

# Interpretation of the Vibrational Spectra of Matrix-isolated Uracil from Scaled Ab Initio Quantum Mechanical Force Fields

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## Abstract

The vibrational spectrum of uracil trapped in an argon matrix has been interpreted based on ab initio Hartree-Fock SCF calculations with a split-valence 4-21 basis set. The directly computed theoretical general valence force field was scaled with empirical scale factors in order to correct for the systematic errors originating in the limitation of the theoretical model. Scale factors transferred from related molecules provided a priori prediction of fundamental frequencies and intensities, permitting several corrections to be proposed for earlier assignments. Using the observed spectrum with the few altered assignments, a new set of scale factors was optimized to give the best force field available from combined consideration of the experimental and the theoretical data. For unknown reasons, the out-of-plane force field predicted a spectrum agreeing slightly less well with experiment than did the in-plane force field. However, the overall agreement between theory and experiment provided additional support for the assumptions involved in the method. The computed force fields were compared with others available from previous work. The comparison demonstrated the importance of expanding the energy surface around the true energy minimum and of using a proper scaling procedure. Previous scaled CNDO/2 calculations were found to be surprisingly good despite the large corrections required and the fact that they were made at an incorrect geometry.

## Introduction

The essential biological importance of uracil and its derivatives has motivated a number of recent studies of the structure and spectroscopy of these molecules [1-5]. Although free pyrimidine and purine bases do not occur in natural biological systems, the interpretation of certain biological processes (e.g., genetic damage) as monitored by infrared and Raman spectroscopy, and the analysis of more complex systems (such as nucleosides and nucleotides), should be based on a sound understanding of the spectra of the free base molecules. Unfortunately, there are serious deficiencies in such understanding in the case of uracil.

The structure of the free uracil molecule has only recently been resolved [6] by gas-phase electron diffraction. Earlier x-ray diffraction studies (e.g., Refs. 7-9) revealed the major impact of the strong intermolecular hydrogen bonds with possible significant distortions in the molecular geometry.

The gas-phase vibrational spectrum of uracil is practically unknown. Apart from an early work by Nowak et al. [10], who studied the  $\nu_{\text{NH}}$  and  $\nu_{\text{CH}}$  stretching region, there is only an unpublished attempt [11] to record the gas-phase spectrum. The results of that experiment are referred to in Ref. 12 and have been used for comparison with a CNDO/2 study [1]. However, since the details of that work have never been made available, we hesitate to use it for our interpretation.

The best available approximation to experimental vibrational spectra of the free uracil molecules comes from spectra in argon matrices [3–5, 13–15]. Spectra in inert gas matrices are, indeed, better resolved than gas-phase data since the low temperature causes them to lack rotational envelopes. There are, however, frequency shifts and intensity variations arising from interaction with the host matrix. For ground-state organic molecules with small dipole moments, the frequency shifts are negligibly small, perhaps up to 0.5%. For highly polar or quasi-ionic molecules, however, the shift can be quite significant, up to 10% or even more. Uracil has a dipole moment of 3.998 [16], so one must be concerned about small but serious frequency shifts owing to matrix effects. The situation is helped if, with Overend and coworkers [17], we believe that the matrix effects are dominated by perturbations of the quadratic term in the intermolecular potential, leaving the higher order terms unaffected. As explained below, certain procedures for using scale factors for the correction of computed force constants can absorb these quadratic matrix perturbations.

Examination of the available experimental data [3–5, 13–15] on the spectra of uracil in argon matrix reveals a lack of full agreement in the assignment of fundamental modes and also, to some extent, in the direct experimental observables of band frequencies and intensities (see Table I). Because of the small but not negligible discrepancies in the experimental data, a degree of caution is required when computed spectra are to be compared with those that are available from the experiments.

Our main purpose in this work is to attempt an unambiguous assignment of the matrix isolation spectra of uracil based on ab initio calculation of the vibrational force field, followed by scaling of the force field using a procedure that has now been shown to be highly successful for a wide range of other molecules. Both the use of an adequate level of computation and the application of a suitable scaling procedure are required to obtain the accuracy desired [18].

The best previous theoretical attempts to deduce force fields for uracil are the CNDO/2 study of Harsányi and Császár [1], which used a scaling procedure essentially identical to that we use here, and the ab initio STO-3G results of Nishimura et al. [19]. The former study suffered from an inadequate level of computation and the latter from use of a circuitous and questionable scaling procedure. Other published force fields include the recent MNDO-MOCIC calculation of Bowman and Spiro [20], the MINDO/3 results of Shibata et al. [21], the force field of Espinosa-Müller and Bravo [22] obtained by an extension of Boyd's method, and the force field from an empirical normal coordinate analysis by Bandekar and Zundel [23]. These force fields refer mainly to the condensed-phase spectra rather than to free uracil and exhibit many mutual disagreements.

### Computational Details

We have computed energy-optimized geometries and force fields by standard methods [18, 24] using the ab initio gradient program TEXAS [25] and the 4-21 basis set [18] of Gaussian orbitals. In separate calculations of the out-of-plane force field, a complete set of  $d$  functions with orbital exponent 0.8 was added to the basis set for both nitrogen and carbon. The matrix of constants was determined from gradients calculated at displaced geometries and scaled by a procedure identical to that we have used for maleimide [26]. Infrared intensities were also evaluated from computed dipole moment derivatives.

A complete, nonredundant set of internal coordinates was used for the calculations (Fig. 1 and Table II). This coordinate system was chosen in accord with our previous recommendations [18] to minimize the contribution of off-diagonal elements in the force constant matrix.

