Rotational Spectra of Nucleobases

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Outline

- Introduction
- Nucleobases
  - Formation Processes
  - Available Data
- Laboratory Measurements on Uracil
- Potential Interstellar Sources
- Summary

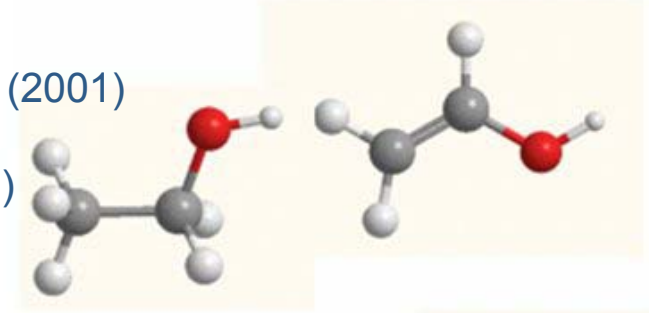
Introduction

Variety of complex organic “prebiotic” molecules found in the ISM:

alcohols

vinylalcohol Turner et al., ApJ 561 (2001)

ethanol Miller et al., A&A 205 (1988)

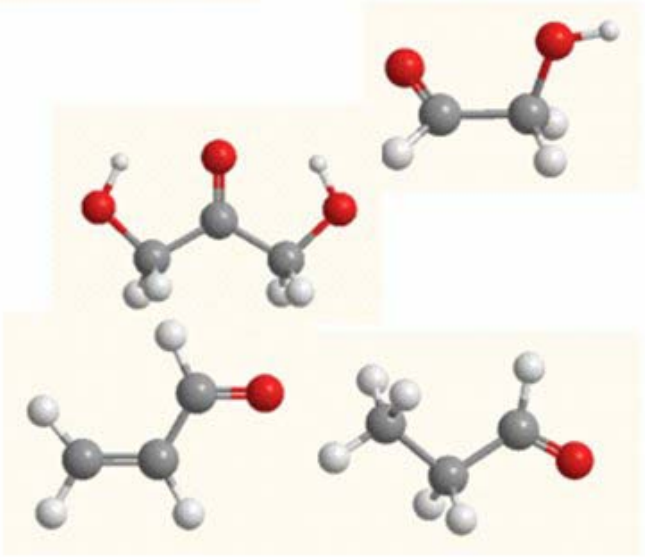


sugars & aldehydes

glycolaldehyde
Hollis et al., ApJ. 540 (2000)

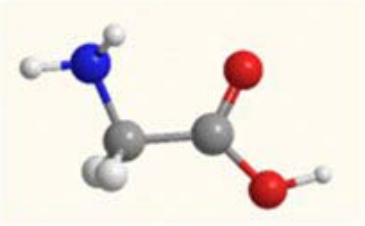
1,3-dihydroxyacetone
Widicus et al., ApJ 624 (2005)

propenal & propanal
Hollis et al., ApJ 610 (2004)

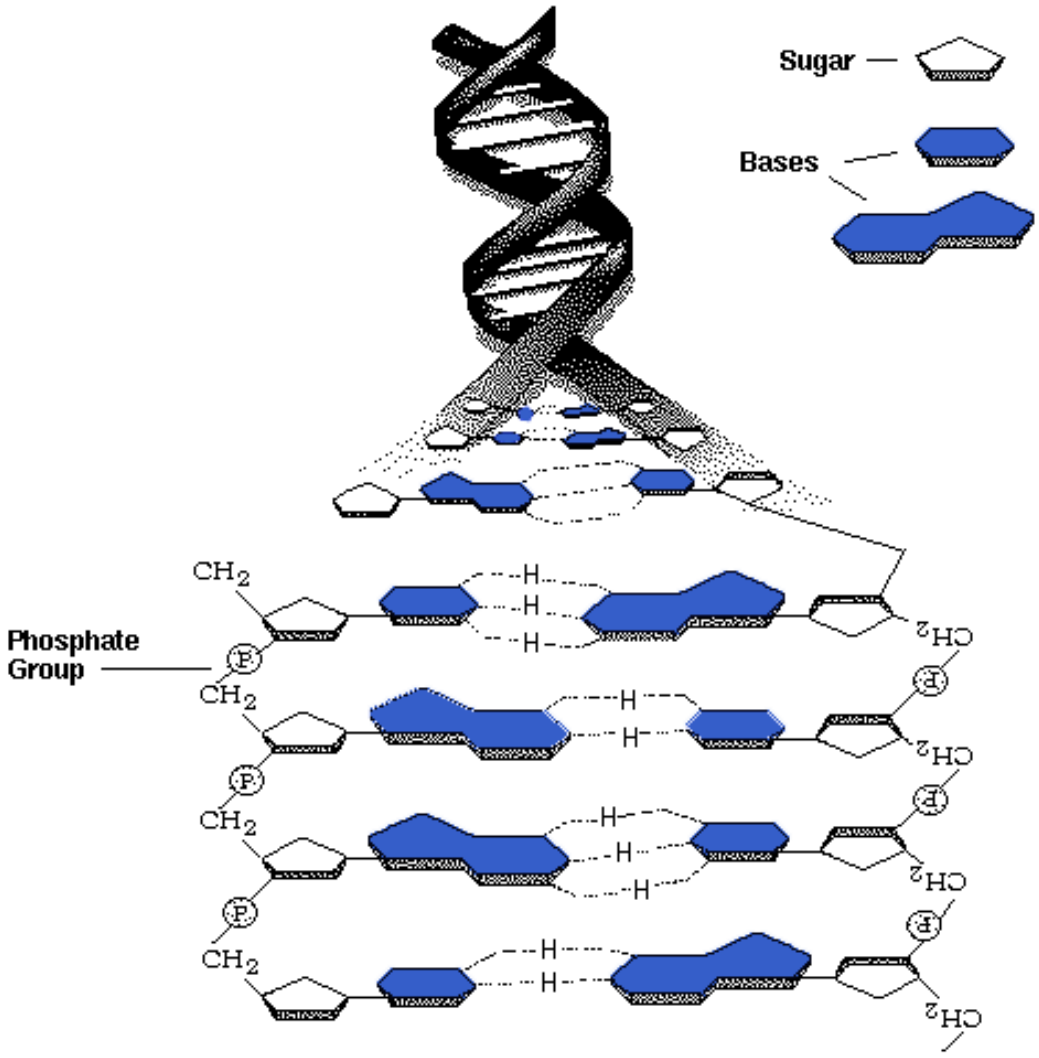


amino acid

glycine (?)
Kuan et al., ApJ 593 (2003)
Snyder et al., ApJ 619 (2005)



