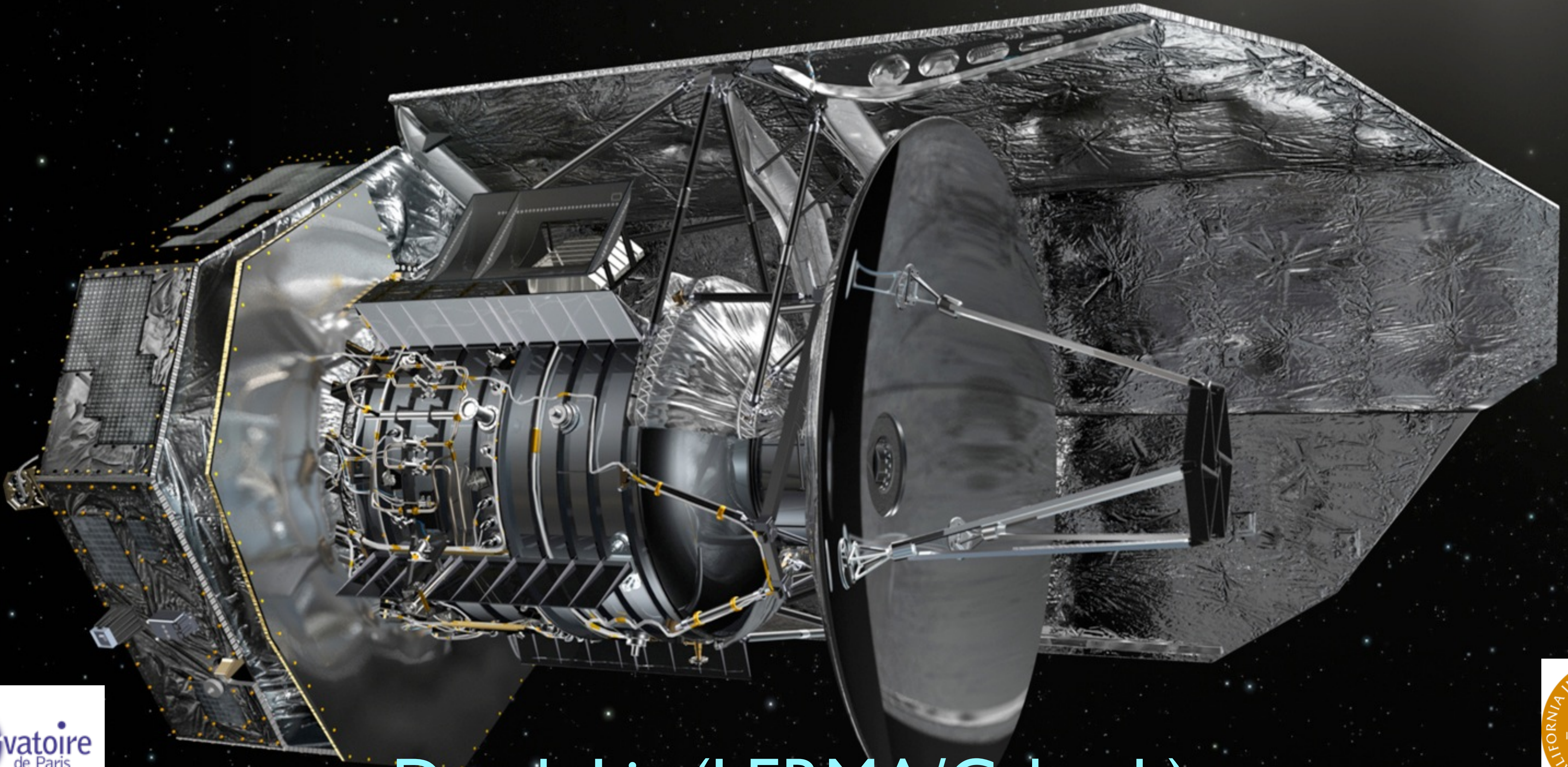
