dideutero compound are not resolved in the i.r. spectra or the Raman effect. The NH and ND stretching modes

Table 1. Observed and calculated in-plane fundamentals of uracil (cm^{-1})

	I.r.	Raman	Calc.	Assignment*	Designation
1	3160 m†	3130(0.1)†	3134	νNH in-phase (99)	
2	3160 m†	3130(0.1)†	3131	νNH out-of-phase (99)	
3	3100 s†	3100(1.0)	3100	νCH in-phase (98)	
4	3080 s†	3085(1.0)	3092	νCH out-of-phase (99)	
5	1716 s‡	1662(1.4)‡	1684	$\nu C_{(2)} = 0$ (74)	U(I)
6	1675 s‡	1648(2.0)‡	1653	$\nu C_{(4)} = 0$, νC═C in phase (68)	U(II)
7	—	1611(0.4)	1605	$\nu C_{(4)} = 0$, νC═C out-of-phase (75)	U(III)
8	1508 m	1507(0.8)	1504	$\delta NH_{(1)}$ (63)	
9	1453 s	1462(1.0)	1465	ν-ring (61)	U(IV)
10	1417 s	1422(1.5)	1424	$\delta NH_{(3)}$ (66)	
11	1390 m	1398(3.4)	1397	δCH in-phase (62)	
12	1238 s	1236(10)	1248	ν-ring (86)	U(V)
13	1217 w	—	1211	δCH out-of-phase (77)	
14	1099 w	1104(1.0)	1125	ν-ring (83)	U(VI)
15	1003 m	1010(0.4)	1028	ν-ring (57)	U(VII)
16	993 m	988(0.8)	980	ν,δ-ring (77)	U(VIII)
17	781 w	792(10)	801	ν,δ-ring (58)	U(IX)
18	585 m	579(2.5)	576	δ-ring (63)	U(X)
19	565 m	558(2.6)	564	δC═O in-phase (77)	U(XI)
20	550 s	540(1.3)	536	δ-ring (63)	U(XII)
21	—	398(0.2)	384	δC═O out-of-phase (72)	U(XIII)

* ν—stretching mode; δ—bending mode; numbers in parentheses refer to the potential energy distribution; s, m, w—strong, medium, weak.

† Center of broad or ill-defined band.

‡ The midpoint between Raman and i.r. frequencies was used for calculations.

Table 2. Observed and calculated in-plane fundamentals of N,N-dideutero uracil

	I.r.	Raman	Calc.	Assignment*	Designation
1	3087 m	3091(2)	3100	νCH in-phase (99)	
2	3087 m	3091(2)	3092	νCH out-of-phase (99)	
3	2330 s	2340(0.3)†	2315	νND in-phase (96)	
4	2277 s	2290(0.4)†	2309	νND out-of-phase (96)	
5	1704 s‡	1661(1.4)‡	1678	$\nu C{=}O_{(4)}$ (75)	U(I)
6	1650 s‡	1630(8.3)‡	1645	$\nu C{=}O_{(2)}$, νC═C in-phase (71)	U(II)
7	1609 w	1597(2.8)	1591	$\nu C{=}O_{(2)}$, νC═C out-of-phase (80)	U(III)
8	1471 s	1470(0.2)	1468	ν-ring (78)	U(IV)
9	1391 w	1397(2.3)	1396	δCH in-phase (59)	
10	1340 m	1343(0.7)	1313	ν-ring (45), δCH (21), δND (21)	
11	—	1258(10)	1237	ν-ring (83)	U(V)
12	1165 w	1167(4)	1181	ν-ring (46), δND (27), δCH (25)	
13	1143 m	—	1155	δND (36), δCH (29)	
14	981 m	987(1.1)	998	δND (41), ν-ring (30)	
15	965 m	969(0.2)	944	ν,δ-ring (62)	U(VIII)
16	883 m	886(0.6)	890	δND (51)	
17	778 w	789(15)	800	ν,δ-ring (55)	U(IX)
18	560 m	569(3.3)	568	δ-ring (60)	U(X)
19	542 m	552(3.6)	549	δC═O in-phase (74)	U(XI)
20	—	533(0.8)	535	δ-ring (63)	U(XII)
21	—	—	383	δC═O in-phase (72)	U(XIII)