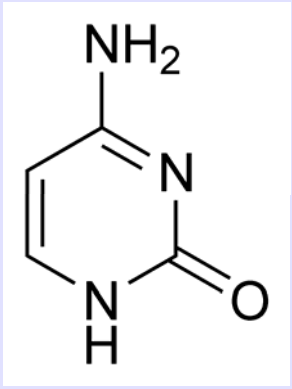
Nucleobases – building blocks of DNA and RNA



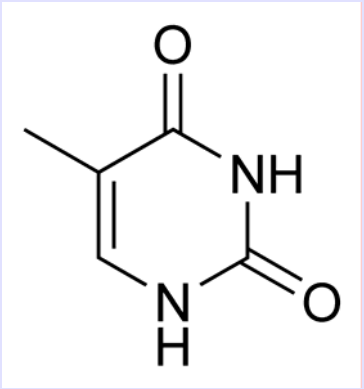
Nucleobases

pyrimidines:

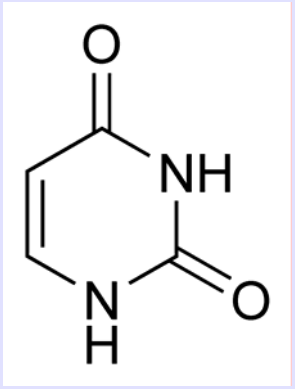
cytosine



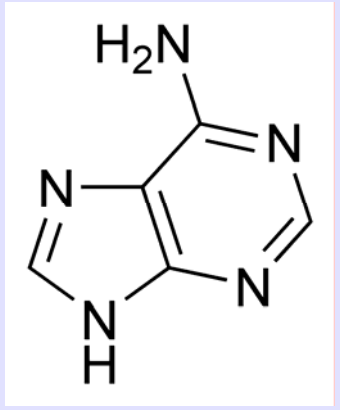
thymine



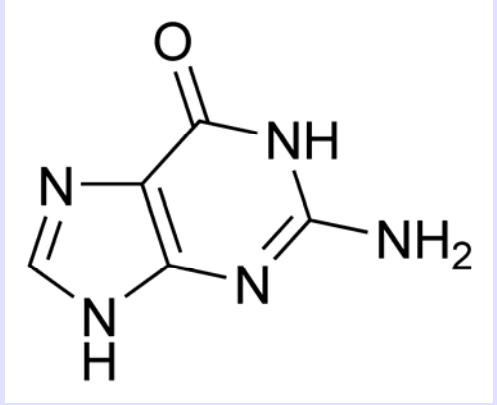
uracil



purines:



adenine

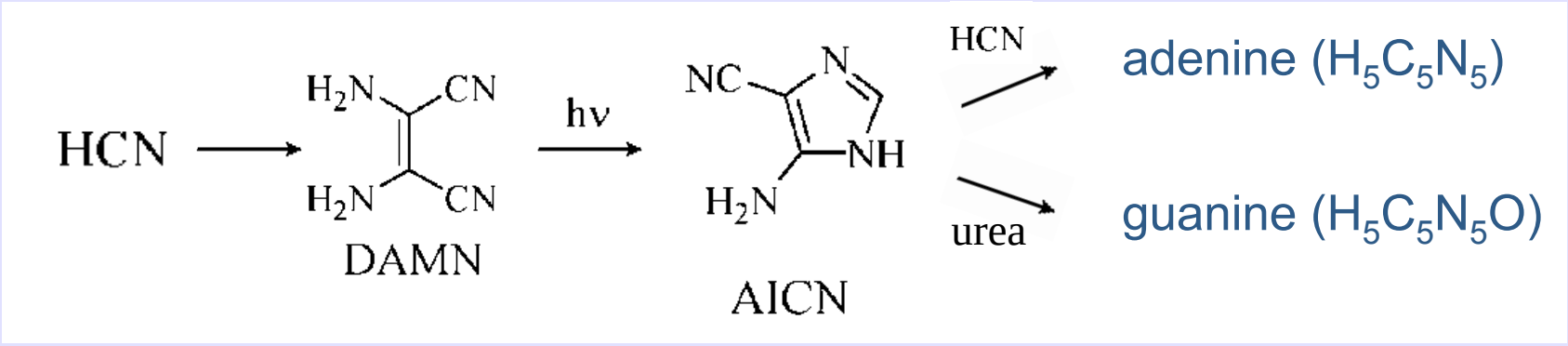


guanine

Formation Processes

Synthesis on icy grains might be similar to processes on the prebiotic earth:

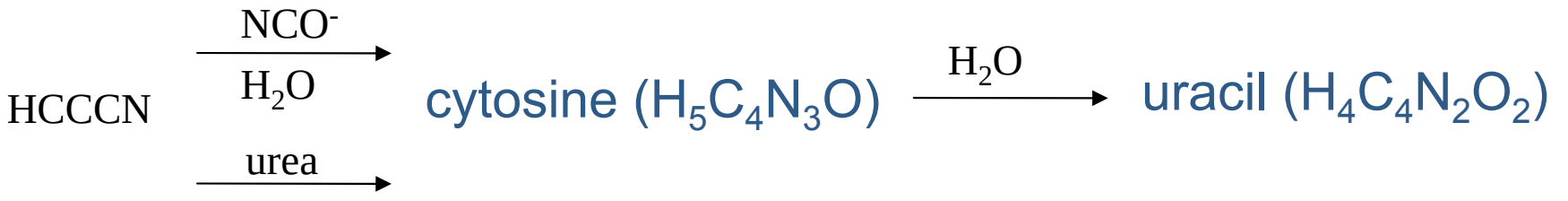
- HCN polymerization forms purine nucleobases:
  (e.g. Ferris et al., Tetrahedron 40, 1093-1120 (1984))



first step, dimerization of HCN unlikely in gas phase at ISM temperatures

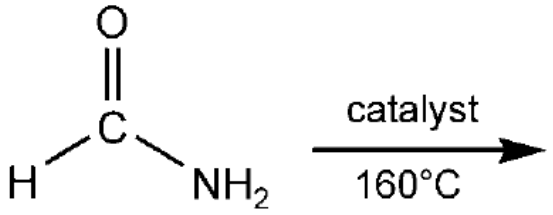
Smith *et al*., *A&A* 369, 611-615 (2001)