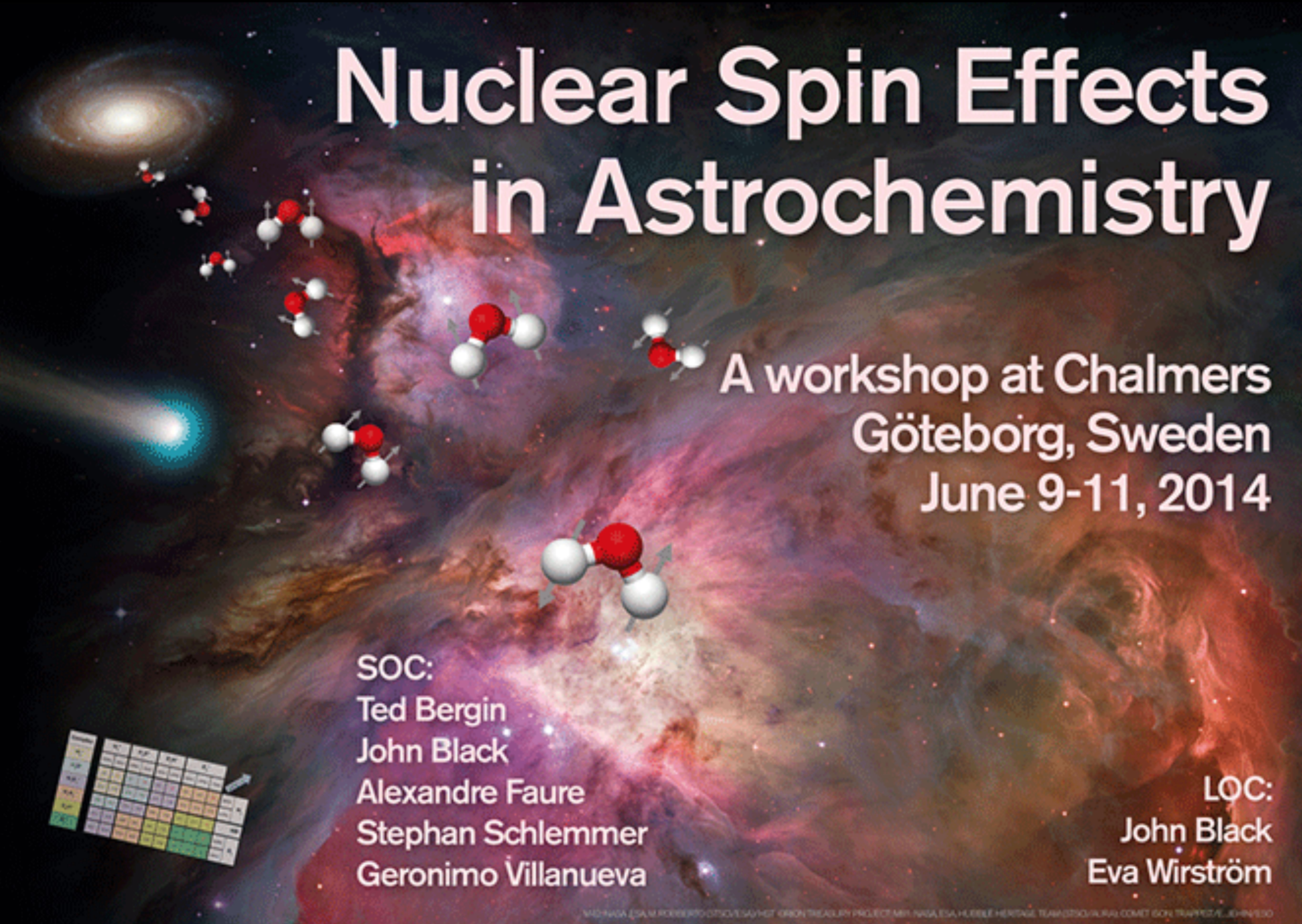
OPR in Water: from ISM to Comets



