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The Structure of Uracil: A Laser Ablation Rotational Study

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The jet-cooled rotational spectrum of uracil has been investigated using laser ablation molecular beam Fourier transform microwave (LA-MB-FTMW) spectroscopy. The quadrupole structure originated by the two ^{14}N nuclei of uracil has been completely resolved and assigned. This provides a definitive method to establish the pyrrolic or pyrimidinic nature of the N nuclei and allows us to conclude that the observed tautomer of uracil in the gas phase is the diketo form. From the rotational constants of the isotopic species detected, a structure of uracil has been determined.

Uracil is a solid with a high melting point (330 °C) and a low vapor pressure, and consequently, it is elusive to gas-phase studies. In 1988 Brown et al.,[1] heating under carefully controlled conditions to avoid decomposition, vaporized uracil and obtained its first rotational spectrum using a Stark-modulation free-jet absorption spectrometer. Since then, advances in instrumentation, mainly as a result of combining molecular beams (MB) and Fourier transform microwave (FTMW) spectroscopy,[2−5] have made it possible to achieve unparalleled sensitivity and resolution. More recently the combination of laser-ablation devices with molecular beam Fourier-transform microwave spectroscopy (LA-MB-FTMW) has become an experimental method generally applicable to the study of organic solids.[6] Hence, neutral aliphatic amino acids in the gas phase have been probed over the last years[7−14] extracting relevant structural information. The glycine−water complex has been generated and characterized for the first time using this technique.[15]

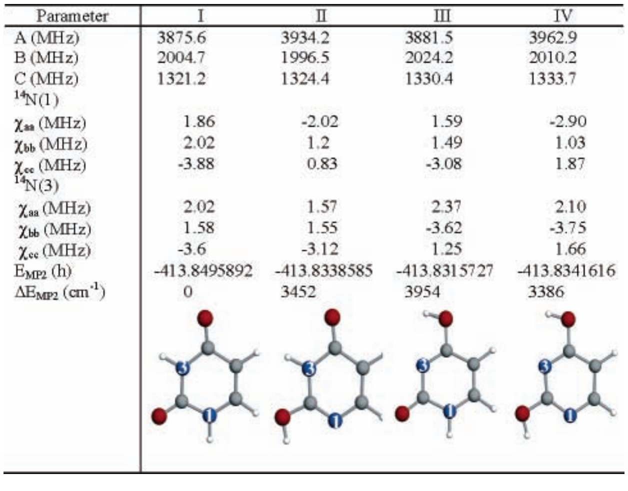
In the present work we have probed uracil in gas phase under high-resolution conditions using our LA-MB-FTMW instrument.[6] Uracil rods obtained by pressing the commercial sample (Aldrich, 98%) with drops of a binder were vaporized by the green light of a pulsed Nd:YAG laser (ca. 50 mJ/pulse). The ablation products were seeded in Ne at backing pressures of 7 bar and expanded supersonically into the Fabry−Pérot resonator to form a molecular beam where the uracil molecules are probed with microwave radiation in the 6−18 GHz range. The molecular emission signals are captured in the time domain and converted to the frequency domain by Fourier transform. Uracil bears two ^{14}N atoms with nonzero quadrupole moments ($I = 1$), which interact with the electric field gradient at the nucleus. As a consequence of this interaction the nuclear spin couples to the rotational angular momentum. Coupling of two ^{14}N nuclei results in a complicated hyperfine structure, with many components spread over several megahertzs (see figure in Supporting Information). After many trials the patterns of seven ^{a}R- and nine ^{b}R-branch transitions were finally assigned. A total of 223 hyperfine transitions were fitted[16] using a Watson's A-reduced semirigid rotor Hamiltonian

TABLE 1: Experimental Rotational Parameters for the Parent and Single ^{15}N Isotopic Species of ^{14}N−^{14}N Uracil