(e.g. Saladino *et al., Top. Cur. Chem.* 259, 29-68 (2005))



Formation Processes

- catalytic processes of formamide on interstellar dust analogues form predominantly pyrimidines
  Saladino et al., ChemBioChem 6, 1368-1374 (2005)



uracil

cytosine

- incorporation of N-heteroatoms and addition of sidegroups in PAHs:

  exchange of HCN for C_2H_2 in ring formation leads to N-heterocycles
  Ricca *et al., Icarus* 154, 516-521 (2001)

  evidence for PANHs in 6.2 **m**m emission feature of PAHs
  Hudgins *et al., ApJ* 632:316-332 (2005)

  incorporation of sidegroups like $–NH_2$, -OH, =O, -CN, $-CH_3$ upon UV-irradiation of coronene in cosmic ice analogues
  Bernstein *et al., ApJ* 576, 1115-1120 (2002)

Formation Processes

- adenine, guanine and uracil were found in the Murchison and Orgueil meteorites
  Stoks *et al., Geoch. et Cosmoch. Acta* 45, 563-569 (1981);
  Stoks *et al. Nature* 282, 709-710 (1979)

large fragment of Orgueil meteorite

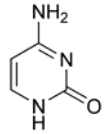
However:

- Searches for N-heterocycles pyrrole (C_4H_4N), pyridine (C_5H_5N), quinoline, isoquinoline (C_9H_7N) so far unsuccessful

  pyrimidine ($C_4H_4N_2$) only tentatively detected towards W51 e1/e2
  Charnley *et al., ASR* 36, 137-145 (2005)
  Myers *et al., ApJ* 241, 155-157 (1980)

- N-heterocycles and nucleobases are unlikely to survive in strong UV-fields
  half life time ~ years in diffuse ISM, ~ Myrs in dense clouds
  Peeters *et al., A&A* 433, 583-590 (2005), Peeters *et al., ApJ* 593, L129-L132 (2003)

Nucleobases: Previous and New Rotational Data

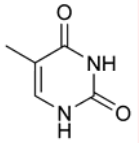


cytosine

Stark measurements: 59-63 GHz (55 lines) - *A, B, C*

Brown *et al., JACS* 111, 2308-2310 (1989) + two isomers

new data: 74-97 GHz (30 lines)



thymine

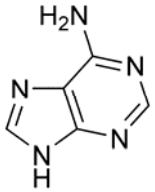
Stark measurements: 59-62 GHz (59 lines)

A, B, C and centrifugal distortion terms

Brown *et al., Chem. Com.* 1, 37-38 (1989) + HFS partly resolved

new data: 73 - 88 GHz on E and A states (28 lines)

7 - 24 GHz, HFS resolved (40 lines)

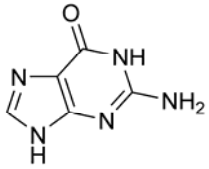


adenine

Stark measurements: 59-64 GHz (58 lines) - *A, B, C*

Brown *et al., Chem. Phys. L.* 156, 61-63 (1989)

new data: 73-90 GHz (12 lines)



guanine

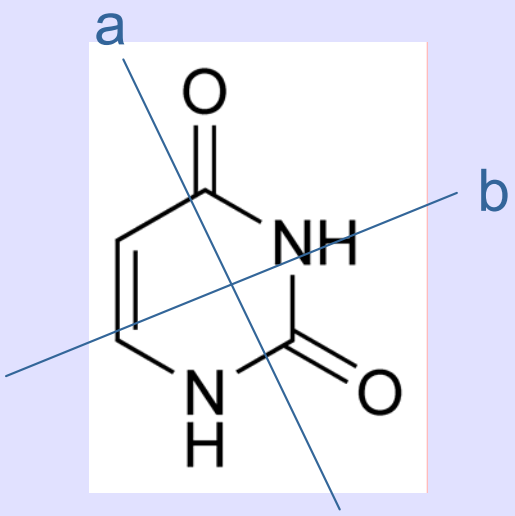
no pure rotational or ro-vibrational measurements to date

but: structure from quantum chemical calculations

MP2/6-31G: Stewart *et al., JACS* 116, 7282-7286 (1994)