*, †, ‡ As in Table 1.

are very weak and shallow in the Raman effect. In the i.r. spectra these modes result in a cluster of bands—evidently caused by Fermi resonance—and overlap with CH or CD stretching bands. The values listed in Tables 1–4 for NH and ND stretching frequencies represent the centers of weak and very broad Raman lines and the best consistent choice of i.r. absorption maxima.

Table 3. Observed and calculated in-plane fundamentals of C,C-dideutero uracil

	I.r.	Raman	Calc.	Assignment*	Designation
1	3120 s†	3130(0.4)†	3134	νNH in-phase (99)	
2	3120 s†	3130(0.4)†	3131	νNH out-of-phase (99)	
3	2315 m	2318(2)	2319	νCD in-phase (92)	
4	2294 m	2298(1.4)	2289	νCD out-of-phase (97)	
5	1715 s‡	1645(sh)‡	1683	νC=O$_{(2)}$ (74)	U(I)
6	1650 s‡	1624(2.6)‡	1686	νC=O$_{(4)}$, νC=C in-phase (67)	U(II)
7	1582 m	1586(1.2)	1588	νC=O$_{(4)}$, νC=C out-of-phase (75)	U(III)
8	1503 w	1499(1.2)	1500	δNH$_{(1)}$ (69)	
9	1450 m	1456(1.0)	1459	ν-ring (69)	U(IV)
10	1413 s	1416(3.3)	1418	δNH$_{(3)}$ (72)	
11	1279 m	1279(10)	1287	ν-ring (86)	U(V)
12	—	1203(4.3)	1208	ν-ring (84)	
13	1091 s	1089(0.4)	1094	ν-ring (61)	
14	988 m	982(1.2)	979	ν,δ-ring (72)	U(VIII)
15	910 w	912(1.9)	891	δCD in-phase (55)	
16	843 s	851(4.6)	851	δCD out-of-phase (83)	
17	796 w	791(4.0)	786	ν,δ-ring (55)	U(IX)
18	575 w	567(3.3)	573	δ-ring (63)	U(X)
19	551 s	539(2.4)	545	δC=O in-phase (70)	U(XI)
20	538 w	525(2.4)	525	δ-ring (62)	U(XII)
21	386 m	390(1.0)	383	δC=O out-of-phase (72)	U(XIII)

*, †, ‡ As in Table 1.

Table 4. Observed and calculated in-plane fundamentals of perdeutero uracil

	I.r.	Raman	Calc.	Assignment*	Designation
1	2326 sh	2326(2)	2321	νCD in-phase (73)	
2	2316 s	—	2315	νND in-phase (82)	
3	2306 sh†	—	2308	νND out-of-phase (90)	
4	2277 s	2302(2)	2289	νCD out-of-phase (96)	
5	1708 s‡	1618(6)‡	1676	νC=O$_{(2)}$ (76)	U(I)
6	1654 s‡	1602(10)‡	1626	νC=O$_{(4)}$, νC=C in-phase (70)	U(II)
7	1571 w	1577 (sh)	1576	νC=O$_{(4)}$, νC=C out-of-phase (77)	U(III)
8	1457 s	1448(1.3)	1456	ν-ring (81)	U(IV)
9	1331 w	1331(5)	1323	ν-ring (68)	
10	—	1261(6)	1237	ν-ring (40), δND (26), δCD (18)	
11	1221 w	1224(7)	1213	ν-ring (92)	U(V)
12	1064 w	1082(1)	1091	δND in-phase (66)	
13	965 m	952(2)	959	ν,δ-ring (61)	U(VIII)
14	938 s	—	908	δND (46), ν-ring (37)	
15	838 m	848(6)	860	δCD out-of-phase (68)	
16	805 m	805(3)	834	δCD (49), δND (16)	
17	772 s	784(5)	785	ν,δ-ring (53)	U(IX)
18	552 s	561(4)	565	δ-ring (64)	U(X)
19	536 s	534(4)	534	δC=O in-phase (68)	U(XI)
20	—	516(1)	522	δ-ring (60)	U(XII)
21	380 w	387(1)	381	δC=O out-of-phase (71)	U(XIII)