Darek Lis (LERMA/Caltech)

Zakopane, May 13, 2015



Nuclear Spin Effects in Astrochemistry

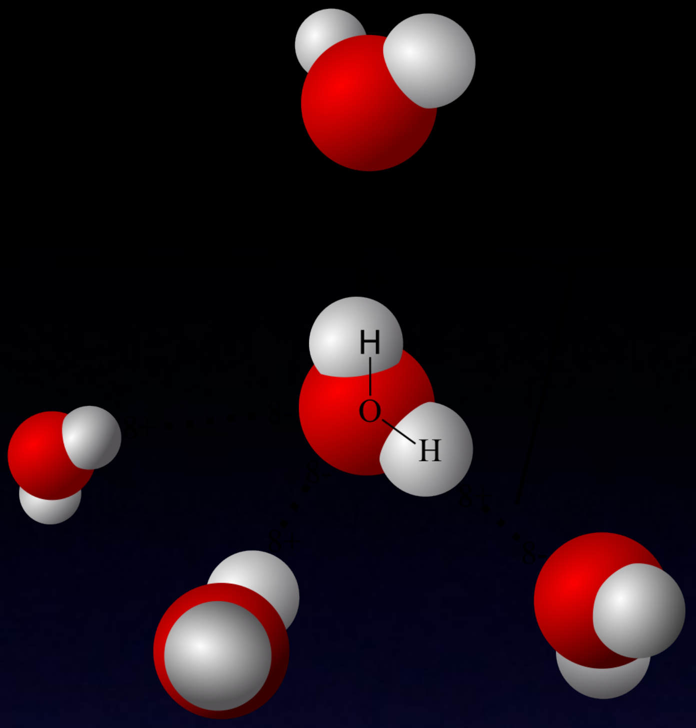
A workshop at Chalmers
Göteborg, Sweden
June 9-11, 2014