MP2/cc-XXX: Wang *et al., JCP* 124, 044303 (2006) … and others

Uracil: Previous Work and Main Characteristics



planar, asymmetric rotor

rot. constants: A = 3884 MHz

B = 2024 MHz **k** = - 0.46

C = 1331 MHz

dipole moments: $\mathbf{m}_a$ = 1.61 D

$\mathbf{m}_b$ = 3.52 D

- Stark measurements: 65 rotational transitions between 57 - 63 GHz

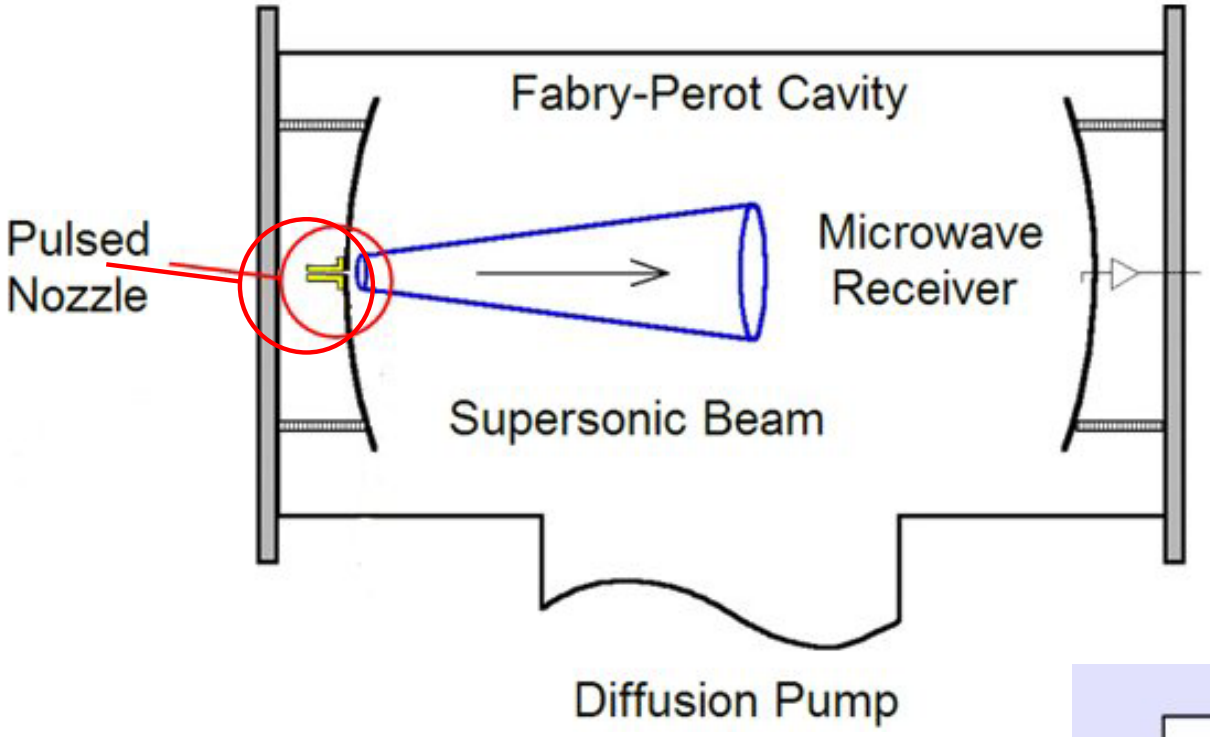
  Brown *et al. JACS* 110 (1988) 2330

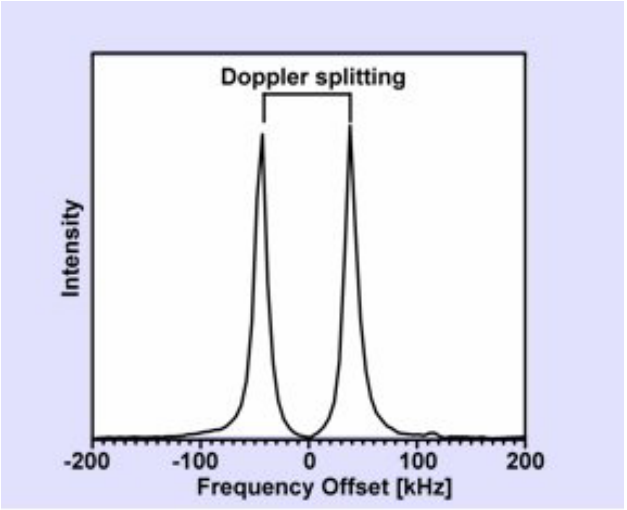
- Hyperfine Structure due to two ^{14}N nuclei ($\mathbf{I}_{N\,i}$ = 1) was not resolved:

  $\mathbf{I_{N1}} + \mathbf{I_{N2}} = \mathbf{F_1}$ $\quad$ $\mathbf{J} + \mathbf{F_1} = \mathbf{F}$

  expected splitting for low J lines: ~ MHz

Experimental Setup – FTMW Spectrometer (Fourier Transform MicroWave)





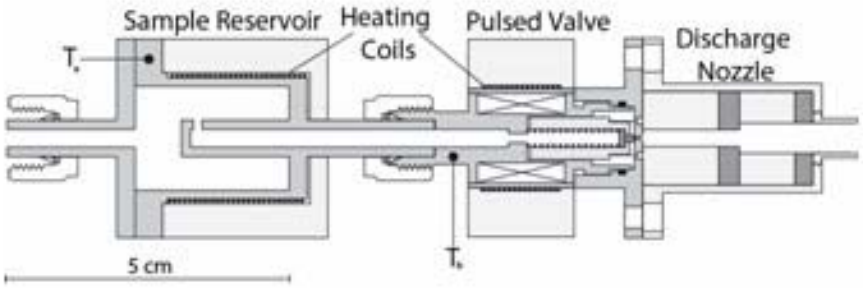
frequency range: 5 – 43 GHz

resolution / accuracy: ~20 kHz / 2 kHz

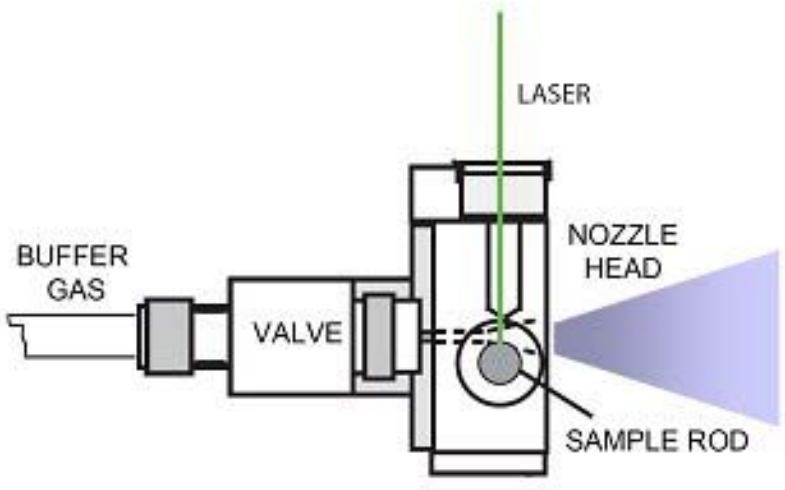
supersonic beam $\rightarrow T_{rot} = 1 - 3$ K