### Results and Discussion

#### Geometry

A crucial point in force field calculations, the importance of which is not always recognized, is the choice of a proper reference geometry around which the energy surface is expanded. This reference point should be the best approximation that can be made, either from experiment or from theory, to the true equilibrium geometry of the molecule [18, 26]. The magnitude of the error introduced by an improper choice of the reference geometry depends on the degree of anharmonicity of the vibrations.

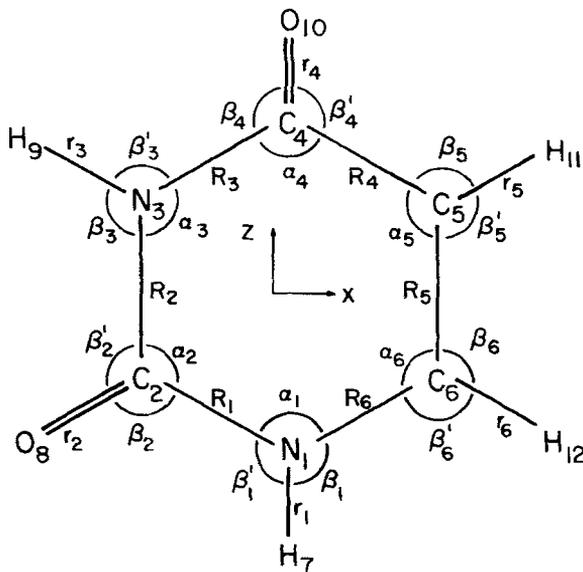


Figure 1.

TABLE I. Experimental frequencies observed in the IR spectra of uracil trapped in low temperature Ar matrices.

Barnes et al. [3]		Szczepaniak and coworkers [4, 5]		Maltese et al. [14]		Radchenko et al. [15]				
$\nu^a$	$I_{rel}^b$	Description <sup>c</sup>	$\nu^a$	$I_{rel}^d$	Description <sup>e</sup>	$\nu^a$	$I_{rel}^b$	Description <sup>f</sup>	$\nu^a$	$I_{rel}^{e,f}$
3485	s	$\nu_{NH}$	3482 (3467)	166	$\nu_{NH}$	3490	m	$\nu_{NH}$	3484	130
3435	s	$\nu_{NH}$	3433 (3422) (3130)	100 (4)	$\nu_{NH}$ $\nu_{CH}$	3477 3440	vw m	$\nu_{NH}$ $\nu_{NH}$	3434	100
3084 <sup>R</sup>		$\nu_{CH}$	2970	8	$\nu_{CH}$	1790	vw			
1774	s		1774			1779	vw			
1764	vs	$\nu_{C=O}$	1762	680		1773	m		1774	150
1761	vs					1769	?		1769	90
1757	vs					1763	vs		1761	450
1761	vs					1761	vs		1760	400
1733	vs		1733		$\nu_{C=O}$	1756	ms		1756	270
1731	s					1760	m		1760	100
1728	vs					1733	ms			
1718	m		1720			1730	ms			
1706	vs	$\nu_{C=O}$	1707	291		1727	s		1728	320
1698	ms		1699			1717	m		1718	50
1643	m	$\nu_{C=C}$	1644 (1525)	33	$\nu_{C=C}$	1706 (1703)	s		1705	260
1515	w					1698	m		1698	120
1472	ms	$\nu_{ring} + \beta_{NH}$	1473	83	$\beta_{NH}$	1683	m		1698	120
			1461	7	$\beta_{NH}$	1643	m	$\nu_{C=C}$	1642	60
1399	vs	$\nu_{ring} + \beta_{CH}$	1401	56	$\beta_{CH}$	1540	w		1515	40
1389	vs	$\beta_{CH} + \beta_{NH}$	1389	21	$\beta_{CH}$	1519	w		1470	60
1360	vw	$\beta_{ring}$	(1366)			1471	m	$\beta_{ring}$		
						1465	mw			
						1458	w			
						1400	m	$\beta_{NH}$	1398	190
						1388	mw	$\beta_{CH}$	1387	60
						1360	vw		1378	20
									1357	20

1313	VW					1306	VW		1302	20
1217	W	$\beta_{CH}$	1219	4	$\beta_{C_5H}$	1216	VW	$\beta_{ring}$	1294	20
1189	VS	$\nu_{ring} + \beta_{NH}$	1186	109	$\beta_{C_6H}$	1192	VW			
982	W	$\beta_{ring}$	963	2	$\beta_{ring}$	1185	m	$\beta_{NH}$	1183	240
958	W	$\nu_{ring} + \beta_{NH}$	958	7	$\beta_{ring}$	1070	W		1068	20
842	VW	$\gamma_{C_6H}$				970	VW			
804	S	$\gamma_{C_4=O} + \gamma_{CH}$	(806)			(811)		$\beta_{ring}$		
759	sh	Ring breath	(769)			806	m	$\gamma_{CH}$	803	170
757	S	$\gamma_{C_2=O}$				759	m	$\gamma_{CH}$	765	110
718	W	$\gamma_{C_3H}$	719	12	Ring breath	720	W	$\tau_{ring}$	759	20
			685	?					717	20
			682	?						
662	m	$\gamma_{N_3H}$	665	?		665	m	$\gamma_{NH}$	661	170
						(660)		657	50	
559	W	$\beta_{ring}$	585	?		587	VW	$\beta_{ring}$		
555	W		557	17	Ring breath	558	W	$\beta_{C=O}$	558	20
						554	m	$\gamma_{NH}$	555	20
551	m	$\gamma_{N_1H}$	551	?		548	m	$I_{ring}$	550	70
536	m	$\beta_{C=O}$	537	7	$\beta_{C=O}$	536	mW	$\gamma_{C=O}$	535	30
						554	m	$\gamma_{NH}$	555	20
516	m	$\beta_{ring}$	516	23	$\beta_{C_4=O} + \beta_{ring}$	(514)			515	70
391	m	$\beta_{C=O}$	393	33	$\beta_{C=O}$	395	m	$\gamma_{C=O}$		
119	?	Ring torsion								