*, †, ‡ As in Table 1.

1750–1550 *cm*$^{-1}$. *Double bond stretching modes*

The i.r. and Raman spectra exhibit complex patterns in this region where three double bond stretching modes, and the overtones and combinations of out-of-plane NH deformation modes are expected. The picture is further complicated by Fermi resonance. It has been suggested [2] that NH in-plane bending modes also absorb in this region, but this is unlikely by general considerations [3] and inconsistent with the spectra of deuterated analogs. In the i.r. spectra the two strongest bands for each analog (1715–1704 and 1681–1648 cm^{-1}) were assumed to be primarily associated with C=O stretching fundamentals. In the Raman spectra corresponding lines

Table 5. Observed out-of-plane modes and lattice modes

Uracil	N,N-dideutero uracil	C,C-dideutero uracil	Perdeutero uracil	$\frac{\nu(H)}{\nu(D)}$	Assignment*	
851 m	621 w	857 sh	622 w	1.37	γNH(ND)	I.r.
867(0.1)	—	—	—			R.
822 s	821 m	598 m	595 m	1.38	γCH(CD)	I.r.
830(0.3)	829(0.3)	602(0.2)	—			R.
807 m	584 w	815 sh	(580 sh)	1.39	γNH(ND)	I.r.
—	—	—	—			R.
760 s	762 m	559 m	552 m	1.38	γCH(CD)	I.r.
—	—	—	—			R.
(782 vw)	(778 w)	764 s	770 s		skel.	I.r.
771(0.1)	—	767(4.8)	761(3.2)			R.
530 w	—	527 w	—		skel.	I.r.
531(1)	521(1)	525(2.4)	—			R.
$\left.\begin{matrix}435\\427\end{matrix}\right\}$ s	$\left.\begin{matrix}431\\421\end{matrix}\right\}$ s	433 s	429 s		skel.	I.r.
431(1)	424(1.4)	416(0.6)	415(0.4)			R.
124(9)	121 $\sim$ (18)	115 $\sim$ (20)	114 $\sim$ (20)		lattice	R.
98(1.5)	95 $\sim$ (0.7)	94 $\sim$ (1)	93 $\sim$ (1)		lattice	R.
70(18)	60 $\sim$ (10)	$\sim$60 $\sim$ (10)	$\sim$60 $\sim$ (16)		lattice	R.

* γ—Out-of-plane bending.

are observed at somewhat lower frequencies (1662–1618 and 1648–1602 cm^{-1}). The relatively large frequency differences between the Raman and i.r. frequencies must be associated with strong intermolecular coupling through hydrogen bonding. A quite similar effect is observed in dimers of carboxylic acids. The mean values of Raman and i.r. frequencies were used for normal coordinate calculations. (No better approximation appears possible until more is known about the intermolecular force field.) For other modes the discrepancy between i.r. and Raman frequencies was small and the latter were used for calculations. The third double bond stretching mode occurs as a weak-to-medium intensity band at 1611–1575 cm^{-1}.