Experimental Setup - Production

- Uracil, m.p. 335 °C, commercially available
  solid with no significant vapour pressure at room temperature

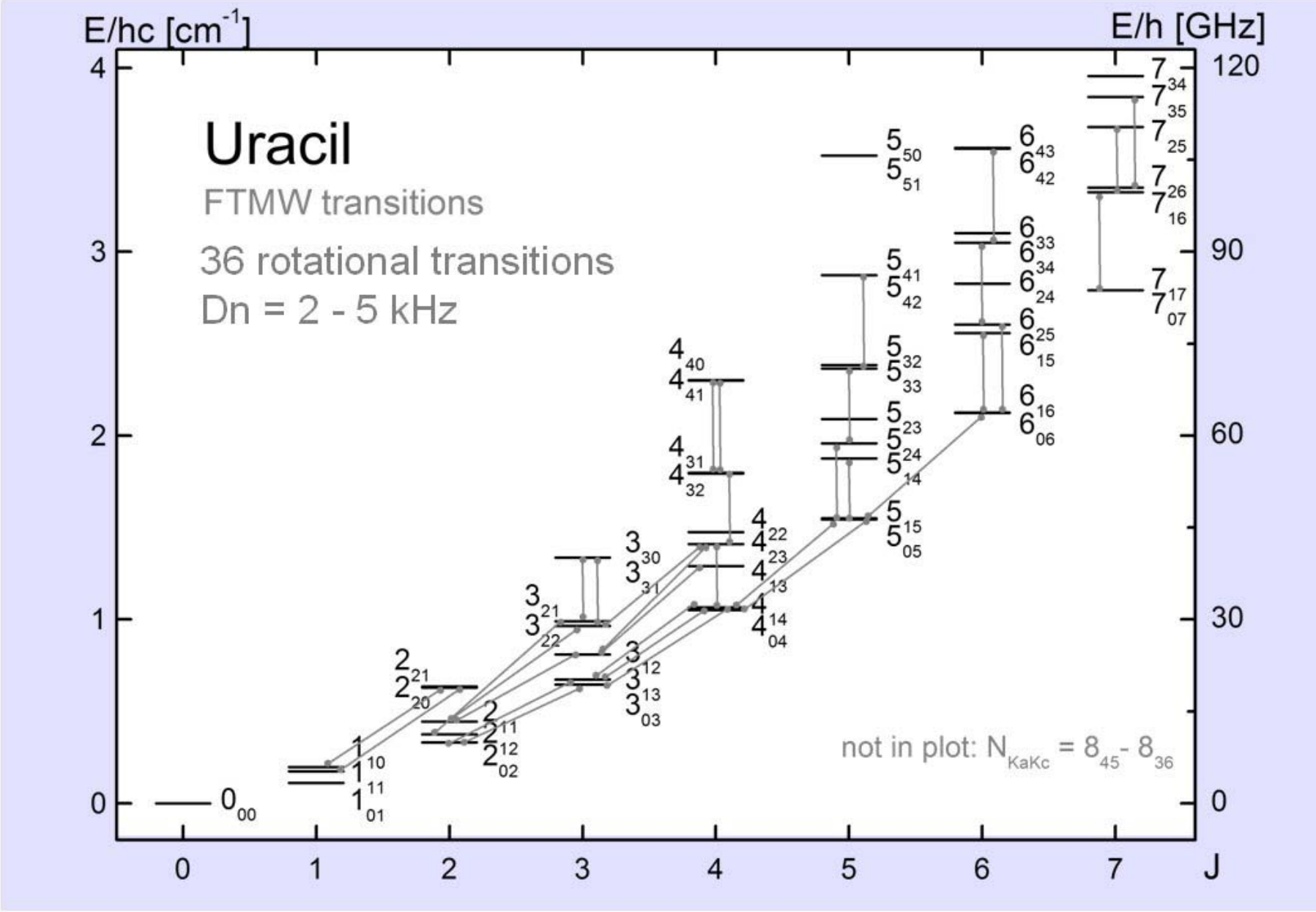


- sample powder resistively heated to 180 °C (limited by solenoid)
- strong increase in signal strength between 150-180 °C