<sup>a</sup>The experimental frequencies are given in  $cm^{-1}$ ; values in parentheses are hardly detectable.  
<sup>b</sup>Notations used for descriptions of relative intensities: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.  
<sup>c</sup>The description of the modes in Refs. 3, 5, and 14 is based on the potential energy distribution; the internal coordinates having dominant contributions are listed only. The notations used:  $\nu_{AB}$  = AB stretching,  $\beta_{AB}$  = AB in-plane bending,  $\gamma_{AB}$  = AB out-of-plane bending; a subscript "ring" refers to a composite coordinate used to describe the motions of the entire ring.  
<sup>d</sup>The values given here are taken from Ref. 5; the figures express the integrated intensities relative to that of  $\nu_2$  having an intensity of 100 units. A question mark in this column is assigned for bonds reported in Ref. 4 but omitted from the later publication [5] by the same authors.  
<sup>e</sup>The figures given here are obtained from the original values reported in Ref. 15 by multiplication with a factor of 100 in order to get values comparable with those of Ref. 5.  
<sup>f</sup>Information in the original publication [15] is insufficient for unambiguous assignment of the bands.

TABLE II. Definition of internal coordinates for uracil.

No.	Description	Symbols	Definition <sup>a</sup>
In-plane			
1	C=C stretching	$\nu_{C=C}$	$R_5$
2	C—C stretching	$\nu_{CC}$	$R_4$
3–6	C—N stretching	$\nu_{CN}$	$R_1, R_2, R_3, R_6$
7, 8	C—H stretching	$\nu_{CH}$	$r_5, r_6$
9, 11	C=O stretching	$\nu_{C=O}$	$r_4, r_2$
10, 12	N—H stretching	$\nu_{NH}$	$r_1, r_3$
13–15	Ring in-plane deformations	$\alpha_{ring,1}$	$\alpha_6 - \alpha_5 + \alpha_4 - \alpha_3 + \alpha_2 - \alpha_1$
		$\alpha_{ring,2}$	$2\alpha_6 - \alpha_5 - \alpha_4 + 2\alpha_3 - \alpha_2 - \alpha_1$
		$\alpha_{ring,3}$	$\alpha_5 - \alpha_4 + \alpha_2 - \alpha_1$
16, 17	C—H bending	$\beta_{CH}$	$\beta_6 - \beta'_6; \beta_5 - \beta'_5$
18, 20	C=O bending	$\beta_{C=O}$	$\beta_2 - \beta'_2; \beta_4 - \beta'_4$
19, 21	N—H bending	$\beta_{NH}$	$\beta_3 - \beta'_3; \beta_7 - \beta'_7$
Out-of-plane			
1–3	Ring torsions	$\tau_{ring,1}$	$\tau_{6123} - \tau_{5612} + \tau_{4561} - \tau_{3456} + \tau_{2345} - \tau_{1234}$
		$\tau_{ring,2}$	$\tau_{6123} - \tau_{4561} + \tau_{3456} - \tau_{1234}$
		$\tau_{ring,3}$	$2\tau_{6123} - \tau_{4561} - \tau_{3456} + 2\tau_{2345} - \tau_{1234} - \tau_{5612}$
4, 5	C—H out-of-plane bending	$\gamma_{CH}$	$\gamma_{11}, \gamma_{12}$
6, 8	C=O out-of-plane bending	$\gamma_{C=O}$	$\gamma_8, \gamma_{10}$
7, 9	N—H out-of-plane bending	$\gamma_{NH}$	$\gamma_7, \gamma_9$

<sup>a</sup>In-plane symbols used are shown in Figure 1. The index of the out-of-plane bending coordinates corresponds to the numbering of the atoms in Figure 1,  $\gamma_i$  is positive if atom  $i$  moves in the positive  $y$  direction. The four indices in the torsion are also numbers of the atoms (i.e.,  $\tau_{2345}$  is the dihedral angle of the 234 and 345 planes). The torsional angle  $\tau_{ijkl}$  is positive if, viewing from the direction of atom  $k$ , a counter-clockwise rotation is needed to bring atoms  $i$  and  $l$  into eclipsed conformation.

As an illustration, it is well known [27, 28] that a computed C—H stretching frequency has an error of  $10 \text{ cm}^{-1}$  for every  $0.001 \text{ \AA}$  error in the reference C—H bond length.

We have optimized the geometry of uracil at the ab initio 4-21 level and also with the addition of  $d$  functions to the basis for carbon and nitrogen. The results are shown in Table III along with calculated CNDO/2 [1], MINDO/3 [29], and experimental geometries. The reliability of the figures obtained from the various approaches is discussed elsewhere [18, 29], but it is of interest to see the results of the different methods compiled in one place.

We have chosen as our reference geometry the structure calculated with the 4-21 basis set and corrected by the small offset values [18, 30] that have been found in many examples to give a close approximation to an  $r_e$  structure. In our opinion, the differences between our computed force field and the force fields calculated by some earlier authors may be largely attributed to their incorrect choice of the reference geometry.

#### Scale Factors

The common practice of scaling the computed force constant matrix to correct for computational errors arising from neglect of electron correlation and use of a finite

TABLE III. Bond lengths (in pm) and angles (in degrees) for uracil.