1550–1350 *cm^{-1}*. CH *and* NH *in-plane deformations*

Uracil shows four bands in this region, C,C-dideutero uracil three bands, N,N-dideutero uracil two, and the perdeutero compound a single band. A detailed comparison of all obtained spectra leads to the conclusion that the bands at 1508–1499 cm^{-1} and 1422–1413 cm^{-1} are essentially caused by NH bending modes, the band at 1398–1390 cm^{-1} by a CH bending mode, and the band at 1470–1448 cm^{-1} by a skeletal mode. The second CH bending mode is difficult to locate. In *cis* olefins it is found around 1260 cm^{-1} [13]. Calculations suggest that in uracil it occurs around 1210 cm^{-1}.

1350–700 *cm^{-1}*. *Skeletal modes.* CH, CD, ND *deformations*

Five Raman lines, two of them very intense (1236, 792 cm^{-1}) are observed in the spectrum of uracil between 790–1300 cm^{-1}, and are assigned to skeletal stretching and "stretch–bend" modes. The corresponding i.r. bands are considerably weaker, except the 1238 cm^{-1} band of uracil. Four i.r. bands between 860–750 cm^{-1} are assigned to out-of-plane NH and CH deformations, as suggested by ANGELL [1].

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(The corresponding Raman lines are very weak.) The latter assignments are confirmed by the i.r. spectra of deuterated analogs. In-plane CD and ND deformation modes in deuterated analogs are evidently strongly coupled with skeletal vibrations; no detailed description is possible on the basis of observed frequenies alone. Eight bands in the spectra of the N,N-dideutero compound (one CH, two ND, five skeletal modes), seven bands in the spectra of the C,C-dideutero compound (two ND, five skeletal modes) and nine bands in the spectra of the perdeutero compound in this frequency range are assigned to mixed planar vibrations. The pattern is in reasonably good agreement with the results of calculations reported further below. A band between 761–782 cm^{-1} is assigned to an out-of-plane skeletal mode.

Frequencies below 700 *cm*$^{-1}$

A cluster of four bands is observed in the i.r. and the Raman spectrum of uracil between 600–530 cm^{-1}. They are assigned to one out-of-plane and three in-plane skeletal deformation modes. (Single crystal studies of 1-methyl thymine suggest out-of-plane ring modes around 530 and around 455 cm^{-1} [14].) In deuterated analogs ND and CD out-of-plane deformations are crowded into the same region. They can be identified by an almost ideal frequency shift ($\nu(H)/\nu(D) = 1.38 \pm 0.01$) and the broad shape of the i.r. branch of NH and ND bending modes. A band in the 415–435 cm^{-1} region is assigned to the third out-of-plane ring deformation [14] and a weak band around 400 cm^{-1} to the lowest in-plane mode. Below 125 cm^{-1} one weak and two very strong Raman lines are observed in all analogs. They are in a region where lattice modes associated with $C{=}O\cdots\cdots H{-}N$ hydrogen bonds are expected [15].

The frequencies associated with out-of-plane modes and lattice modes are summarized in Table 5. Unfortunately, the obtained data provide no concise picture regarding the skeletal out-of-plane modes.

FORCE CONSTANTS

Four isotopic species and a total of 83 experimental frequencies were available for normal coordinate calculations of the planar modes. Nevertheless, it did not appear to be possible to obtain a reasonable potential energy force field by the usual iterative methods [4, 16] without assigning fixed values to a number of force constants. Various sets of transferred Urey–Bradley force constants were used in initial zero order trial calculations. No calculated frequencies and potential energy distributions [17] could be obtained which would agree with the assignments discussed in the previous section, in particular with the assignments of CH and NH deformation modes which can be made with confidence by comparing the spectra of uracil and its deuterated analogs.

