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In-Plane Vibrational Modes in the Uracil Molecule from an ab Initio MO Calculation

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Abstract: Ab initio SCF MO calculations have been made for the equilibrium geometry, harmonic force constants, in-plane vibrational frequencies, and in-plane vibrational modes of uracil. The energy gradient method was employed, and the STO-3G basis set was used. The "STO-3G force constants" thus reached were corrected into "4-31G force constants", by estimating proper correction factors on the basis of the results of two sets of force constant calculations of fragments of the uracil molecule, namely, acrolein, urea, and formamide: one with the STO-3G basis set and the other with the 4-31G basis set. The corrected set of force constants could reproduce observed frequencies of uracil, uracil-d_2 (at positions 1 and 3), uracil-d_2 (at 5 and 6), uracil-d_4 (at 1, 3, 5, and 6), and uracil-$^{15}N_2$ residues, except that all the calculated normal frequencies are 8% (on the average) greater than the observed fundamental frequencies. Therefore, the vibrational modes calculated from this new set of force constants are significant and useful.

Introduction

For a proper use of the vibrational spectra of nucleic acids, including their resonance Raman spectra, in biophysical research, it is essential to have a reliable knowledge of the normal mode of vibration for each Raman line or infrared band. In the course of our work[2,3] to improve such knowledge, we have recently examined ^{15}N isotope effects on the Raman spectra of β-uridine-5′-phosphoric acid both in ^1H_2O and ^2H_2O solutions.[4] In combination with the infrared and Raman spectra of a number of uracil derivatives accumulated by previous investigators,[5-11] we now have a good amount of experimental data of the vibrational modes of the uracil residue.

In this work, therefore, we have now attempted to reach the best available set of force constants of uracil on the basis of an ab initio MO calculation. For this size of molecule, it is not practical to make a mere estimation of the force constants in an empirical manner. Even if an empirically estimated set of force constants is found to reproduce observed frequencies and other experimental values in a satisfactory extent, it should be suspected that this might be accidental. While, if an ab initio set of force constants is found to reproduce experimental values equally well, it must be given a much higher qualification. The vibrational modes derived from this set of force constants are considered to be significant.

Computational Details

General Method. For the uracil molecule, the ab initio SCF-MO method with the STO-3G basis set with standard parameters[12] was applied. The energy gradient technique[13] was employed for the geometry optimization and force calculation, by the use of IMSPACK program.[14] Force constants of the in-plane vibrations were obtained by numerical differentiation (three point method) of analytically calculated energy gradients (forces) in the Cartesian coordinate system and then transformed into an internal coordinate system. The internal coordinates **S** adopted are shown in Figure 1. Here, the redundancy of the angular coordinates caused by the ring system has already been removed. The vibrational frequencies and normal modes of vibrations were calculated from the force constants by the use of a program (NCTB) written by Shimanouchi and his collaborators.[15] The normal modes are given, not only by the **L** matrix elements in eq 1 but also by the

$$\mathbf{S} = \mathbf{LQ} \qquad (1)$$

percentage potential energy distribution, $F_{ii}L_{ik}^2\ 100/\lambda_k$, among the internal coordinates (i), where **Q** is the normal coordinates (k), **F** is the force constant matrix, and λ_k is related with the normal frequency (cm^{-1}), ν_k, as

$$\lambda_k = 4\pi^2c^2\nu_k^2 \qquad (2)$$

Table I. STO-3G to 4-31G Conversion Factors

	urea	acrolein	formamide	average
C=O str	0.790	0.844	0.813	0.82
C=C str		0.828		
C–C str		0.938		0.96
C–N str	0.974[a]		0.968	
N–H str	0.871[a] 0.892[a]		0.865 0.873	0.87
C–H str		0.818[b]	0.839	0.82
C=O bend	1.171	1.028	1.063	1.08
NCN bend	1.084			
CCC bend		1.043		
CH_2 bend		0.885	0.923	0.91
N–H bend	0.929	0.909[c]	0.917	
NH_2 rock	1.033		1.00	1.00
CH_2 rock		0.939		

[a] An average of the factors for two force constants. [b] An average of the factors for four force constants. [c] For C–H bend of acrolein.

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(1) (a) University of Tokyo. (b) Institute for Molecular Science.

(2) M. Tsuboi, S. Takahashi, and I. Harada, "Physico-chemical Properties of Nucleic Acids", Vol. 2, J. Duchesne, Ed., Academic Press, London, New York, 1973, p 91.

(3) Y. Nishimura, A. Y. Hirakawa, and M. Tsuboi, "Advances in Infrared and Raman Spectroscopy", Vol. 5, R. J. H. Clark and R. E. Hester, Eds., Heydon, London, 1978, Chapter 4.