Parameter <sup>a</sup>	Experimental					<i>Ab-initio</i>			
	x-ray		ED <sup>b</sup>	CNDO/2 <sup>c</sup>	MINDO/3 <sup>d</sup>	STO-3G		4-21	
	$r_x^c$	$r_x^f$	$r_g/r_\alpha$	$r_e^g$	$r_e^g$	$r_e^{g,h}$	$r_e^{g,i}$	$r_e^g$	$r_{ref}^j$
R <sub>1</sub>	137.1	138.1	139.5	138.4	139.0	142.5	142.7	138.0	136.9
R <sub>2</sub>	137.1	138.2	139.1	137.9	138.0	142.0	141.9	137.5	136.5
R <sub>3</sub>	137.1	138.1	141.5	138.9	140.1	143.6	143.2	139.9	138.9
R <sub>4</sub>	143.0	143.9	146.2	143.5	147.0	149.7	149.2	145.9	145.8
R <sub>5</sub>	134.0	133.6	134.3	134.3	135.9	132.1	132.3	132.5	134.5
R <sub>6</sub>	135.8	137.6	139.6	137.9	136.7	140.5	140.5	138.0	137.0
r <sub>1</sub>	83.6	—	100.2 <sup>k</sup>	106.4	102.7	101.8	101.9	99.5	100.0
r <sub>2</sub>	121.5	121.6	121.2	127.8	121.6	121.9	121.9	121.5	121.0
r <sub>3</sub>	88.7	94.7	100.2 <sup>k</sup>	106.7	103.4	102.0	101.9	99.8	100.3
r <sub>4</sub>	124.5	122.5	121.2	127.8	121.1	122.1	122.1	121.4	120.9
r <sub>5</sub>	93.1	96.1	107.2 <sup>k</sup>	111.2	110.2	107.8	107.2	106.5	107.0
r <sub>6</sub>	95.7	95.4	107.2 <sup>k</sup>	111.7	111.3	108.7	108.6	106.9	107.4
α <sub>1</sub>	122.7	120.7	123.2	121.7	126.6	123.3	122.7		123.3
α <sub>2</sub>	114.0	114.8	114.6	114.9	109.9	112.6	112.7		113.6
α <sub>3</sub>	126.7	127.2	126.0	126.2	131.6	127.5	127.9		128.5
α <sub>4</sub>	115.6	114.6	115.5	115.1	111.1	113.3	112.6		113.4
α <sub>5</sub>	118.9	119.0	119.7	119.3	121.2	120.7	121.2		119.3
α <sub>6</sub>	122.3	123.7	122.1	122.4	119.6	122.7	122.6		121.8
β <sub>1</sub>	122.2	120.2	121.1 <sup>k</sup>	119.5	115.8	119.8	120.7		121.0
β <sub>2</sub>	123.7	121.5	123.8	121.9	123.0	124.1	123.8		122.7
β <sub>3</sub>	117.8	116.4	115.4 <sup>k</sup>	115.7	112.8	117.0	115.4		115.4
β <sub>4</sub>	119.0	126.3	120.2	118.0	120.4	126.3	120.4		120.7
β <sub>5</sub>	118.0	122.5	118.1 <sup>k</sup>	119.1	119.1	121.7	117.5		118.1
β <sub>6</sub>	123.2	113.4	122.8 <sup>k</sup>	123.8	123.8	114.5	122.2		122.8

<sup>a</sup>For notations see Figure 1.<sup>b</sup>Ref. 6.<sup>c</sup>Ref. 1.<sup>d</sup>Ref. 29.<sup>e</sup>Refs. 7, 9; x-ray structures for uracil.<sup>f</sup>Ref. 19, from x-ray structure for cyclohexyl uracil.<sup>g</sup>Uncorrected theoretical equilibrium values.<sup>h</sup>Ref. 19.<sup>i</sup>Ref. 21.<sup>j</sup>Obtained from the theoretical  $r_e$  values, applying the small correction suggested in Ref. 18. The correction used for the C—N distance is somewhat arbitrary.<sup>k</sup>Assumed values, kept fixed during evaluation of ED data.

basis set may have either of two objectives. If the spectrum of a molecule is unknown or uncertain, scale factors may be transferred from closely related molecules on the assumption that the computational error is similar for similar types of vibrations in similar molecules. This leads to an a priori prediction of the spectrum and can be used to make or correct assignments of the fundamental modes. Alternatively, the computed force field may be corrected by a set of scale factors that have been opti-

mized to give the best fit of the computed spectrum to the observed spectrum, or to some portion of it that is known with certainty. In this case, the object is to obtain the best possible force field from a combination of all the available evidence, both experimental and theoretical. We have used both approaches here.

The scale factors we have used are shown in Table IV. Set A is transferred from calculations on a group of small aliphatic molecules [24] and set B is transferred from the closely related molecule maleimide [26]. Set C is optimized to give the best fit to the uracil spectrum. Both a priori predictions, with either set A or set B, suggested some inconsistencies in the experimental assignments [3–5, 13–15], leading to a number of changes that are proposed below. The mean-square deviations between the computed frequencies and the experimental frequencies are  $21.1 \text{ cm}^{-1}$  of the in-plane frequencies and  $21.7 \text{ cm}^{-1}$  for the out-of-plane modes using the set A scale factors. These values are reduced to 11.3 and  $21.5 \text{ cm}^{-1}$  using the more closely related scale factors of maleimide, set B. The rather large discrepancies in the out-of-plane modes call attention to the possible misassignments that are examined in a subsequent section. After making these corrections, the set C scale factors were obtained by least-squares optimization to the observed uracil matrix spectrum.

Limited calculations with  $d$  functions on all of the ring atoms gave results in accord with our earlier observations on maleimide [26]. Scale factors were nearer unity with the higher-level calculation, but there was nothing to suggest that any improvement in the quality of the scaled force field is obtained from calculations at higher than the 4-21 level.