SOC:
Ted Bergin
John Black
Alexandre Faure
Stephan Schlemmer
Geronimo Villanueva

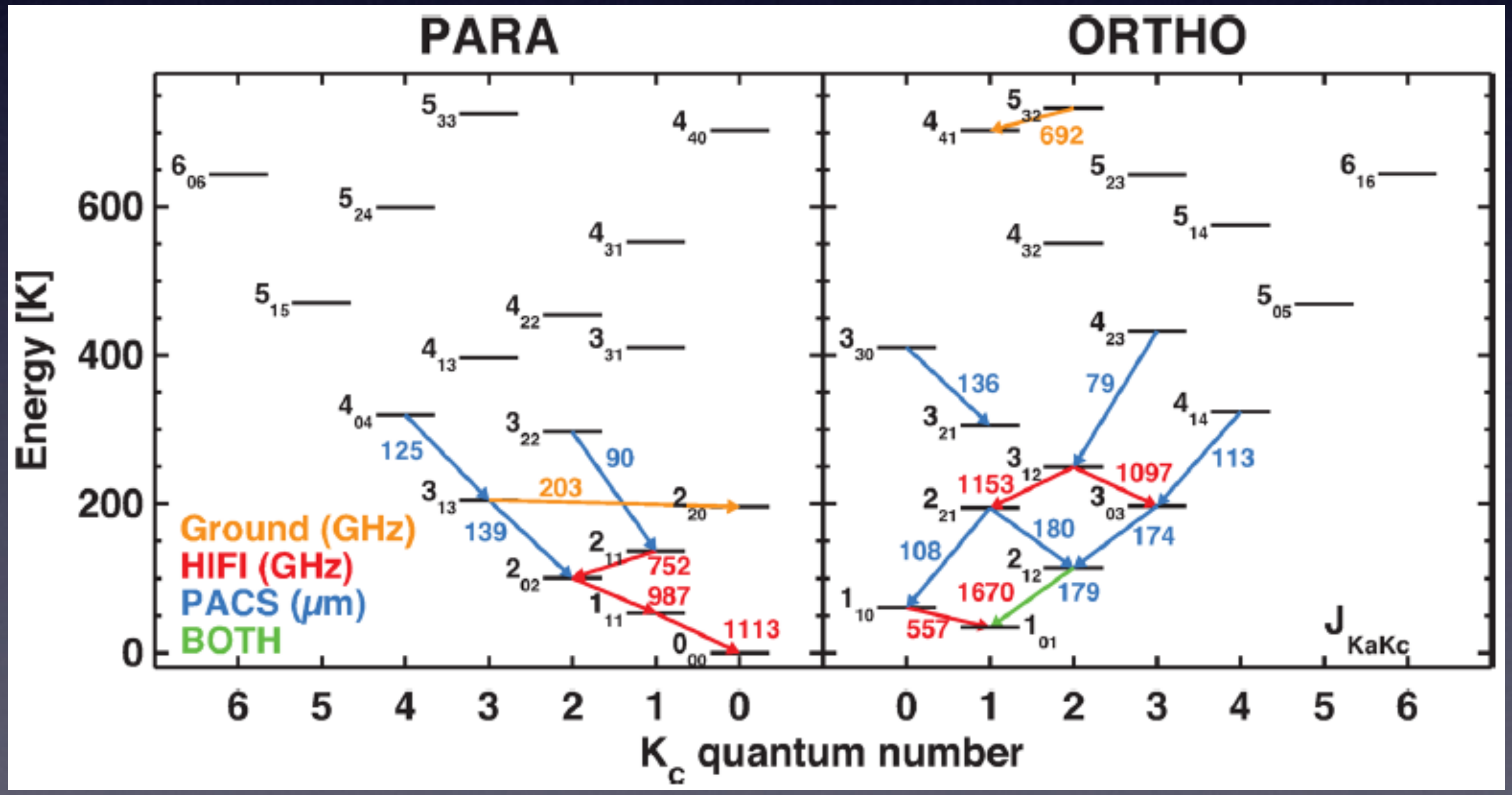
LOC:
John Black
Eva Wirström

M42: NASA, ESA, M. ROBBERTO (STScI/ESA)/HST ORION TREASURY PROJECT; M81: NASA, ESA, HUBBLE HERITAGE TEAM (STScI/AURA); COMET ISON: TRAPPIST/E. JEHIN/ESO

Water

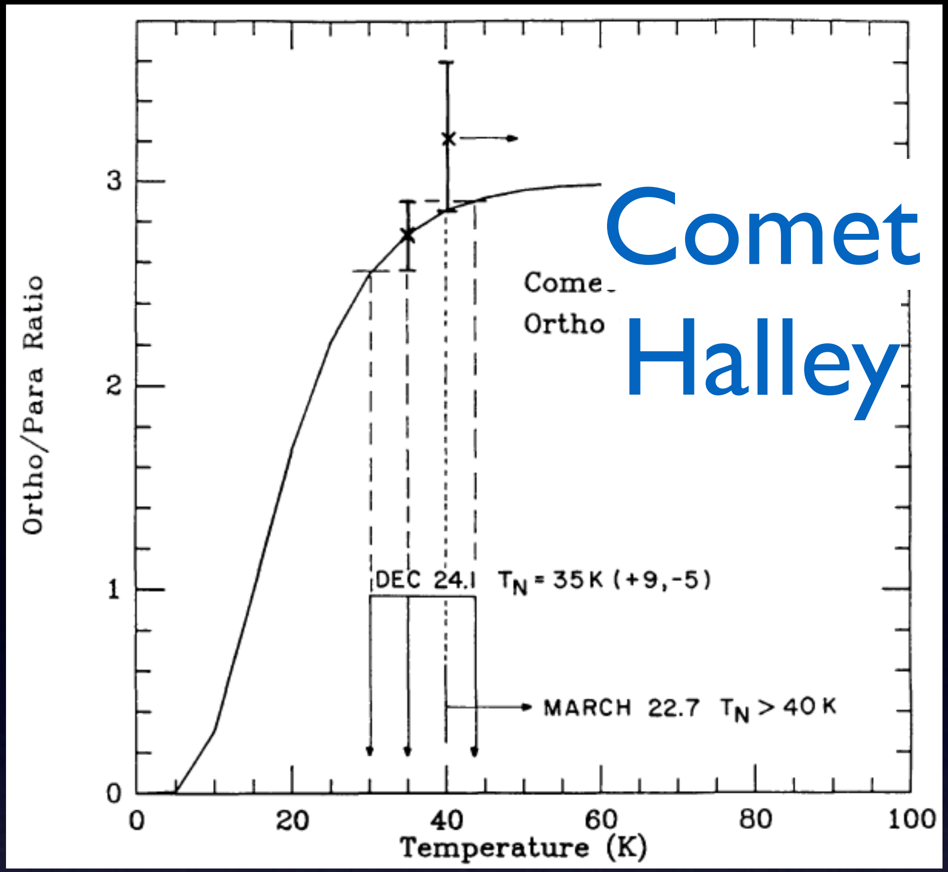


- Asymmetric top with two spin isomers: total hydrogen spin I=1 (ortho), I=0 (para)
- Energy difference 34.2 K
- High temperature limit OPR=3 (T>50 K)
- Spin temperature provides (maybe) some information about formation of water molecules on dust grains
- Herschel/HIFI has allowed for the first time high-resolution spectroscopy of the fundamental rotational transitions of both ortho- and para-water in the ISM