(4) Y. Nishimura, H. Haruyama, K. Nomura, A. Y. Hirakawa, and M. Tsuboi, *Bull. Chem. Soc. Jpn.*, **52**, 1340 (1979).

(5) M. Tsuboi, Y. Kyogoku, and T. Shimanouchi, *Biochim. Biophys. Acta*, **55**, 1 (1962).

(6) R. C. Lord and G. J. Thomas, Jr., *Spectrochim. Acta, Part A*, **23A**, 2551 (1967).

(7) M. Tsuboi, "Proceeding of the 23rd International Congress of Pure and Applied Chemistry", Vol. 7, Butterworth, London, 1971, p 145.

(8) H. T. Miles, T. P. Lewis, E. D. Becker, and J. Fragier, *J. Biol. Chem.*, **248**, 1115 (1973).

(9) H. Susi and J. S. Ard, *Spectrochim. Acta, Part A*, **27A**, 1549 (1971).

(10) H. Susi, *Spectrochim. Acta, Part A*, **30A**, 1843 (1974).

(11) Y. Nishimura, A. Y. Hirakawa, and M. Tsuboi, *Chem. Lett. (Tokyo)*, 907 (1977).

(12) W. J. Hehre, R. E. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(13) P. Pulay in "Applications of electronic structure theory", H. F. Schaefer III, Ed., Plenum Press, New York, 1977, Chapter 4.

(14) K. Morokuma, S. Kato, K. Kitaura, I. Ohmine, and S. Sakai, to be submitted for publication.

(15) T. Shimanouchi, Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules, Department of Chemistry, University of Tokyo.

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$S_1=\Delta r_1$	νN_1C_2 str.
$S_2=\Delta r_2$	νC_2N_3 str.
$S_3=\Delta r_3$	νN_3C_4 str.
$S_4=\Delta r_4$	νC_4C_5 str.
$S_5=\Delta r_5$	νC_5C_6 str.
$S_6=\Delta r_6$	νC_6N_1 str.
$S_7=\Delta r_7$	νN_1H str.
$S_8=\Delta r_8$	νC_2O str.
$S_9=\Delta r_9$	νN_3H str.
$S_{10}=\Delta r_{10}$	νC_4O str.
$S_{11}=\Delta r_{11}$	νC_5H str.
$S_{12}=\Delta r_{12}$	νC_6H str.
$S_{13}=(\Delta\beta_{13}-\Delta\beta_{14}+\Delta\beta_{15}-\Delta\beta_{16}+\Delta\beta_{17}-\Delta\beta_{18})/\sqrt{6}$	δRing deform. I
$S_{14}=(2\Delta\beta_{13}-\Delta\beta_{14}-\Delta\beta_{15}+2\Delta\beta_{16}-\Delta\beta_{17}-\Delta\beta_{18})/\sqrt{12}$	δRing deform. II
$S_{15}=(\Delta\beta_{14}-\Delta\beta_{15}+\Delta\beta_{17}-\Delta\beta_{18})/\sqrt{2}$	δRing deform. III
$S_{16}=(\Delta\beta_{19}-\Delta\beta_{25})/\sqrt{2}$	δN_1H bend.
$S_{17}=(\Delta\beta_{20}-\Delta\beta_{26})/\sqrt{2}$	δC_2O bend.
$S_{18}=(\Delta\beta_{21}-\Delta\beta_{27})/\sqrt{2}$	δN_3H bend.
$S_{19}=(\Delta\beta_{22}-\Delta\beta_{28})/\sqrt{2}$	δC_4O bend.
$S_{20}=(\Delta\beta_{23}-\Delta\beta_{29})/\sqrt{2}$	δC_5H bend.
$S_{21}=(\Delta\beta_{24}-\Delta\beta_{30})/\sqrt{2}$	δC_6H bend.

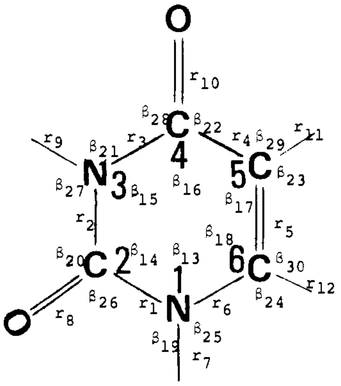

Figure 1. Internal coordinates of the uracil molecule.