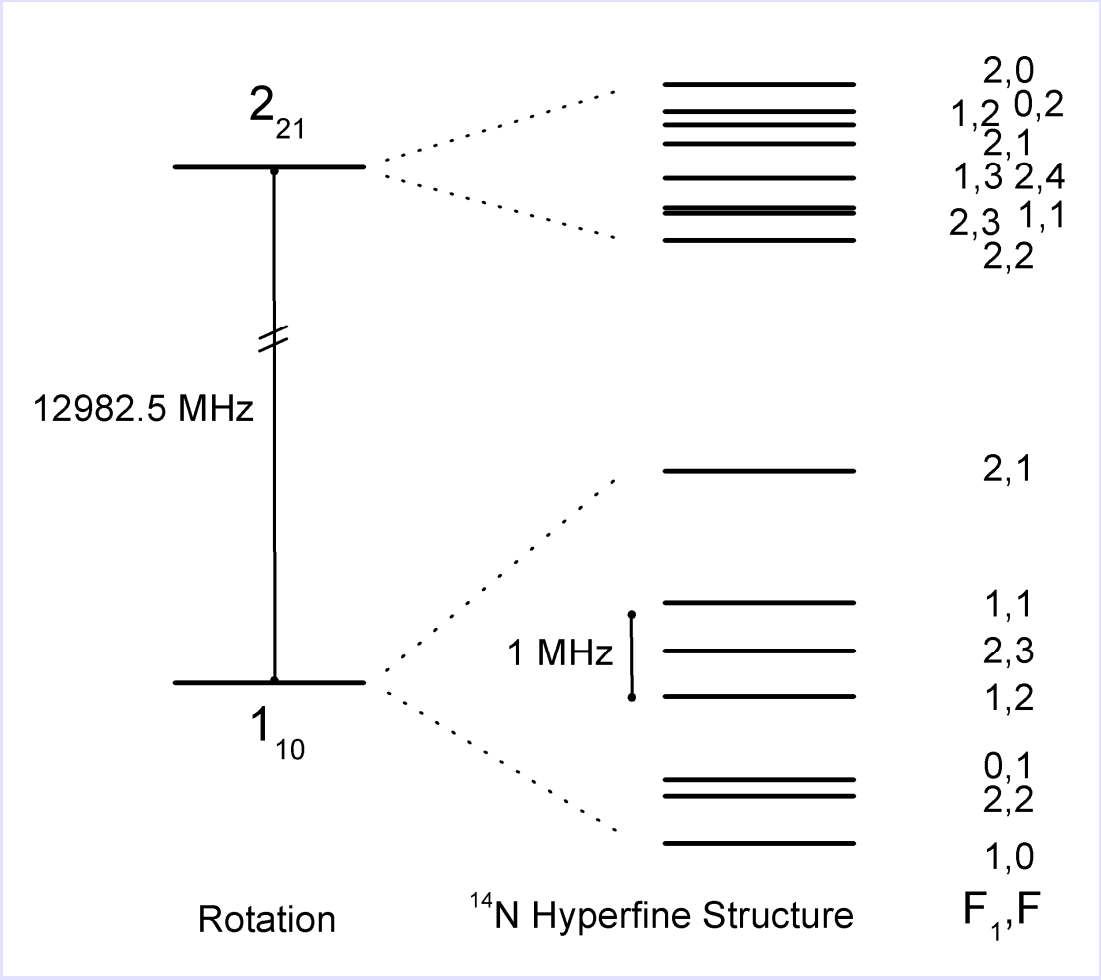


- production of stable rods from uracil with a commercial binder
- Nd:YAG laser ablation with short (5 ns), intense (28 mJ) pulses at a wavelength of 1064 nm
- factor 4 - 5 higher signal strength
- perpendicular arrangement

Uracil - Energy Level Scheme



Uracil: Hyperfine Structure of the $J_{KaKc}= 2_{21}-1_{10}$ Transition



Selection rules:

DJ = 0, ±1

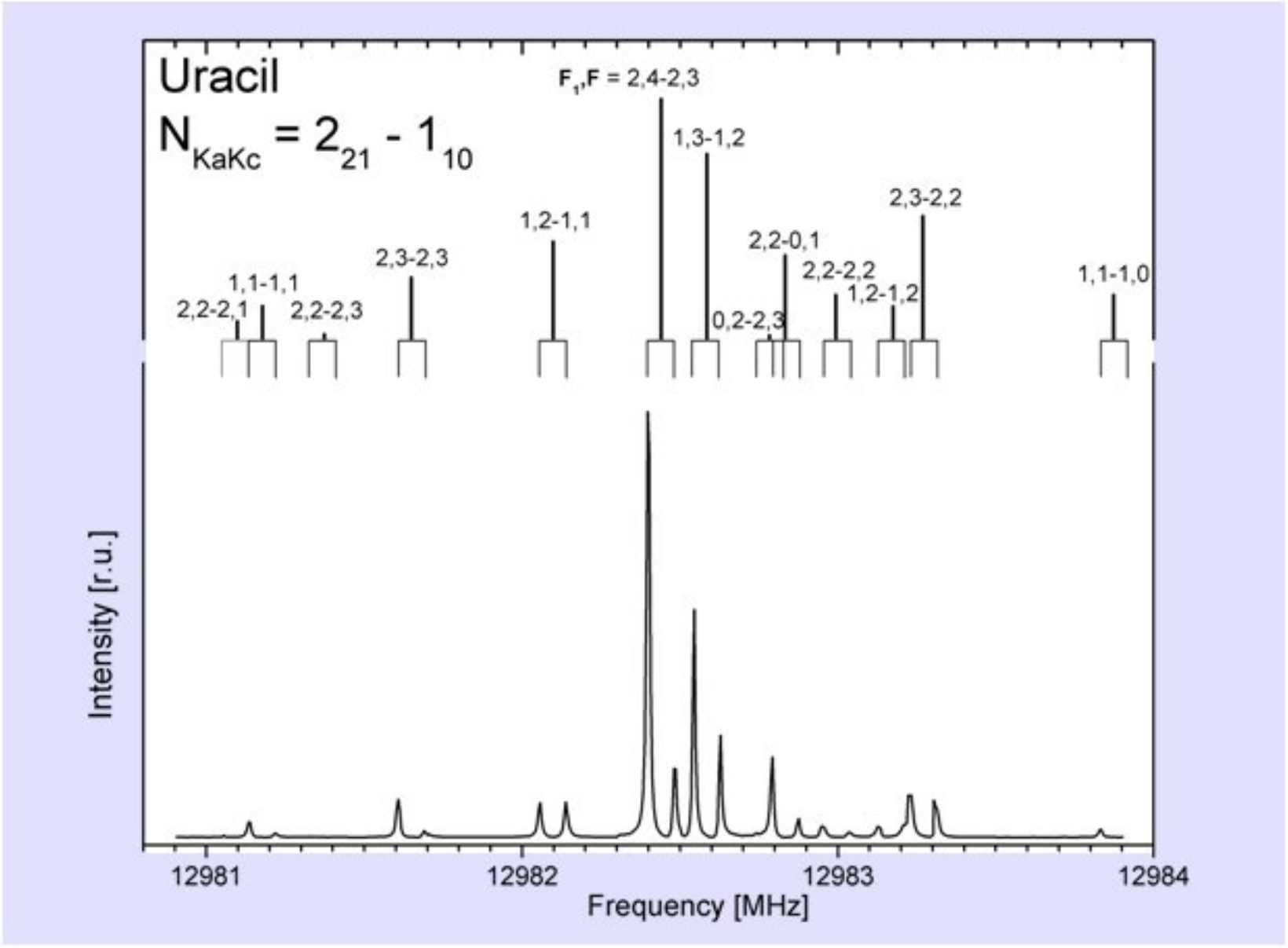
DKa = 0, DKc = 1 a-type

DKa = 1, DKc = 1 b-type

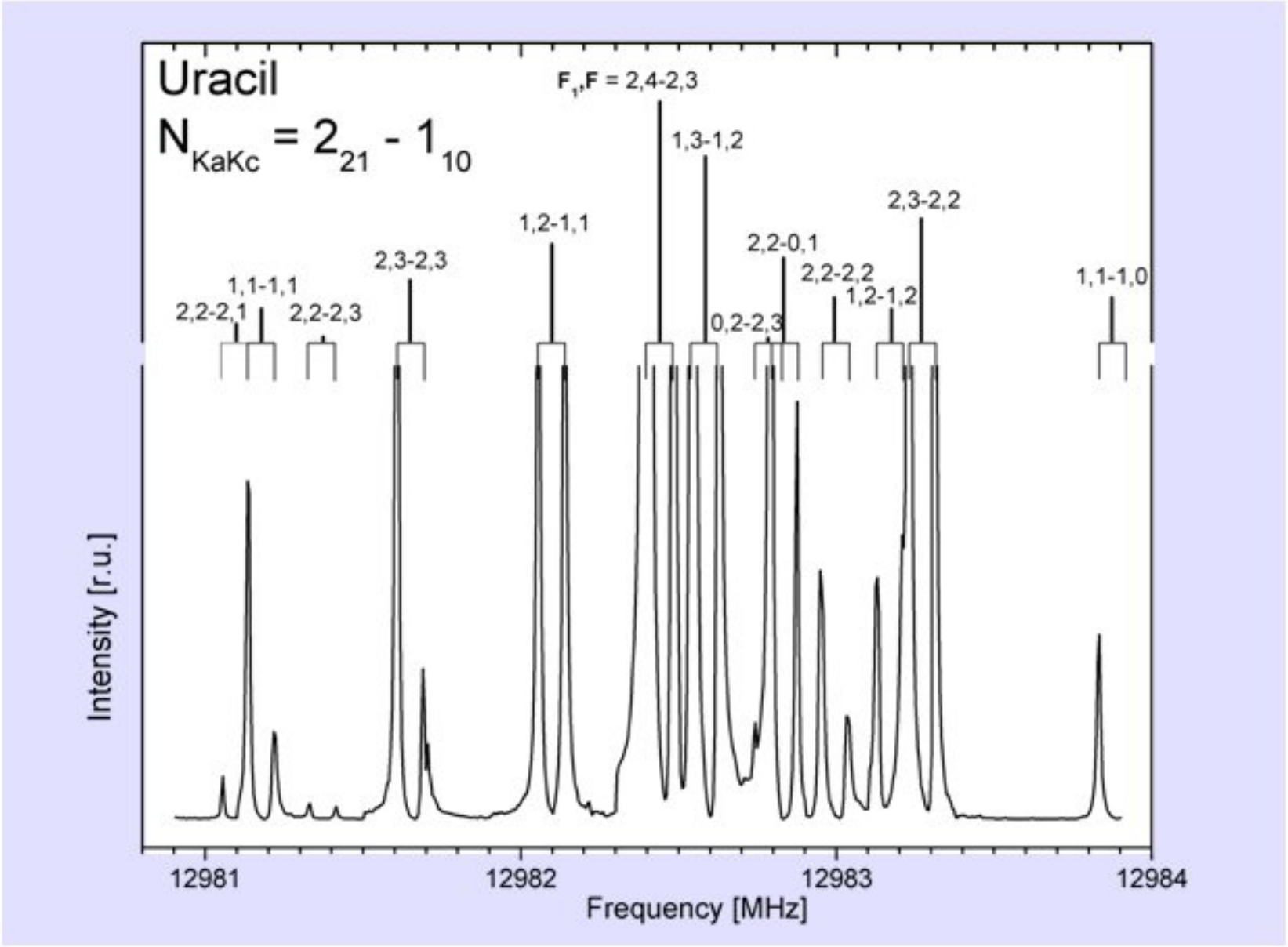
DF = 0, ±1

38 hfs-transitions in total

Uracil: FTMW Spectrum of the 2_{21}-1_{10} Transition



Uracil: FTMW Spectrum of the 2_{21}-1_{10} Transition



Uracil - Stark Measurements

Monash University:

- conventional Stark cell with solid state oscillators: 70 – 100 GHz
- solid uracil sample heated to 300-350 ºC
- adiabatic expansion in a continuous flow of Argon
- rotational temperature: 10 K

44 rotational transitions: J_{max} = 18, $K_{a\,max}$ = 12, $E_{low\,max}$ = 23 cm^{-1}

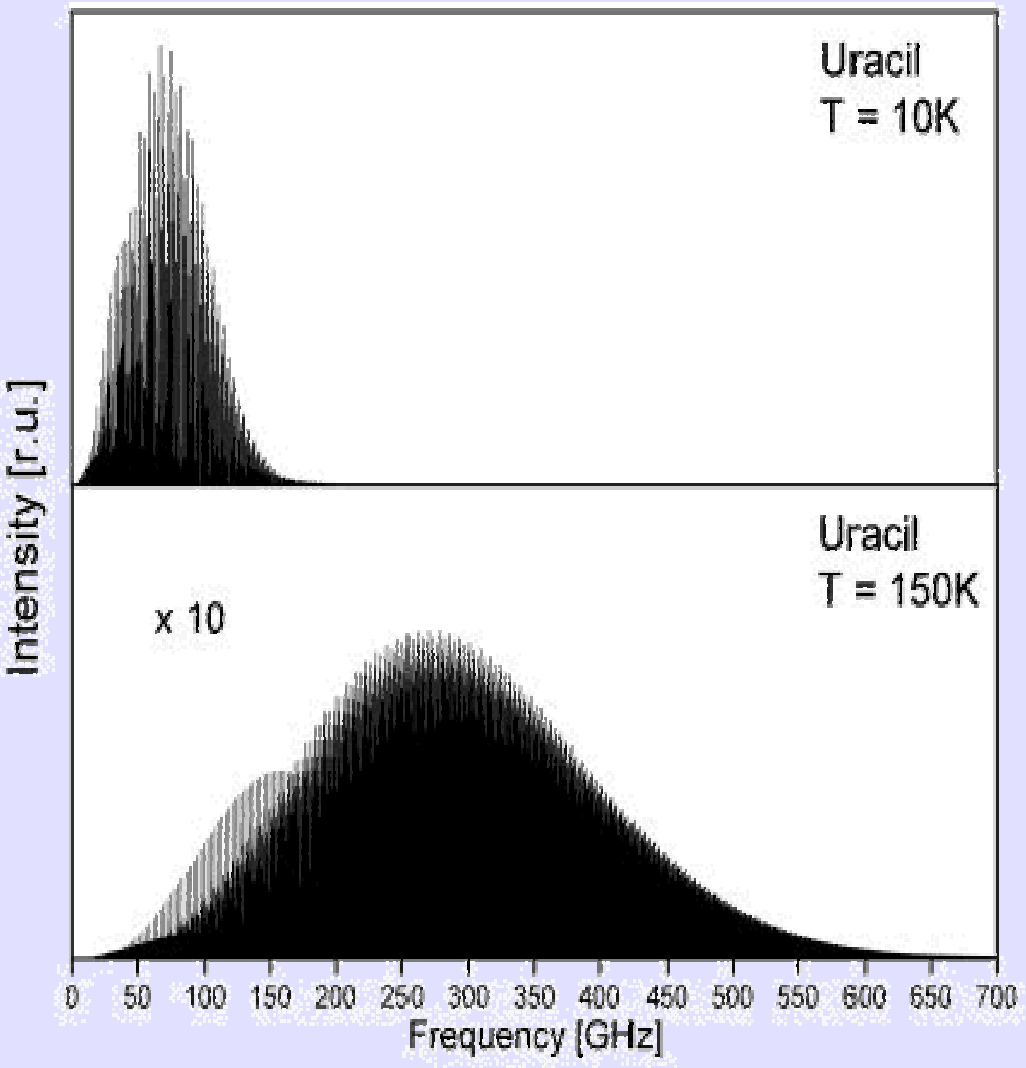
experimental uncertainty ~ 50 kHz or 0.15 km/s