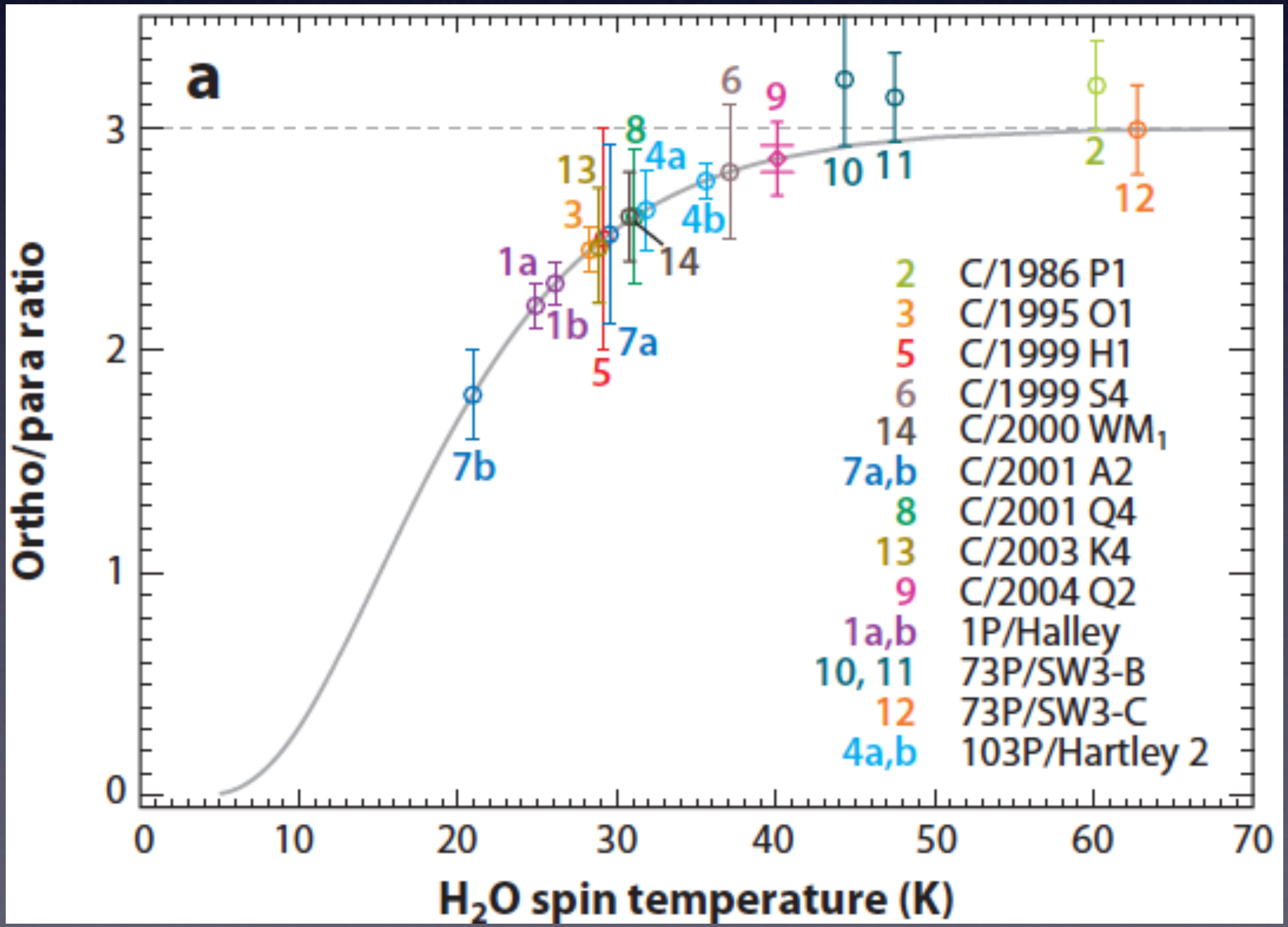
van Dishoeck et al. 2013

OPR in Cometary Water



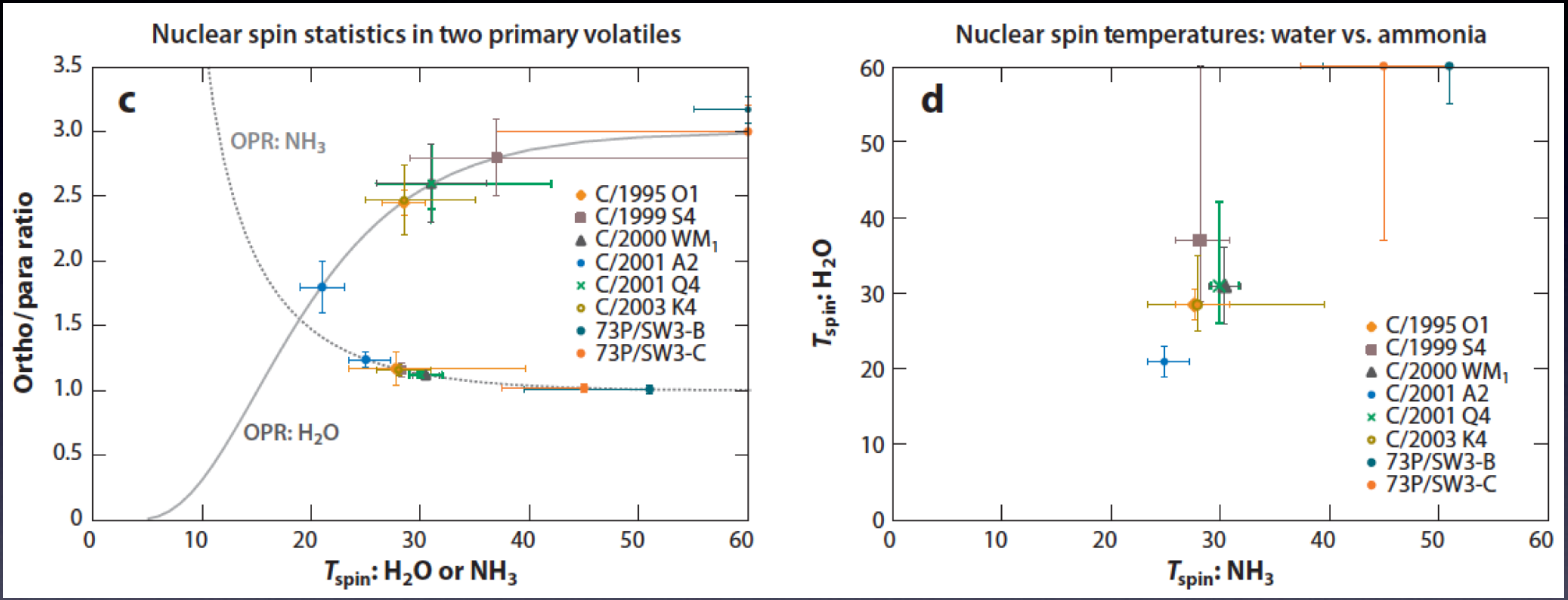
Mumma et al. 1987

- OPR studied extensively in cometary atmospheres
- Optical or IR spectroscopy
- KAO, ISO, IRTF, Keck…
- Spin temperatures often ~30 K
- Some values consistent with LTE
- No values below ~20 K