Over the past years, detailed correlations have been proposed between some bond stretching force constants and bond lengths [8, 9]. The correlations have been successfully applied to molecules of moderate complexity; in favorable instances, they permit calculation of interaction force constants which can otherwise not be

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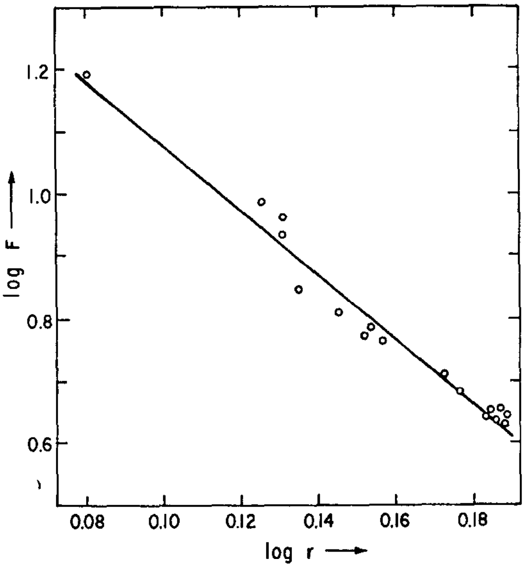

Fig. 3. Relation between stretching force constant and interatomic distance for CC bonds.

obtained [10]. The relationship used by LADD *et al.* [8] for CO bonds and by DECIUS [9] for NN bonds has the form:

$$F = ar^{-b}$$

or

$$\log F = -b \log r + \log a$$

where r is the equilibrium bond length, a and b are constants characteristic for a particular type of bond. For CO bonds, $a = 35.5$, $b = 5.79$ [8]. For CC and CN bonds we estimated a and b by least squares calculations using literature data for bond distances and force constants [4–6, 18–26]. A plot of $\log F$ vs. $\log r$ for CC bonds is shown in Fig. 3. It leads to $a(\text{CC}) = 40.1$, $b(\text{CC}) = 5.21$. For CN bonds the following values were obtained: $a(\text{CN}) = 43.2$, $b(\text{CN}) = 6.09$.

A valence force field (VFF) for uracil was constructed in the following manner:

(a) Skeletal stretching force constants for CO, CC, and CN bonds were estimated by the described procedure.

(b) Bending force constants were transferred from acetone [5], *cis* olefins [18], and *n*-methyl acetamide [27]; the two bending constants on either side of an outer atom were assumed to be equal.

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(c) In general, only stretch–stretch interaction constants (one common atom) and stretch–bend interaction constants (two common atoms) were assumed to have nonzero values. (These are the VFF interaction terms resulting from a Urey–Bradley force field with *gem* interactions [16].)

(d) The following exceptions were made in the scheme (c) for interaction constants: (i) interactions involving CH or NH stretching modes could not be determined and were set equal to zero; (ii) *meta* and *para* ring stretch–stretch interactions were added; (iii) a C=C, C=O stretch–stretch interaction was added for the conjugated double bonds to obtain a reasonable frequency fit in the double bond region.

A zero order calculation with force constant values transferred from molecules listed under (b), and benzene [28], reproduced the experimental frequencies within acceptable limits and lead to a reasonable potential energy distribution.

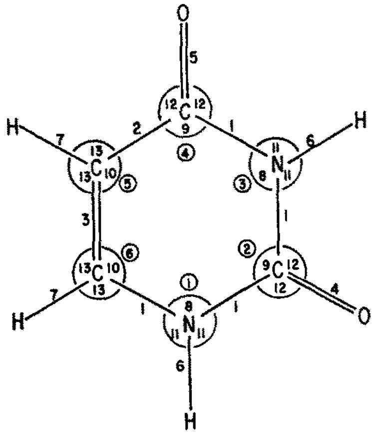

Fig. 4. Numbering of ring atoms and diagonal force constants.

Subsequently, the bending and interaction force constants as well as the NH and CH stretching constants were refined by iteration [4, 16] while the skeletal stretching constants were not varied. The refinement was based on Raman frequencies, except for modes which were not observed in the Raman effect and the CO stretching modes (cf. Assignments). A rapid convergence was obtained. The nomenclature of diagonal force constants is given in Fig. 4, the final values and dispersions of the refined constants in Table 6, calculated frequencies in the fourth column of Tables 1–4. The average error for 83 frequencies was 7.6 cm^{-1} (*ca.* 0.8%).