The uracil force field of Chin et al. [5] was based on the STO-3G calculations of Nishimura et al. [19]. These calculations were apparently made at a reference ge-

TABLE IV. Scale factors for Uracil.

Coordinate <sup>a</sup>	Set A <sup>b</sup>	Set B <sup>b</sup>	Set C <sup>b</sup>	STO-3G <sup>b</sup>
<i>In-plane</i>				
$\nu_{\text{NH}}$	0.880	0.844	0.850	0.705
$\nu_{\text{CH}}$	0.866	0.835	0.822	0.664
$\nu_{\text{C=O}}$	0.826	0.818	0.831	0.664
$\nu_{\text{NC}}$	0.880	0.878	0.842	0.778
$\nu_{\text{CC}}$	0.920	0.901	0.896	0.778
$\nu_{\text{C=C}}$	0.866	0.869	0.909	0.664
$\beta_{\text{NH}}$	0.800	0.790	0.793	0.737
$\beta_{\text{CH}}$	0.800	0.785	0.768	0.737
$\beta_{\text{C=O}}$	0.836	0.875	0.847	0.875
$\beta_{\text{ring}}$	0.800	0.793	0.813	0.875
<i>Out-of-plane</i>				
$\gamma_{\text{NH}}$	0.500	0.510	0.583	—
$\gamma_{\text{CH}}$	0.730	0.697	0.733	—
$\gamma_{\text{C=O}}$	0.800	0.831	0.765	—
$\tau_{\text{ring}}$	0.800	0.731	0.791	—

<sup>a</sup>For notations of the internal coordinates see Table II and Figure 1.

<sup>b</sup>See text for specifications of the scale factor sets.

ometry far from the true equilibrium geometry, a procedure which can introduce serious errors. Scaling was done in two steps. First, the STO-3G force field was multiplied by a set of scale factors that had been derived to convert STO-3G force constants to 4-31 quality. Next, computed vibrational frequencies were multiplied by the constant factor of 0.9 to predict experimental frequencies. The latter step is equivalent to multiplying the force constants by the single factor of  $0.9^2 = 0.81$ . The two steps may be combined to give the scale factors shown in Table IV that give in one step the same values as those obtained by the previous authors [5]. It must be emphasized that these are scale factors for correcting the STO-3G computed results to agree with experiment and that the earlier work was not based on any 4-31 computations on uracil.

### *Force Constants*

The computed force field of uracil using the optimized scale factors of set C is given in Table V for the in-plane modes and in Table VI for the out-of-plane modes. Table V also gives the in-plane force field obtained by CNDO/2 calculations [1] and by STO-3G [5, 19], both scaled as described above. The STO-3G results have been transformed into our coordinate system for ready comparison. The most striking observation that can be drawn from an inspection of this table is that the scaled CNDO/2 force field shows better agreement with the ab initio 4-21 values than might be expected considering the large error that appears in the directly calculated CNDO/2 force field. Apparently the error is sufficiently systematic, even at this level of calculation, that the scaling procedure, properly applied, can correct for most of it. A close comparison of the results is not warranted because the CNDO/2 calculations were made at a considerably different geometry (the CNDO/2 energy minimum geometry, see Table III), and a somewhat different interpretation of the experimental spectrum was used to refine the CNDO/2 scale factors. These two considerations may well account for a good part of the differences seen in the diagonal force constants and particularly in the ortho interactions of the  $\nu_{\text{CH}}$  and  $\nu_{\text{NH}}$  stretchings with the  $\nu_{\text{CC}}$  and  $\nu_{\text{CN}}$  stretchings. The prediction of the exocyclic bond lengths was particularly poor by CNDO/2 (Table III). It would be extremely interesting to see CNDO/2 force constants for uracil calculated at the true equilibrium geometry and fitted to the uracil spectrum as we have interpreted it here.

Aside from the ortho interactions mentioned above, CNDO/2 predicted the off-diagonal elements of the force constant matrix reasonably well. Although about 20 of the 84 off-diagonal elements differ in sign when compared with either of the ab initio force matrices, all but one of these elements is smaller than 0.05. Regardless of sign, such small elements can have little effect on a predicted spectrum. In general, it appears that CNDO/2 calculations can give highly useful information at little expense, provided care is taken in using the correct reference geometry and in the scaling procedure. On the other hand, the analysis is fully as complicated as for the ab initio computations so that the greater certainty of higher accuracy from the ab initio calculations make them preferable if computer facilities permit. The level of calculation was probably adequate for the STO-3G calculations, and better agreement with our present results would be anticipated if they had been made at the equilibrium geometry and if our scaling procedure had been used.