Mumma et al. 2011

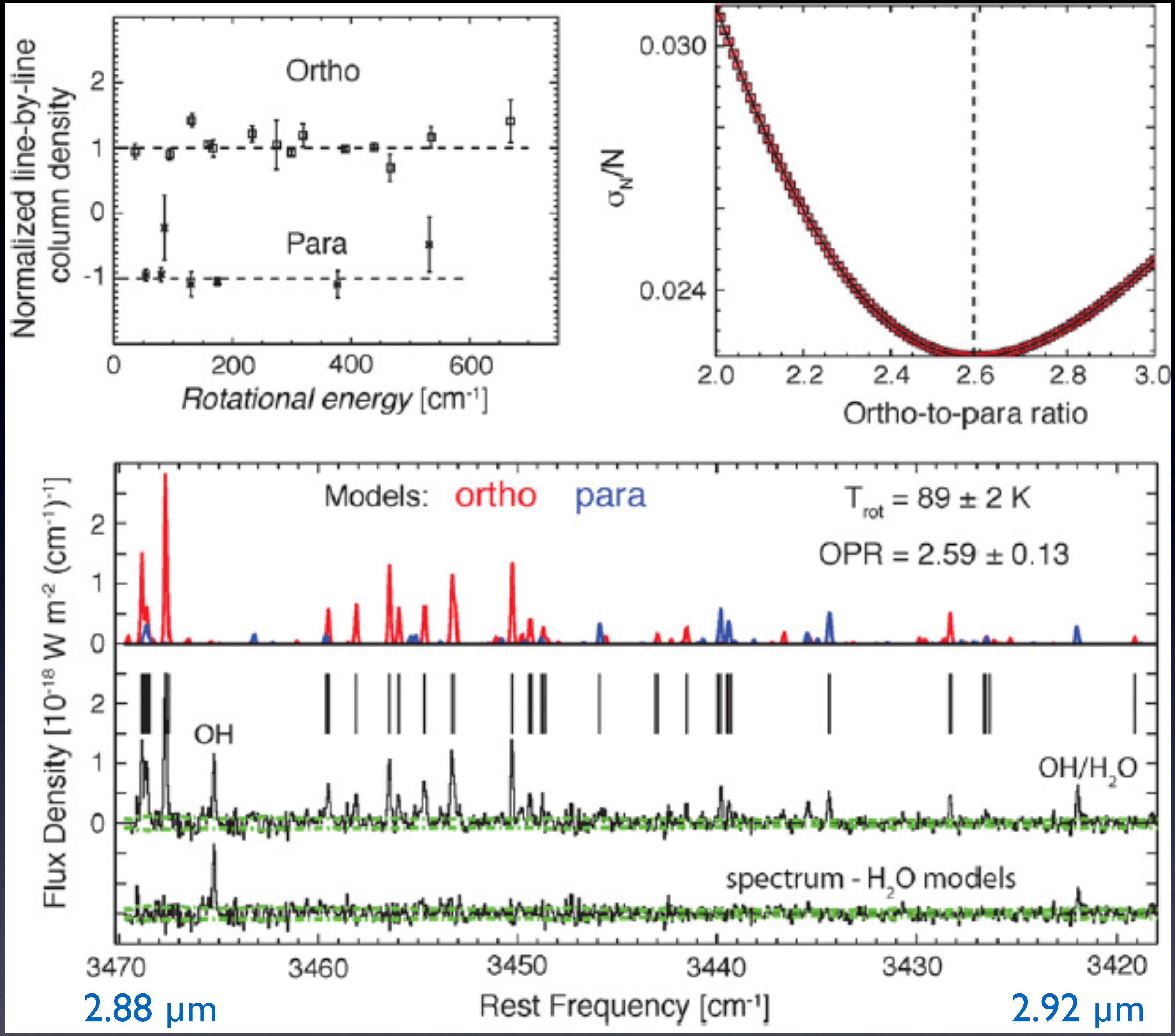
OPR: Water vs. Ammonia



Mumma et al. 2011

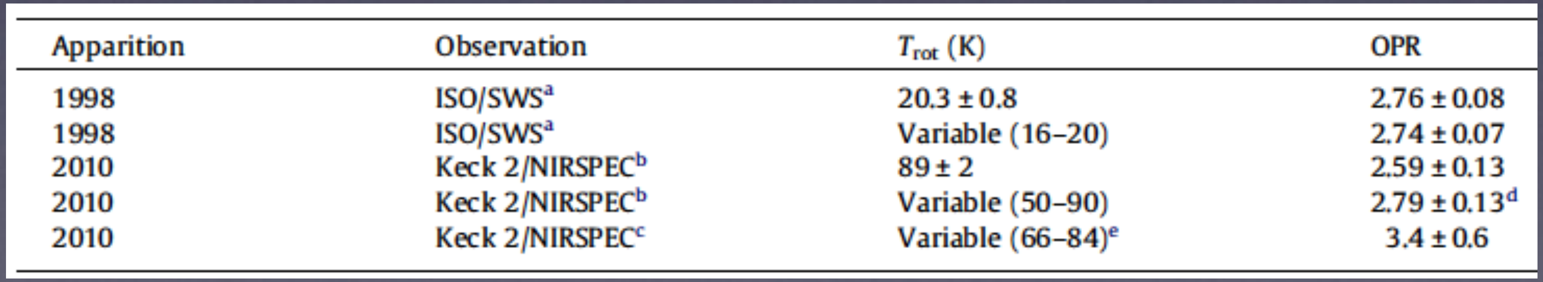
- Similar spin temperatures derived for other cometary volatiles, e.g. ammonia, methane
- "Standard" interpretation: a measure of some *physical temperature*, at which molecules formed or condensed on grain surfaces