Force Constant Correction. The ab initio STO-3G force constants of the uracil molecule were subjected to a correction, on the basis of the results of more extensive calculations on urea, acrolein, and formamide molecules, all of which are considered to be fragments of the uracil molecule. For all of these three smaller molecules, the force constant calculations were performed with both the STO-3G and 4-31G[16] basis sets. It has been found that in every case the 4-31G set of force constants gives a better reproduction of the observed vibrational frequencies than the STO-3G set. For acrolein, for example, the 4-31G force field gave in-plane vibrational frequencies, all of which are nearly equally (10–14%) higher than the observed frequencies, whereas the STO-3G force field gave vibrational frequencies, which show wide variety (7–27%) of differences from the observed frequencies depending on the vibrational modes, especially depending upon whether the stretching motions or the bending motions are mainly involved. Such a situation, in general, must cause a serious difficulty in reproducing a particular set of vibrational modes, in which stretching and bending motions are coupled with one another. In Table I, the correction factors c_{ii} found in the calculations are given for some of the diagonal elements F_{ii} of the force constant matrix, where

$$F_{ii}(\text{4-31G}) = c_{ii}F_{ii}(\text{STO-3G}) \qquad (3)$$

For each off diagonal element F_{ij}, the correction factor c_{ij} was assumed to be given by eq 4. The results of our STO-3G and

$$c_{ij} = \sqrt{c_{ii}c_{jj}} \qquad (4)$$

4-31G calculations of urea and acrolein will be detailed elsewhere. The results of 4-31G calculation of formamide has been reported.[17]

Table II. Geometry of the Uracil Molecule

		calcd on STO-3G	obsd[b]
N_1C_2	r_1[a]	1.425	1.381
C_2N_3	r_2	1.420	1.382
N_3C_4	r_3	1.436	1.381
C_4C_5	r_4	1.497	1.439
C_5C_6	r_5	1.321	1.336
C_6N_1	r_6	1.405	1.376
N_1H	r_7	1.018	
C_2O	r_8	1.219	1.216
N_3H	r_9	1.020	0.947
C_4O	r_{10}	1.221	1.225
C_5H	r_{11}	1.078	0.961
C_6H	r_{12}	1.087	0.954
$C_6N_1C_2$	β_{13}	123.3	120.7
$N_1C_2N_3$	β_{14}	112.6	114.8
$C_2N_3C_4$	β_{15}	127.5	127.2
$N_3C_4C_5$	β_{16}	113.3	114.6
$C_4C_5C_6$	β_{17}	120.7	119.0
$C_5C_6N_1$	β_{18}	122.7	123.7
HN_1C_2	β_{19}	116.9	119.1
OC_2N_3	β_{20}	124.1	121.5
HN_3C_4	β_{21}	117.0	116.4
OC_4C_5	β_{22}	126.3	126.3
HC_5C_6	β_{23}	121.7	122.5
HC_6N_1	β_{24}	114.5	113.4

[a] See Figure 1. r is in A. β is in deg. [b] Reference 18.

We have never attempted to correct the STO-3G or 4-31G force constants by fitting them to experimental data. It seems to be important for us to grasp what ab initio calculation can reach by itself in our present stage.

Results and Discussions

Equilibrium Geometry. The structural parameters calculated using the STO-3G basis set are given in Table II. In this calculation, the equilibrium geometry of the free uracil molecule showed a good coincidence with the geometry found in an X-ray crystallographical analysis of a 1-cyclohexyluracil crystal.[18] Thus, it is suggested that the skeletal structure of C, N, and O of the uracil molecule is not greatly affected by a crystalline force field. Calculated C–H and N–H bond lengths are, however, considerably greater than what are given by the crystallographic result. One should be reminded that the X-ray analysis gives a C–H or N–H distance on the basis of the electron distribution, and here an exceptionally great error may be involved in locating a proton.

STO-3G Force Constants (Uncorrected). The force constants calculated from the STO-3G basis set are given in the supplementary material. The force constant values which were estimated previously[4] (for 1-methyluracil) on an empirical basis are also given there. From the comparisons, it has been shown that many of the values (and signs) of off-diagonal elements previously estimated have now firm grounds. In addition, it has now been suggested that the off-diagonal elements between two adjacent bonds (let us call them "ortho") do not always have equal values; the interaction between $C^5{=}C^6$ and $N^1{-}C^6$ is great (0.624 mdyn A^{-1}) whereas that between $N^3{-}C^4$ and $C^4{-}C^5$ is small (0.341 mdyn A^{-1}). An idea, previously proposed,[4] that the bond-stretch bond-stretch cross terms for two bonds "next door but one" from each other (meta) and for two bonds two doors away from each other (para) must have appreciable values has now been supported. Some of them ($C^4{-}C^5/N^1{-}C^6$, for example) are suggested, however, to have relatively greater values (−0.378 mdyn A^{-1}), whereas some ($C^2{-}N^3/C^4{-}C^5$, for example) relatively smaller values (−0.179 mdyn A^{-1}).