Uracil - Global Analysis

- standard Watson Hamiltonian in *S* – reduction (prolate representation)
- inclusion of nuclear quadrupole interaction terms for both ^{14}N nuclei
- assignment of HFS aided by quantum chemical calculations (B3LYP/6-31G)

Parameter		this work	Brown *et al.*
A	MHz	3883.873021(60)	3883.87825(110)
B	MHz	2023.732581(45)	2023.73267(101)
C	MHz	1330.928108(33)	1330.92380(60)
D_J	kHz	0.06336(44)	0.06029(77)
D_{JK}	kHz	0.10551(232)	0.1047(14)
D_K	kHz	0.4530(32)	0.4724(43)
d_1	kHz	−0.026229(179)	−0.02738(28)
d_2	kHz	0.006803(132)	−0.006532(94)
$\chi_{aa}(N1)$	MHz	1.92548(241)	
$\chi_{bb}(N1)$	MHz	1.52731(318)	
$\chi_{aa}(N2)$	MHz	1.76000(247)	
$\chi_{bb}(N2)$	MHz	1.98111(288)	
No. lines		142	
wrms		1.1	

Uracil - Predictability



at T = 10 K:

- maximum intensities at ~ 70 GHz
- strongest transitions

J =8…12 K_a= 8…12

- uncertainty < 10 kHz ⇘ 0.05 km/s

at T = 150 K:

- maximum intensities at ~ 270 GHz
- strongest transitions

J = 32…40 K_a= 32…40

- uncertainty < 300 kHz ⇘ 0.3 km/s

Uracil - Astronomical Sources

- circumstellar shells around C-rich late type stars
  (e.g. CRL 618, IRC+10216, NGC7027)

  rich in PAHs, complex molecules (benzene, cyanopolyynes,…)

  but: deficient in oxygen (adenine?)

  high excitation temperatures → high partition function

- dark clouds (e.g. TMC-1)

  low rotational temperatures, grain chemistry assumed

  but: ejection into the gas phase?

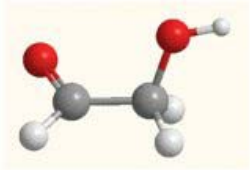
- low and high mass star forming regions
  (e.g. Orion KL, IRAS16293-2422, …)

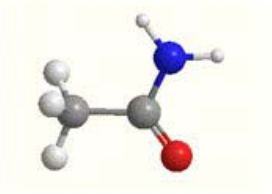
  harbour a variety of complex, organic molecules

  but: high excitation temperatures → high partition function

Uracil – Astronomical Sources

Evidence of extended (> 60”), cold (8 K) halo around SgrB2(N)

glycolaldehyde CH_2OHCHO  Hollis *et al.*, *ApJ* 613, L45-L48 (2004)

acetamide CH_3CONH_2  Hollis *et al.*, *ApJ* accepted (2006)

formation on dust grains → evaporation due to shocks → expansion & cooling

low excitation temperatures + complex chemistry → IDEAL SOURCE

Uracil - Column Density Upper Limits in SgrB2(N)

Survey data towards SgrB2-N(LMH) with Kitt Peak ARO 12m telescope

A. Apponi, private communication

14 lines between 70 - 110 GHz, E_{up} = 12 - 28 cm^{-1}

10 coincide with emission features (< 100 mK)

2 coincide with absorption features

2 are not detected at a significant level above noise (5 - 10 mK)

assuming T_{rot} = 10 K, Dv = 20 km/s and extended emission (Q_S>Q_B=60”-90”):

→ column density upper limit: N < 3 ·10^{13} cm^{-2}

Observations with the GBT 100 m radio telescope are scheduled

→ less contamination

→ lines in absorption?

→ identification via HFS

Summary

- new, highly accurate experimental data on adenine, cytosine, thymine and uracil are available
- precise rotational transition frequency predictions for astrophysical searches up to 300 GHz
- astronomical searches for uracil towards SgrB2(N) in the mm- and cm- wavelength region are in preparation

THANKS!

- Sam Palmer — for designing the laser ablation source
- Jens-Uwe Grabow — for the blue-prints of his rod press
- Maria Sanz — for helpful advice regarding the production of stable rods
- Aldo Apponi — for looking for uracil lines in his KP data
- Carl Gottlieb
  Harshal Gupta
- Thomas Giesen
  Holger Müller

  — for interesting and helpful discussions