$\beta_{N_1H}$	-0.043	-0.001	-0.028	-0.033	0.024	0.058	0.010	0.000	-0.017	-0.001	-0.013	6.690
	-0.050	0.012	-0.020	-0.031	-0.030	-0.021	0.000	0.003	-0.006	0.001	-0.029	6.688
	0.001	-0.009	-0.019	0.008	0.167	0.185	0.000	0.001	-0.007	0.000	-0.008	6.671
$\alpha_{ring,1}$	0.036	-0.034	-0.001	0.044	-0.030	0.087	-0.073	0.090	-0.275	0.096	-0.264	1.464
	0.053	-0.030	-0.035	-0.011	-0.067	0.111	-0.056	0.065	-0.235	0.075	-0.223	0.059
	0.078	-0.004	-0.017	-0.011	-0.022	0.057	-0.168	0.154	-0.231	-0.155	-0.204	0.143
$\alpha_{ring,2}$	0.016	-0.200	0.039	0.066	-0.207	0.183	-0.072	0.033	0.174	-0.098	0.200	1.236
	0.050	-0.173	0.096	0.116	-0.176	0.178	-0.055	0.031	0.153	-0.066	0.151	1.288
	0.059	-0.123	0.076	0.088	-0.126	0.122	-0.184	0.085	0.130	-0.168	0.136	1.600
$\alpha_{ring,3}$	0.252	0.101	-0.123	0.113	-0.029	-0.207	0.006	-0.085	0.306	0.007	-0.311	0.081
	0.198	0.097	-0.067	0.069	-0.068	-0.158	0.005	-0.055	0.244	-0.005	-0.246	0.050
	0.142	0.066	-0.058	0.050	-0.061	-0.105	0.017	-0.155	0.264	-0.009	-0.235	0.140
$\beta_{c,H}$	0.128	0.001	0.014	0.011	0.014	-0.250	-0.006	-0.003	0.012	0.000	-0.016	0.010
	0.109	-0.002	0.015	0.003	0.017	-0.183	-0.007	-0.010	0.008	0.000	-0.012	0.016
	0.138	0.014	0.014	0.004	0.000	-0.152	-0.010	-0.006	0.001	0.000	-0.008	0.008
$\beta_{c,3H}$	-0.173	0.126	0.003	-0.024	0.038	0.002	0.006	0.009	-0.001	0.003	0.000	-0.003
	-0.157	0.101	0.004	-0.029	0.039	0.009	0.012	-0.001	-0.018	0.003	0.000	-0.001
	-0.157	0.177	0.015	-0.016	0.017	-0.008	0.010	-0.009	-0.006	0.004	-0.001	-0.003
$\beta_{c,4=0}$	0.046	-0.224	0.455	-0.094	0.041	-0.114	-0.006	0.023	0.085	-0.035	0.040	0.006
	0.046	-0.199	0.394	-0.068	0.030	-0.081	0.004	0.011	0.057	-0.026	0.002	0.005
	0.018	-0.225	0.300	-0.021	0.022	-0.064	-0.009	0.010	0.050	-0.006	0.016	0.003
$\beta_{N_3H}$	0.024	0.027	-0.090	0.137	-0.020	-0.038	0.000	-0.005	-0.019	0.005	0.018	0.003
	0.029	0.014	-0.039	0.081	-0.007	-0.048	0.001	-0.003	0.008	0.007	-0.011	0.004
	0.022	-0.016	-0.120	0.140	0.023	-0.027	0.000	-0.006	-0.018	0.012	0.010	0.005
$\beta_{c_2=0}$	0.049	-0.046	0.127	-0.423	0.422	-0.105	0.009	-0.004	-0.048	0.034	0.020	-0.030
	0.024	-0.025	0.096	-0.331	0.340	-0.091	0.007	-0.007	-0.036	0.025	0.003	-0.019
	0.038	-0.029	0.033	-0.270	0.277	-0.046	0.007	-0.001	-0.017	0.005	-0.001	-0.003
$\beta_{N_1H}$	-0.019	-0.033	0.023	0.013	-0.122	0.178	-0.001	0.004	0.000	-0.002	-0.021	-0.063
	-0.015	-0.036	0.029	0.007	-0.057	0.150	-0.015	0.001	-0.003	-0.001	0.006	-0.019
	0.018	-0.020	0.015	-0.021	-0.122	0.164	-0.007	0.005	-0.003	-0.004	-0.021	-0.012
												0.085
												0.002
												0.009
												-0.004
												0.055
												0.519
												0.005
												0.510
												0.045
												0.010
												0.640

<sup>a</sup> Units are consistent with energy measured in aJ, stretching coordinates in Å, and bending coordinates in radians. For notations of internal coordinates see Figure 1 and Table II.

<sup>b</sup> The first entries in vertical triads are the directly calculated ab initio 4-21 force constants scaled with Set C scale factors, the second ones are the scaled STO-3G force constants of Ref. 19, and the third ones are scaled CNDO/2 values from Ref. 1.



Table VI shows the out-of-plane force fields from our 4-21 calculations, our 4-21\* calculations, and the CNDO/2 results. These force constants were not reported in the earlier STO-3G work. Again, comparison bears out the high quality of the CNDO/2 results. Differences in sign are seen for 3 out of 45 off-diagonal elements, but all of these have absolute values less than 0.03.

#### *Assignment of In-plane Fundamentals*

The vibrational fundamentals of uracil calculated at various levels of approximation are given in Table VII. As described in the Introduction, we choose to compare our results only with matrix isolation data [3-5, 13-15]. Of the available experiments, we can select that of Barnes et al. [3] for comment, since the assignments given there correspond most closely to our own. Our proposed assignment of the in-plane fundamentals differs from that of Barnes et al. [3] for only three bands,  $\nu_5$ ,  $\nu_6$ , and  $\nu_{16}$ . The C=O stretching region that contains  $\nu_5$  and  $\nu_6$  is noted for being strongly influenced by Fermi interactions. In the uracil spectrum there are 10 bands reported in this region [3], but only two fundamentals,  $\nu_5$  and  $\nu_6$ , are expected. As in the case of maleimide [26], the assignment of any of the observed bands can be questioned, and our choice of the bands at 1764 and 1741  $\text{cm}^{-1}$  is based largely on the calculated frequency difference between  $\nu_5$  and  $\nu_6$ , which is 15-20  $\text{cm}^{-1}$  by all methods considered here and on the predicted ratio of the absolute intensities. We do not consider this to be a definitive assignment, however.