We realize here that, for such a big molecule, many of the bond-stretch angle-bend cross terms, as well as the bend bend cross terms, are difficult to estimate by a trial-and-error method even

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(16) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(17) Y. Sugawara, Y. Hamada, A. Y. Hirakawa, M. Tsuboi, S. Kato, and K. Morokuma, *Chem. Phys.*, **50**, 105 (1980).

(18) T. Katsura, K. Morikawa, M. Tsuboi, and Y. Iitaka, to be submitted for publication.

Table III. Vibrational Frequencies (cm^{-1}) of the Uracil Molecule (Calculated ω and Observed ν)

numbering of normal coord (k)	calcd ω on STO-3G with all the elements	calcd ω on STO-3G with 143 elements	calcd ω on modified STO-3G with 143 elements	vibrational modes^a	obsd ν^b	ratio of $\nu_{obsd}/\omega_{calcd}$
1	4145	4143	3865	N_1H str (99)	3395^c	0.88
2	4116	4113	3837	N_3H str (99)	3395^c	0.88
3	3768	3764	3409	C_5H str (95)	3100	0.91
4	3717	3717	3368	C_6H str (95)	3085	0.92
5	2110	2112	1972	C_2=O str (53)	1716	0.87
6	2094	2096	1942	C_4=O str (56), UrI	1662	0.86
7	2009	2006	1849	C=C str (57), UrII	1611	0.88
8	1712	1708	1648	ring str (50), N_1H bend (26) UrIII	1507	0.92
9	1627	1623	1552	ring str (55), N_3H bend (32)	1462	0.93
10	1613	1611	1531	N_3H bend (20), CH bend (35)	1422	0.93
11	1549	1546	1525	ring str (39), N_1H bend (30) UrIV	1398	0.92
12	1426	1424	1386	ring str (63), Kekulé UrV	1236	0.89
13	1358	1360	1301	CH out-of-phase bend (64)	1217	0.93
14	1231	1234	1188	ring str (55)	1104	0.93
15	1065	1065	1087	ring deform I (75)	1010	0.93
16	1054	1056	1036	ring str (61)	988	0.96
17	839	838	822	ring breathing (67), UrVI	792	0.95
18	601	601	612	ring deform III (57)	579	0.96
19	578	578	591	C=O in-phase bend (60)	558	0.96
20	541	541	558	ring deform II (67)	540	0.99
21	406	406	416	C=O out-of-phase bend (69)	398	0.96
						(average 0.92)

[a] Potential energy distribution (%) calculated is given in parentheses. For UrI–UrVI, see ref 4. [b] Reference 9 (uracil). [c] NH stretching frequency observed for 1-cyclohexyluracil.

with the aid of good amount of data, including those of small fragment molecules, and a physical model of the force field. At present, only the ab initio MO method would provide a reliable first guess. For example, the rather great cross terms between the C=O stretching (S_8 or S_{10}) and the ring deformation (S_{13}, S_{14}, or S_{15}) are what are newly realized by our present calculation.

$$\begin{array}{ccc} & S_8 & S_{10} \\ S_{13} & 0.293 & 0.308 \\ S_{14} & 0.180 & -0.378 \\ S_{15} & -0.333 & -0.013 \end{array}$$

unit = mdyn

It should be pointed out, however, that our previous effort[4] to reproduce the observed effects of the position 3 deuteration and position 5 deuteration on the vibrational frequencies caused a fairly good set of the force constants; all of the greater cross terms found by the present STO-3G calculation among N^1H bending (S_{16}), N^3H bending (S_{18}), C^5H bending (S_{20}), C^6H bending (S_{21}), and C—C (or C—N) stretchings were properly predicted.

STO-3G Frequencies. The in-plane normal frequencies calculated with the STO-3G force constant values are given in the first column of Table III. It has been shown that 88 of the total 210 off-diagonal elements of the force constant matrix are very small, and probably they are essentially zero. The vibrational frequencies calculated with the STO-3G force constants but with an assumption that all of these 88 elements are zero are given in the second column of Table III. As is expected, the result is practically the same as that given in the first column. Thus, in the uracil molecule, only the remaining 143 force constants are taken to be significant.

All of the 21 in-plane frequencies calculated are readily correlated with the observed frequencies,[9] and the calculated normal modes of vibrations are not contradictory with the available experimental data at all. The calculated frequencies, however, are always higher than the observed ones, and the differences are distributed in the range of 0–25%.