The described potential energy force field is admittedly constrained, redundant and, to a degree, arbitrary. On the other hand, it does reproduce the observed frequencies with fair accuracy, leads to a reasonable potential energy distribution, makes maximum use of transferred force constants, and possesses a certain degree of internal logic. For molecules of this size and no symmetry except the molecular plane, it appears that such a model offers the only way to obtain some insight regarding the nature of the normal vibrations.

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[28] J. R. Scherer, *Spectrochim. Acta* **20**, 345 (1964).

Table 6. Valence force constants

Description*	Value†	Dispersion	Description	Value	Dispersion
$F(1)$	6.38	—	$f(\nu, \nu\ ortho)$	0.896	0.058
$F(2)$	6.202	—	$f(\nu, \nu\ meta)$	−0.204	0.066
$F(3)$	8.702	—	$f(\nu, \nu\ para)$	0.511	0.077
$F(4)$	11.000	—	$f(\nu_{\mathrm{C=O}}, \nu_{\mathrm{ring}})$	1.397	0.260
$F(5)$	10.500	—	$f(\nu_{\mathrm{C=O(4)}}, \nu_{\mathrm{C=C}})$	−0.225	0.113
$F(6)$	5.397	0.018	$f(\delta_{\mathrm{ring}}, \nu_{\mathrm{ring}})$	0.295	0.059
$F(7)$	5.204	0.018	$f(\delta_{\mathrm{C=O}}, \nu_{\mathrm{ring}})$	0.304	0.065
$F(8)$	1.166	0.234	$f(\delta_{\mathrm{NH}}, \nu_{\mathrm{ring}})$	0.222	0.015
$F(9)$	1.620	0.421	$f(\delta_{\mathrm{CH}}, \nu_{\mathrm{ring}})$	0.253	0.028
$F(10)$	0.539	0.098	$f(\delta_{\mathrm{C=O}}, \nu_{\mathrm{C=O}})$	0.857	0.246
$F(11)$	0.417	0.005			
$F(12)$	1.034	0.035			
$F(13)$	0.403	0.006			

* See Fig. 4.

† Stretching force constants: mdyn/Å; bending force constants: mdyn Å/rad^2; stretch bend interactions: mdyn/rad.

POTENTIAL ENERGY DISTRIBUTION. CHARACTERISTIC URACIL MODES

The predominant term(s) in the potential energy distribution (PED) [17] of each vibrational mode are given in parentheses in the fifth column of Tables 1–4. For modes which necessarily involve more than one internal displacement coordinate, the figure represents the sum of the fractions of potential energy associated with the primarily involved force constants, i.e. for ring stretching modes, the sum over all six stretching terms; for ring bending modes, the sum over all six bending terms. In this way, it is possible to classify the vibrations in a general way, but it is not possible to determine the form of the vibration from PED data alone. The same is true for mixed modes involving, for instance, CD bending, ND bending, and skeletal motions of the ring (cf. Tables 2 and 4).

NH, ND, CH, and CD stretching modes are essentially pure in all studied uracil analogs. The descriptions "in-phase" and "out-of-phase" (Tables 1–4) are based on calculated Cartesian displacements (see below). Table 1 indicates that for non-deuterated uracil most fundamentals can be classified as group vibrations by PED criteria. In view of earlier discussions and assignments of the spectra of uracil and related molecules [1–3], it is interesting to note that the NH and CH bending modes are reasonably well identified and the NH bending contribution to C=C and/or C=O stretching modes is relatively small (7% for ν_5, 6% for ν_6, 14% for ν_7). To permit a comparison with the spectra of deuterated analogs and with uracil derivatives, the 13 planar skeletal modes are labeled U I to U XIII in decreasing order of frequency, and in analogy with a similar nomenclature used for secondary amides and polypeptides [29, 30].