In the 950-980  $\text{cm}^{-1}$  region of the spectrum, there should be three fundamentals,  $\nu_{15}$ ,  $\nu_{16}$ , and  $\nu_{22}$ , all of very low intensity. Barnes et al. [3] observe only two bands in this region, and the situation is very similar in most of the other experimental spectra [4-5, 13-15]. Only Maltese et al. [14] report three bands in this region. One of these, however, is described as uncertain, and only one is considered by them to be a fundamental. Since our calculations show  $\nu_{15}$  to be the most intense, we assign the band at 958  $\text{cm}^{-1}$  reported in all four experimental spectra to it. The predicted intensity of the other two bands is extremely low, and it is possible that neither of them has actually been observed. There is, however, some evidence for very weak bands at 982 [3], 970 [14], and 963  $\text{cm}^{-1}$  [5]. We have chosen, somewhat arbitrarily, to assign  $\nu_{22}$  at 963  $\text{cm}^{-1}$  and  $\nu_{16}$  at 982  $\text{cm}^{-1}$ . Despite these small uncertainties, we consider the overall agreement between the assignments of Barnes et al. and our calculations to be excellent.

#### *Assignment of Out-of-plane Fundamentals*

The assignment of the out-of-plane fundamentals is more problematical than for the in-plane modes. The C-H out-of-plane bends in  $\gamma$ -pyrone [31] and in maleimide [26], which have structures similar to that of uracil, lie in the 940-980  $\text{cm}^{-1}$  region. This supports our assignment of the 963  $\text{cm}^{-1}$  band [5] in uracil as  $\nu_{22}$ , in disagreement with the suggestions of a much lower frequency made in the experimental work (see Tables I and VII).

TABLE VII. Experimental and calculated vibrational fundamentals for uracil.<sup>a</sup>

Assign.	Description <sup>g</sup>	Ab initio 4-21 <sup>b</sup>												Experimental	
		CNDO/2 <sup>c</sup>		STO-3G <sup>d</sup>		Set A		Set B		Set C		Ar matrix <sup>e</sup>		Gas <sup>f</sup>	
		$\nu_i$	$I_{\text{abs}}$	$\nu_i$	$I_{\text{abs}}$	$\nu_i$	$I_{\text{abs}}$	$\nu_i$	$I_{\text{abs}}$	$\nu_i$	$I_{\text{abs}}$	$\nu_i$	$I_{\text{rel}}$	$\nu_i$	$I_{\text{rel}}$
<i>In-plane</i>															
$\nu_1$	$\nu_{\text{NH}}$	3450	0.3	3479	70	3535	131	3462	131	3476	131	3485	s	3450	w
$\nu_2$	$\nu_{\text{NH}}$	3427	0.1	3454	98	3505	94	3433	95	3445	95	3435	s	3427	w
$\nu_3$	$\nu_{\text{CH}}$	3119	1	3070	11	3162	2	3105	2	3081	2	3084 <sup>b</sup>		3101	w
$\nu_4$	$\nu_{\text{CH}}$	3074	64	3029	9	3114	3	3058	3	3034	3	(3034) <sup>f</sup>		3076	w
$\nu_5$	$\nu_{\text{C=O}}$	1744	179	1780	912	1759	571	1751	590	1760	449	1764	vs	1734	vs
$\nu_6$	$\nu_{\text{C=O}}$	1715	68	1756	555	1746	809	1737	910	1746	926	1741	vs	1688	vs
$\nu_7$	$\nu_{\text{C=C}}$	1621	4	1672	2	1627	111	1625	100	1645	99	1643	m	1632	vs
$\nu_8$	$\nu_{\text{NH}} + \nu_{\text{N}_1\text{C}_6}$	1505	9	1494	91	1478	98	1472	100	1466	94	1472	ms	1480	s
$\nu_9$	$\nu_{\text{CN}} + \beta_{\text{NH}}$	1453	2	1405	22	1421	161	1423	179	1409	138	1399	vs	1396	ms
$\nu_{10}$	$\beta_{\text{NH}}$	1400	21	1396	108	1398	35	1392	28	1389	77	1389	vs	1380	s
$\nu_{11}$	$\nu_{\text{NH}} + \beta_{\text{C}_5\text{H}}$	1371	1	1390	4	1380	18	1371	6	1362	15	1360	vw	1360	m
$\nu_{12}$	$\beta_{\text{C}_6\text{H}} + \beta_{\text{C}_5\text{H}}$	1238	1	1258	17	1254	13	1249	13	1233	12	1217	w	1228	m
$\nu_{13}$	$\nu_{\text{N}_3\text{C}_4} + \beta_{\text{C}_5\text{H}}$	1115	4	1182	43	1203	101	1196	97	1182	102	1184	vs	1089	s
$\nu_{14}$	$\beta_{\text{C}_6\text{H}} + \beta_{\text{C}_3\text{H}}$	1058	2	1074	28	1072	14	1069	13	1060	17	1073	w	999	w
$\nu_{15}$	$\nu_{\text{N}_1\text{C}_6} + \beta_{\text{C}_3\text{H}}$	997	1	991	9	979	7	976	7	980	6	982	w	974	w
$\nu_{16}$	$\beta_{\text{ring}}$	949	3	935	1	964	0.5	961	0.5	952	2	958	w	946	vw
$\nu_{17}$	$\nu_{\text{CC}}$	781	3	761	5	768	4	764	12	760	4	759	sh	769	s
$\nu_{18}$	$\nu_{\text{C}_4\text{C}_5}$	604	2	562	11	559	4	562	2	559	5	559	w	588	w
$\nu_{19}$	$\beta_{\text{ring},2} + \beta_{\text{C}_4=\text{O}}$ $\beta_{\text{ring},2} + \beta_{\text{C}_2=\text{O}}$	553	3	538	6	539	4	542	7	540	6	536	m	556	m