Corrected Force Constants and Frequencies. The 143 force constants (21 diagonal and 122 off-diagonal) just mentioned were corrected by the above described method (cf. eq 3 and 4 and Table I). The normal frequencies of the in-plane vibrations calculated with this corrected set of force constants are given in the third column of Table III. The normal modes of vibration found in this calculation are shown in the fourth column of Table III and in more detail in Table IV. The calculated frequencies are still higher than the observed frequencies, but the differences are much smaller with the corrected force constants than otherwise. The calculated N–H stretching frequencies are to be compared with the experimental values obtained for the molecule free from any intermolecular hydrogen bondings. In Table III are given the N–H

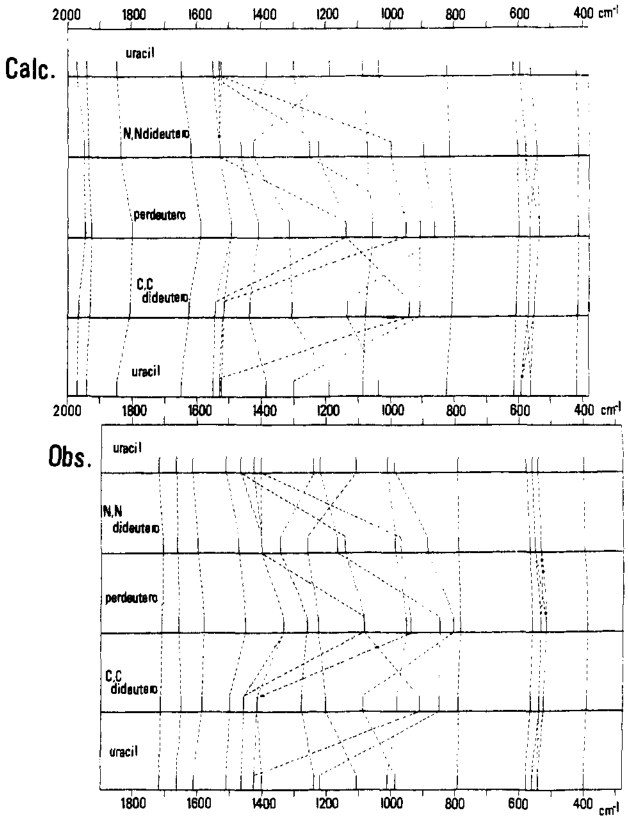

Figure 2. Calculated (upper) and observed[9] (lower) frequencies of uracil and its deuterated species.

Table IV. Normal Modes of Vibration in the Uracil Molecule[a]