	^{14}N$_1$−^{14}N$_3$	^{15}N$_1$−^{14}N$_3$	^{14}N$_1$−^{15}N$_3$
A/MHz	3883.86951(14)^d	3854.02926(36)	3857.09261(28)
B/MHz	2023.73119(19)	2012.58402(61)	2023.79925(46)
C/MHz	1330.926922(56)	1322.60527(22)	1327.80675(17)
Δ^a/u Å^2	−0.12933(17)	−0.1308(4)	−0.1320(3)
χ_{aa}(N$_1$)/MHz	1.7672(68)		1.7604(61)
χ_{bb}(N$_1$)/ MHz	1.9748(83)		1.9832(54)
χ_{cc}(N$_1$)/ MHz	−3.7420(83)		−3.7436(54)
χ_{aa}(N$_3$)/ MHz	1.9161(68)	1.9293(82)	
χ_{bb}(N$_3$)/ MHz	1.5344(90)	1.5128(73)	
χ_{cc}(N$_3$)/ MHz	−3.4505(90)	−3.4421(73)	
σ^b/kHz	2.7	2.4	1.8
N^c	223	15	15

[a] $\Delta = I_c - I_a - I_b$ is the inertial defect. Conversion factor: 505379.1 MHz u Å^2. [b] rms deviation of the fit. [c] Number of measured transitions. [d] Standard error in parentheses in units of the last digit.

TABLE 2: Calculated Rotational Constants, Quadrupole Coupling Constants, and Relative Energies of the Lower-Energy Tautomers of Uracil at the MP2/6-311++G(d,p) Level of Theory



Parameter	I	II	III	IV
A (MHz)	3875.6	3934.2	3881.5	3962.9
B (MHz)	2004.7	1996.5	2024.2	2010.2
C (MHz)	1321.2	1324.4	1330.4	1333.7
^{14}N(1)				
χ_{aa} (MHz)	1.86	-2.02	1.59	-2.90
χ_{bb} (MHz)	2.02	1.2	1.49	1.03
χ_{cc} (MHz)	-3.88	0.83	-3.08	1.87
^{14}N(3)				
χ_{aa} (MHz)	2.02	1.57	2.37	2.10
χ_{bb} (MHz)	1.58	1.55	-3.62	-3.75
χ_{cc} (MHz)	-3.6	-3.12	1.25	1.66
E_{MP2} (h)	-413.8495892	-413.8338585	-413.8315727	-413.8341616
ΔE_{MP2} (cm^{-1})	0	3452	3954	3386

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TABLE 3: Experimental Rotational Parameters of $^{15}N-^{15}N$ Uracil and Its Single ^{13}C and ^{18}O Isotopomers

	$^{15}N_1-^{15}N_3$	$^{15}N_1-^{15}N_3-^{13}C_2$	$^{15}N_1-^{15}N_3-^{13}C_4$	$^{15}N_1-^{15}N_3-^{13}C_5$	$^{15}N_1-^{15}N_3-^{13}C_6$	$^{15}N_1-^{15}N_3-^{18}O_7$	$^{15}N_1-^{15}N_3-^{18}O_8$
A/MHz	3827.19193(41)[c]	3823.19727(39)	3824.72909(19)	3789.65954(26)	3741.91665(12)	3773.29559(57)	3781.20776(33)
B/MHz	2012.63959(73)	2001.26041(69)	1999.40114(33)	2001.11195(46)	2012.66429(23)	1935.75876(98)	1929.54712(57)
C/MHz	1319.46170(24)	1314.08962(24)	1313.46776(11)	1310.04303(15)	1309.18212(7)	1279.83296(34)	1278.01958(20)
Δ/u Å^2	−0.13307(51)	−0.13300(49)	−0.13281(24)	−0.13363(33)	−0.13186(15)	−0.13223(72)	−0.13214(42)
σ^a/kHz	1.8	1.7	0.8	1.1	0.5	2.5	1.5
N^b	6	6	6	6	6	6	6

[a] rms deviation of the fit. [b] Number of measured transitions. [c] Standard error in parentheses in units of the last digit.

(I^r representation),[17] $H_R^{(A)}$, supplemented with a term to account for the nuclear quadrupole coupling contribution, H_Q,[18] set up in the coupled basis set (I_1 I_2 I J F), $I_1 + I_2 = I$, $I + J = F$.[19] The energy levels involved in each transition are thus labeled with the quantum numbers J, K_{-1}, K_{+1}, I, F. The determined rotational constants A, B, and C and quadrupole coupling constants χ_{aa}, χ_{bb}, and χ_{cc} are given in Table 1.