$\nu_{20}$	$\beta_{\text{ring},3}$	532	4	512	31	513	23	512	22	516	23	516	m	527	m
$\nu_{21}$	$\beta_{\text{C=O}}$	370	3	375	25	386	32	392	31	397	31	391	m	377	m
	Mean square deviations <sup>1</sup>	(18) <sup>1</sup>		16.6		21.1		11.3		6.1					
<i>Out-of-plane</i>															
$\nu_{22}$	$\gamma_{\text{C}_6\text{H}}$	875	7			971	0.5	952	1	975	1	963	w <sup>k</sup>	974	w
$\nu_{23}$	$\gamma_{\text{C=O}}$	832	19			839	121	848	134	832	147	804	s	810	s
$\nu_{24}$	$\gamma_{\text{C}_3\text{H}} + \gamma_{\text{C}_2=\text{O}}$	755	22			808	0.1	810	1	801	0.4	842	vw	841	m
$\nu_{25}$	$\gamma_{\text{C}_3\text{H}} + \gamma_{\text{C}_4=\text{O}}$	684	1			715	16	706	12	709	14	718	w	672	vw
$\nu_{26}$	$\gamma_{\text{N}_3\text{H}}$	496	40			602	81	605	68	645	60	662	s	633	m
$\nu_{27}$	$\gamma_{\text{N}_1\text{H}}$	472	16			522	115	527	120	563	118	551	m	556	m
$\nu_{28}$	$\tau_3 + \tau_1$	338	14			415	28	401	23	412	18	411	m	411	m
$\nu_{29}$	$\tau_2$	119	11			189	5	181	7	187	7	185	w	185	w
$\nu_{30}$	$\tau_3$	66	0.3			173	5	165	5	172	6	(170) <sup>m</sup>		(170) <sup>m</sup>	
	Mean square deviations <sup>1</sup>	(20) <sup>1</sup>		—		21.7		21.5		13.6					

<sup>a</sup>Vibrational frequencies in  $\text{cm}^{-1}$ , absolute intensities in  $\text{km mol}^{-1}$ .  
<sup>b</sup>Present work,  $\nu_i$  (Set A),  $\nu_i$  (Set B), and  $\nu_i$  (Set C) refers to the frequencies calculated with the respective set of scale factors.  
<sup>c</sup>Ref. 1.  
<sup>d</sup>The frequencies are calculated using the force constants of Ref. 19 scaled in one step as described in the text. The intensities are of Ref. 5, calculated ab initio using 4-31G basis set, at a corrected x-ray geometry of cyclohexyl-uracil.  
<sup>e</sup>If not otherwise stated, data of this column are taken from Ref. 3.  
<sup>f</sup>Ref. 11.  
<sup>g</sup>For notations see Table II.  
<sup>h</sup>Raman data.  
<sup>i</sup>This band is not observed either in the infrared or in the Raman. The value shown is the calculated value of column  $\nu_i$  (Set C).  
<sup>j</sup>Calculated with scale factors fitted to reproduce experimental frequencies slightly different from those used here, taken from Ref. 1.  
<sup>k</sup>Taken from Ref. 5.  
<sup>l</sup>The mean square deviation characterizes the agreement between the calculated and experimental frequencies (for details see Ref. 24).  
<sup>m</sup>Assumed values.

The assignments of  $\nu_{23}$  and  $\nu_{24}$  present a special problem. The intensity of a  $\gamma_{C=O}$  band is usually high, in agreement with our calculated intensity. This supports the assignment of the  $804\text{ cm}^{-1}$  band, the strongest one in this region of the spectrum, as  $\nu_{23}$ . We feel that this is correct despite the better agreement with the computed frequencies that would have been obtained by reversing the assignments of  $\nu_{23}$  and  $\nu_{24}$ .

From experimental evidence (e.g., isotopic shifts [3]) it is quite certain that the  $\gamma_{NH}$  bands,  $\nu_{26}$  and  $\nu_{27}$ , are at  $662$  and  $551\text{ cm}^{-1}$ , respectively. These vibrations are particularly susceptible to matrix effects, which may account for the larger than normal differences between experimental and computed intensities.

There is little evidence to support the assignments of the last three modes,  $\nu_{28}-\nu_{30}$ . The  $411$  and  $185\text{ cm}^{-1}$  frequencies assigned to  $\nu_{28}$  and  $\nu_{29}$  are taken from gas-phase spectra [11, 12]. For the lowest frequency, the ring torsion mode, we have used the calculated value.

### Conclusions

Use of scale factors transferred from related molecules permits us to make an a priori prediction of the in-plane spectrum of uracil of sufficient quality to confirm most of the previously assigned fundamental modes and to suggest three likely alterations. Scale factors (set C) derived from combined use of the observed spectra and the calculations allow us to obtain what should be the best currently available uracil force field. Since these scale factors must partly compensate for quadratic effects resulting from intermolecular potentials, they should partially correct for matrix interactions of a systematic nature.

The out-of-plane force field produces a predicted spectrum that agrees less well with experiment than we have come to expect from computations at this level. For example, the out-of-plane modes for the related molecules maleimide [26],  $\gamma$ -pyrone [31], and pyridine [32] could be calculated with at least as much accuracy and reliability as the in-plane modes. Particularly disturbing are the apparent reversal of several bands compared with experiment. We have no ready explanation for the greater errors in the out-of-plane spectrum of uracil unless they can be attributed to matrix effects on the experimental spectra.

We intend to use the computed force fields to investigate the spectra of a variety of isotopic species of uracil. These spectra contain a larger number of uncertainties in assignment, and we expect the force fields we have obtained to make a useful contribution in sorting out at least some of the difficulties.

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