normal coord (k)	5	6	7	8	9	10	11	12	13	14	15	16	17
ω_{calcd}, cm^{-1}	1972	1942	1849	1648	1552	1531	1525	1386	1301	1188	1087	1035	822
ν_{obsd}, cm^{-1}	1716	1662	1611	1507	1462	1422	1398	1236	1217	1104	1010	988	792
internal coord (i)													
S_1	6.6	2.9	*0.8*	*7.6*	*11.8*	*9.6*	*7.7*	9.7	0.0	*2.8*	*2.0*	*24.8*	*14.8*
S_2	11.5	0.2	0.0	2.0	17.7	2.9	16.0	*12.3*	*5.9*	*0.8*	*2.1*	*10.9*	*6.9*
S_3	*4.1*	3.2	0.8	4.3	*12.7*	6.6	5.2	25.7	2.1	*2.3*	*7.2*	7.0	*8.2*
S_4	*1.0*	9.8	*0.0*	*8.1*	7.3	0.0	*9.4*	*11.7*	*0.2*	0.6	*2.8*	16.6	*28.8*
S_5	4.1	*9.2*	56.9	0.6	*4.1*	*3.3*	0.0	0.8	*1.8*	13.8	*0.2*	0.0	*2.3*
S_6	*3.6*	0.1	*11.8*	27.7	1.1	*0.6*	*0.3*	*2.8*	6.7	34.3	*0.2*	*1.9*	*6.4*
S_7	*0.0*	0.0	*0.1*	0.0	*0.0*	*0.0*	*0.0*	0.0	0.0	0.1	*0.0*	*0.0*	*0.0*
S_8	*53.3*	*14.0*	0.8	*10.5*	3.3	*4.7*	4.6	0.0	0.1	*0.3*	1.9	*1.6*	*3.4*
S_9	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	*0.0*	*0.0*	*0.1*	*0.0*	*0.0*
S_{10}	7.3	*56.0*	*16.8*	*1.1*	*2.6*	6.2	*2.8*	*0.1*	*0.3*	0.1	1.5	1.2	*3.6*
S_{11}	0.0	*0.0*	0.3	*0.0*	0.0	*0.0*	*0.0*	*0.0*	0.0	0.2	*0.1*	0.0	*0.1*
S_{12}	0.0	*0.1*	0.3	0.2	*0.0*	*0.0*	*0.0*	*0.0*	0.0	0.1	0.0	*0.0*	*0.1*
S_{13}	1.4	7.2	0.8	4.0	*0.1*	*0.2*	*0.0*	0.0	0.5	*1.2*	75.4	0.3	*5.2*
S_{14}	5.1	*4.1*	0.9	0.4	0.3	1.1	0.8	*0.9*	*0.7*	*0.0*	0.5	0.8	*2.6*
S_{15}	*3.8*	*1.2*	*0.0*	5.7	*0.0*	0.2	4.3	0.7	0.5	*0.0*	2.0	*0.9*	*6.5*
S_{16}	*3.8*	*1.8*	1.1	25.8	8.8	0.2	*30.2*	1.8	*13.9*	*9.8*	*0.8*	*0.1*	0.0
S_{17}	*0.0*	0.0	*0.4*	*0.2*	*0.7*	*6.1*	*8.7*	3.3	0.9	1.9	0.1	*5.3*	1.3
S_{18}	7.3	*0.8*	*1.4*	*0.0*	31.5	*20.2*	2.4	21.4	1.4	0.0	*0.2*	10.0	*0.1*
S_{19}	*0.0*	*0.0*	*0.5*	1.7	*0.1*	1.8	6.0	10.1	0.0	*3.1*	*0.2*	*4.6*	*0.2*
S_{20}	*0.6*	3.6	*1.2*	*7.8*	5.3	18.0	*0.5*	16.5	*19.6*	21.5	2.9	*0.7*	*0.1*
S_{21}	0.7	*0.7*	13.0	*3.4*	8.0	17.5	*6.0*	1.6	44.1	*0.7*	*0.2*	*5.3*	0.2

[a] The calculated percentage potential energy distribution ($F_{ii}L_{ik}^2 100/\lambda_k$) among internal coordinates (i) is given here. The italicized numbers mean that the corresponding eigenvector element (L matrix element) has the negative sign.

stretching frequencies observed for 1-cyclohexyluracyl in dilute $CDCl_3$ solution.[19]

^{15}N Isotope Shifts. In Table V, ^{15}N isotope shifts calculated with the corrected STO-3G force constants of uracil are shown. Observed ^{15}N isotope shifts are available only for stronger Raman lines of β-uridine-5′-phosphoric acid. As long as the comparisons are possible, however, agreement between the calculated and observed values are found to be satisfactory. It should be concluded that the amplitudes of the nitrogen motions in the normal modes of vibration are well reproduced by our present calculation.

Deuteration Effects. As is shown in Figure 2, the calculated pattern of the N-H and C-H deuteration effects on the in-plane vibrational spectra is quite similar to the observed pattern; they can be taken as topologically identical with each other.

Normal Modes of Vibration. It has become clear that as far as the in-plane vibrations are concerned, the corrected STO-3G (nearly 4-31G) calculation is sufficient to reproduce experimental results. Therefore, by examining the calculated modes of vibration (see Table IV) as well as the available experimental data, comments are given below for some of the vibrations which appear in a resonance Raman spectrum.[4] They are called UrI, UrII, UrIII, UrIV, UrV, and UrVI. The vibrational frequencies given in the parentheses are those observed for uracil.[9] What are observed for β-uridine-5′-phosphoric acid (5′-UMP) are the following: 1680, 1630, 1475, 1397, 1231 and 783 cm^{-1} respectively.

UrI (1662 cm^{-1}): A great amount of the $C^4{=}O$ stretching and a smaller amount of the $C^5{=}C^6$ stretching vibrations take place in-phase.

UrII (1611 cm^{-1}): A great amount of the $C^5{=}C^6$ stretching and a smaller amount of the $C^4{=}O$ stretching vibrations take place with a 180° phase difference.

UrIII (1507 cm^{-1}): The $N^1{-}C^6$ plus $N^3{-}C^4$ stretchings take place with a 180° phase difference from the $N^1{-}C^2$ plus $C^4{-}C^5$ stretchings. Note that a great amount of the $N^1{-}H$ in-plane bending mode is involved in this vibration.

UrIV (1398 cm^{-1}): The $C^2{-}N^3$ stretching and $C^4{-}C^5$ stretching vibrations take place with a 180° phase difference. Here is again a great amount of the $N^1{-}H$ bending contribution.