In deuterated analogs the identity of ND and CD bending modes is to a large

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[29] T. MIYAZAWA, T. SHIMANOUCHI and S. MIZUSHIMA, *J. Chem. Phys.* **29**, 611 (1958).

[30] T. MIYAZAWA, in *Polyamino Acids, Polypeptides, and Proteins*, (Edited by M. R. STAHMANN). Univ. of Wisconsin Press, Madison (1962).

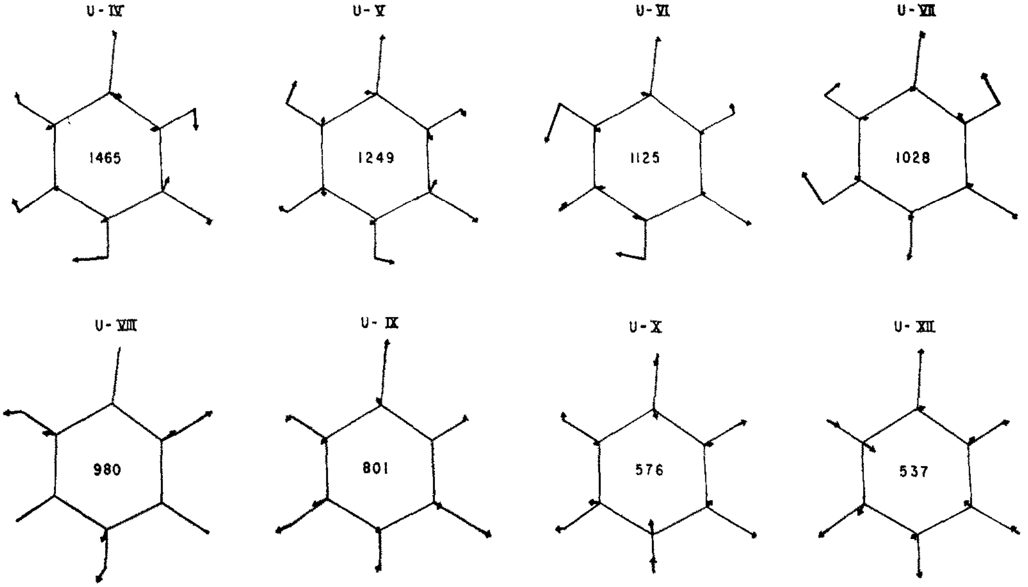

Fig. 5. Cartesian displacements for some planar ring modes of uracil. (Position of ring as in Fig. 4.)

degree lost. The unperturbed vibrations would be expected around 1100–1000 cm^{-1}, close to the U VI and U VII modes. Indeed, the U VI and U VII modes cannot be identified as such in any of the deuterated derivatives; instead, mixed modes are observed which in the perdeutero molecule fall into the broad range of 1331–805 cm^{-1}. The U I to U V and U VIII to U XIII modes nevertheless retain their essential characteristics, particularly if judged by Cartesian displacements.

CARTESIAN DISPLACEMENTS

The Cartesian displacements for the U IV to U X modes and the U XII mode of uracil are shown in Fig. 5. The nature of the remaining modes can be deduced from the potential energy distribution and qualitative statements based on the Cartesian displacements (cf. Tables 1–4). The displacements are drawn to the same scale as the equilibrium geometry and represent twice the unit changes in the normal coordinates.

It is interesting to observe that many skeletal ring modes retain a certain resemblance to the pseudo normal modes of a hypothetical C_6 ring [31] and the skeletal modes of benzene [32], although the uracil ring has no symmetry within the molecular plane. The A_{1g} breathing mode of a C_6 ring is an exception, i.e. no similar vibration is observed in uracil. Because of the loss of symmetry the comparisons are of course somewhat approximate and the parallelism in the designations "stretching" and "bending" does not hold for all skeletal vibrations. By PED criteria the skeletal uracil modes above 1000 cm^{-1} are essentially stretching vibrations, the modes

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[31] J. R. Scherer, *Spectrochim. Acta* **21**, 321 (1965).