Uracil may exist in various tautomeric forms (see Table 2) differing from each other by the position of the hydrogens, which may be bound to either nitrogen or oxygen atoms (keto-enolic equilibrium). The rotational and quadrupole coupling constants obtained from structures optimized at the MP2/6-311++G(d,p) level[20] for the lower-energy tautomers (I to IV) are reported in Table 2. The particular tautomer observed in the supersonic expansion cannot be conclusively identified considering only the rotational constants. Comparison between experimental and predicted rotational constants in Tables 1 and 2 seems to indicate that the form observed in gas phase is the keto-enolic form III, in sharp contrast with the relative stabilities predicted ab initio. Fortunately, the values of the quadrupole coupling constants provide an independent approach to identify the tautomers. Specifically, χ_{cc} corresponds with one of the principal quadrupole coupling tensor elements and provides information on the electric field gradient along the direction of an axis perpendicular to the heterocyclic ring. For pyrrolic nitrogens (−N<) χ_{cc} is negative.[21−23] In contrast, pyridinic nitrogens (−N=) have positive values of χ_{cc}.[22−24]

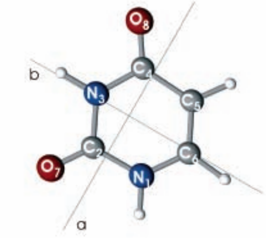
The experimental χ_{cc} values of −3.74 and −3.45 MHz in Table 1 correspond to two pyrrolic nitrogens and thus allow us to establish unambiguously the presence of the diketo tautomer of uracil in our supersonic expansion. The quadrupole hyperfine structure can thus be taken as a unique fingerprint to distinguish between different conformers or tautomers of a molecule when their rotational constants are alike.[12]

To obtain the structure, the investigation of the rotational spectrum was extended to the monosubstituted species. Due to the high sensitivity reached in the experiment, transitions of the $^{14}N-^{15}N$ species (natural abundance 0.4%) were detected. Analysis of the spectra was performed using the same Hamiltonian as above, but with a simplified term for H_Q corresponding to only one nitrogen nucleus. The coupling scheme $I + J = F$ was employed. The determined spectroscopic constants are displayed in Table 1. An enriched sample with two ^{15}N was employed to favor the observation of the ^{13}C and ^{18}O isotopic species in their natural abundances, because no quadrupole coupling interaction can occur. Thus the intensity of each transition is not shared by several hyperfine components. The rotational constants of the ^{13}C and ^{18}O isotopomers are given in Table 3.

The practical invariance of the inertial defect $\Delta = I_c - I_a - I_b$ through all isotopic substitutions, and its small value points to the planarity of the diketo tautomer of uracil. All measured transition frequencies for the observed isotopomers are provided as Supporting Information.

TABLE 4: Substitution (r_s) Structure for the Diketo Tautomer of Uracil (Distances in Å and Angles in Degrees)

r(N_1–C_2)	1.386(5)[a]
r(N_3–C_4)	1.38(2)
r(C_4–C_5)	1.451(4)
r(C_5–C_6)	1.379(4)
r(C_6–N_1)	1.352(14)
r(C_2–O_7)	1.219(4)
r(C_4–O_8)	1.22(2)
$\angle N_1C_6C_5$	122.3(6)
$\angle C_2N_1C_6$	123.0(11)
$\angle C_5C_4N_3$	115.4(16)
$\angle C_6C_5C_4$	118.8(12)
$\angle N_1C_2O_7$	122.3(8)
$\angle C_5C_4O_8$	118.8(7)



[a] Derived errors in parentheses in units of the last digit.

The rotational constants of Tables 1 and 3 for the monosubstituted and $^{15}N-^{15}N$ species have been used to determine the structure using the substitution method of Kraitchmann,[25] which yields the coordinates of the substituted atoms in the principal axis system (see Table S6, Supporting Information). From these coordinates, the substitution structure r_s, shown in Table 4, was derived.

The high sensitivity and resolution reached in our LA-MB-FTMW experiment made it possible to obtain the structure of uracil and to analyze the quadrupole hyperfine structure originated by the two ^{14}N nuclei. Hence the pyrrolic nature of nitrogen atoms has been conclusively established. The present results constitute a first step to the investigation of other pyrimidinic and purine bases with the forementioned technique to assign their different tautomers in gas phase. In fact, thymine, cytosine, adenine, and guanine are already under study in our laboratory, and their quadrupole coupling hyperfine structures are being analyzed.

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Supporting Information Available: Tables of the rotational frequencies of the parent and isotopic species of uracil together with a figure showing a section of a rotational transition of parent uracil, the coordinates of the atoms in the principal axis system, and complete ref 20. This material is available free of charge via the Internet at http://pubs.acs.org.

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