UrV (1236 cm^{-1}): A ring stretching vibration that corresponds essentially to the Kekulê vibration of the benzene ring, in which every bond in the ring stretches and contracts with a 180° phase difference from the stretching and contraction of the adjacent bond. In undeuterated uracil, however, the contribution of the $N^3{-}C^4$ stretching is the greatest, and the mode is somewhat deformed from a typical Kekulê mode. In this vibrational mode, the contributions of the $N^3{-}H$ bending and $C^5{-}H$ bending are also great, and its frequency (1236 cm^{-1} for uracil and 1231 cm^{-1} for 5′-UMP) is lower than the intrinsic Kekulê vibration. Thus, if the vibrational coupling with the $N^3{-}H$ bending is removed by N^3-deuteration, the UrV frequency is elevated to 1303 cm^{-1}, and the vibrational mode now becomes more typical Kekulê mode. A similar high-frequency shift is caused also by C^5-deuteration.

UrVI (792 cm^{-1}): All of the eight bonds, C=C, C—C, C—N, and C=O, stretch and contract in-phase (ring-breathing vibration).

Table V. Calculated and Observed ^{15}N Isotope Shifts in the Vibrational Frequencies of the Uracil Molecule

normal vibr (k)	calcd[a]	obsd[b]	calcd (ω)[d]	obsd (ν)[e]
1	3546	3395[c]	−9	
2	3520	3395[c]	−9	
3	3128	3100	0	
4	3090	3085	0	
5	1809	1716	−7	
6	1782	1662	−1	−2
7	1696	1611	−2	−3
8	1512	1507	−15	−13
9	1424	1462	−18	
10	1405	1422	−8	
11	1398	1398	−6	−7
12	1272	1236	−3	−8
13	1194	1217	−2	
14	1090	1104	−11	
15	997	1010	−15	
16	950	988	−15	
17	754	792	−5	−2
18	561	579	−3	−6
19	542	558	−3	−5
20	512	540	−5	
21	382	398	−2	−2

[a] Normal frequency calculated on the modified STO-3G force constants times 0.92. [b] Reference 9 (for uracil). [c] Observed in 1-cyclohexyluracil. [d] Calculated with the 143 force constants, obtained by STO-3G to 4-31G conversion (corresponding to the 4th column of Table IV). [e] Reference 4 (for 5′-UMP).

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[19] Y. Kyogoku, R. C. Lord, and A. Rich, *J. Am. Chem. Soc.*, **89**, 496 (1967).

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Supplementary Material Available: Force constants of the uracil molecule, calculated on the STO-3G basis set, in comparison with what were empirically determined (2 pages).[4] Ordering information is given on any current masthead page.

VCNDO/S Method for Second-Row Atoms

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Abstract: A CNDO method has been constructed for the study of molecules containing second-row atoms. Empty, low-lying 3d orbitals are included, and the 3d orbital exponents, core integrals, and repulsion integrals involving X-ray orbitals are calculated after SCF convergence and used as input for a new SCF calculation. In this fashion the "size" and involvement of the 3d orbitals are calculated in a self-consistent manner for each molecule. Orbital occupations and calculated UV band maxima are presented for molecules containing sulfur.

Much has been written on the involvement of d orbitals in the chemistry of sulfur and other second-row elements.[1,2] The idea that d orbitals contract in an electron-withdrawing environment and thus become more effectively involved in bonding has been advanced[1,3] and has been under investigation in this laboratory since 1953.[3] Ab initio calculations with optimized scaling factors have shown that such factors for 3d orbitals on sulfur vary widely with the atoms to which the sulfur is bonded.[4] Binding energy, geometry, dipole moment, and other molecular properties are affected by the presence of d orbitals, particularly if the sulfur atoms would be strongly positive without their use.

CNDO level studies of molecules containing second-row elements have been reported, by many authors.[5-13] While most of these papers deal with ground-state properties of molecules, several attempts have been made to parameterize a CNDO method to reproduce spectroscopic data for molecules containing second-row atoms.[9,11-13]

However, none of the methods presented have incorporated adjustment of the size of the 3d orbitals to the electronegativity of the environment; this problem was first addressed here by Kuehnlenz.[14]

A method is presented here to extend the CNDO/S method to second-row elements; the heart of the method is a self-consistent optimization of 3d orbital exponents to account for the environment of the second-row element. This method has also been applied to CNDO/2 in a preliminary study.