[32] T. C. Duinker and I. M. Mills, *Spectrochim. Acta* **24A**, 417 (1968).

Table 7. Planar ring modes of uracil

Pseudo normal mode of a hypothetical C_6 ring*	Similar uracil mode†	Corresponding benzene frequency‡
E_{2g} (stretch)	U(III) (1611)	1599
	U(IV) (1462)	
B_{2u} (stretch)	U(V) (1236)	1309
E_{1u} (stretch–bend)	U(VI) (1104)	1037
	U(VII) (1010)	
B_{1u} (bend)	U(VIII) (988)	1010
A_{1g} (stretch)	—	993
	U(IX) (792)	
E_{2g} (bend)	U(X) (579)	606
	U(XII) (540)	

* Ref. [31].
† Raman frequencies in parentheses.
‡ Ref. [32].

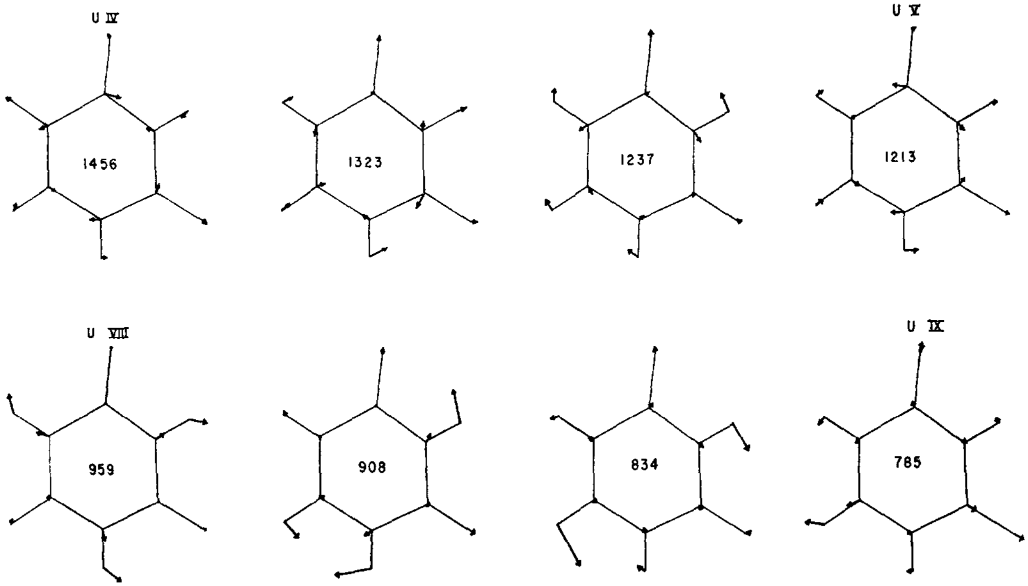

Fig. 6. Cartesian displacements for some planar ring modes and mixed ring-XD bending modes of perdeutero uracil. (Position of ring as in Fig. 4.)

between 1000 cm^{-1} and 750 cm^{-1} are stretch–bend vibrations, and the ones below 600 cm^{-1} essentially ring bending vibrations. Table 7 presents a correlation between the pseudo normal modes of a C_6 ring [31], the skeletal modes of uracil, and the similar modes of benzene [32].

In deuterated species the U VI and U VII modes are heavily mixed with CD and ND deformation vibrations, but the remaining skeletal ring modes retain a considerable similarity to the corresponding modes of nondeuterated uracil. Figure 6 presents the Cartesian displacements of the ring modes and mixed modes of perdeutero uracil in the 1500–700 cm^{-1} range.

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