Table I. Converged Values of Quantities Adjusted to Self-Consistency

	ζ_d	$\frac{1}{2}(I_d + A_d)$	orbital occupation d	orbital occupation sp	total charge on sulfur
thiophenol	0.842	−11.085	0.16	6.11	0.27−
thioanisole	0.851	−10.795	0.27	6.06	0.32−
methyl *p*-aminophenyl thioether	0.850	−10.820	0.27	6.06	0.33−
methyl *p*-tolyl thioether	0.851	−10.812	0.27	6.06	0.33−
methyl phenyl sulfoxide	0.965	−7.705	0.56	5.52	0.08−
methyl phenyl sulfone	1.078	−0.965	1.59	4.50	0.10−
methyl merceptan	0.842	−11.059	0.15	6.10	0.26−
sulfur dioxide	1.053	−3.543	0.72	4.88	0.41+
thioformaldehyde	0.812	−11.766	0.10	6.23	0.34−
thiopyran-4*H*-one	0.868	−10.288	0.26	5.96	0.22−
pyran-4*H*-thione	0.781	−12.674	0.12	6.41	0.53−
thiopyran-4*H*-thione					
keto S	0.788	−12.479	0.12	6.37	0.50−
ring S	0.871	−10.184	0.26	5.95	0.20−
thiopyran-2*H*-thione					
keto S	0.798	−12.201	0.12	6.32	0.43−
ring S	0.879	−9.901	0.27	5.90	0.17−
thiophene	0.859	−10.528	0.26	6.01	0.27−
thiourea	0.767	−13.055	0.11	6.48	0.59−

Method

The method here developed is completely analogous to the method of Del Bene and Jaffe[15] as modified by Ellis, Kuehnlenz, and Jaffe.[16] For first-row atoms, all matrix elements are chosen exactly as described by these authors, except that for oxygen β° has been modified.[17]

For d orbitals, semiempirical integrals were made a function of the electron occupation of the secod-row atom; an iterative procedure is employed to calculate new parameters from the results of one iteration as input to the next. With use of Burns' rules,[18] at each iteration, ζ_d, the d orbital exponent, is calculated from the density matrix obtained in the previous iteration. ζ_d is then used to evaluate new I_d, A_d, $S_{\mu\nu}$, γ_{sd}, γ_{dd}, and $\beta_{\mu\nu}$. The value of the two-center integral, $\gamma_{\mu\nu}$, depends *only* on the atoms on which the atomic orbitals ϕ_μ and ϕ_ν are centered, and their azimuthal

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(1) H. Kwart and K. King, "d-orbitals in the Chemistry of Silicon, Phosphorus, and Sulfur", Springer-Verlag, New York, 1979.

(2) (a) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); (b) D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956); (c) D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601, 609 (1962).

(3) H. H. Jaffe, *J. Phys. Chem.*, **58**, 185 (1953).

(4) (a) J. B. Collins, P. von R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5742 (1976); (b) F. J. Marsh and M. S. Gordon, *Chem. Phys. Lett.*, **45**, 255 (1977).

(5) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

(6) (a) D. P. Santry, *J. Am. Chem. Soc.*, **90**, 3309 (1968); (b) J. R. Sabin, D. P. Santry, and K. Weiss, *ibid.*, **94**, 6651 (1972).

(7) G. Höjer and S. Meza, *Acta Chem. Scand.*, **26**, 3723 (1972).

(8) K. A. Levison and P. G. Perkins, *Theor. Chim. Acta*, **14**, 206 (1969).

(9) (a) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 73, 78 81 (1972); (b) *J. Chem. Soc. A*, 3579 (1971).

(10) M. Ohsaku, N. Bingo, W. Sugikawa, and H. Murata, *Bull. Chem. Soc. Jpn.*, **52**, 355 (1979).

(11) K. W. Schulte and A. Schweig, *Theor. Chim. Acta*, **33**, 19 (1974).

(12) D. Gonbeau, Ph.D. Dissertation, Universite' de Pau, 1978.

(13) A. Serafini, J.-M. Savariault, P. Cassoux, and J.-F. Labarre, *Theor. Chim. Acta*, **36**, 241 (1975).

(14) G. Kuehnlenz, Ph.D. Dissertation, University of Cincinnati, 1972.

(15) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807 (1968).

(16) R. L. Ellis, G. Kuehnlenz, and H. H. Jaffe, *Theor. Chim. Acta*, **26**, 131 (1972).

(17) P. Jacques, J. Faure, O. Chalvet, and H. H. Jaffe, *J. Phys. Chem.*, in press.

(18) G. Burns, *J. Chem. Phys.*, **41**, 1521 (1964).

0002-7863/81/1503-1358$01.25/0