Hartley 2



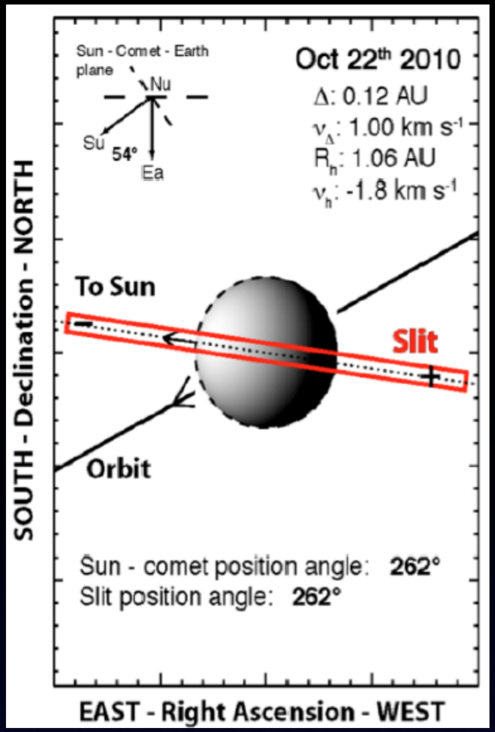
- State-of-the-art NIR, Keck 2/ NIR-SPEC (2 µm water vibrational "hot-bands")
- Many lines of both ortho- and para-water
- OPR values retrieved in very good agreement with the 1998 ISO SWS results (ν_3 full fundamental band at 2.7 µm)

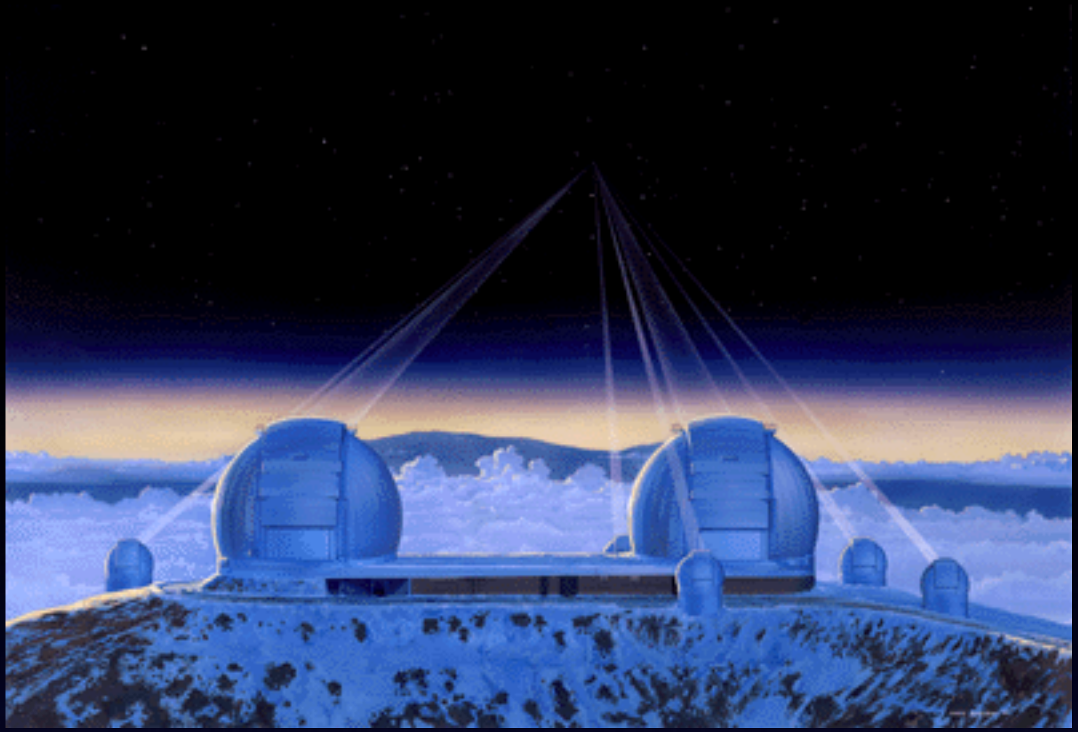
- No evidence for variation of OPR with depth



Apparition	Observation	T_{rot} (K)	OPR
1998	ISO/SWS[a]	20.3 ± 0.8	2.76 ± 0.08
1998	ISO/SWS[a]	Variable (16–20)	2.74 ± 0.07
2010	Keck 2/NIRSPEC[b]	89 ± 2	2.59 ± 0.13
2010	Keck 2/NIRSPEC[b]	Variable (50–90)	2.79 ± 0.13[d]
2010	Keck 2/NIRSPEC[c]	Variable (66–84)[e]	3.4 ± 0.6

Bonev et al. 2013

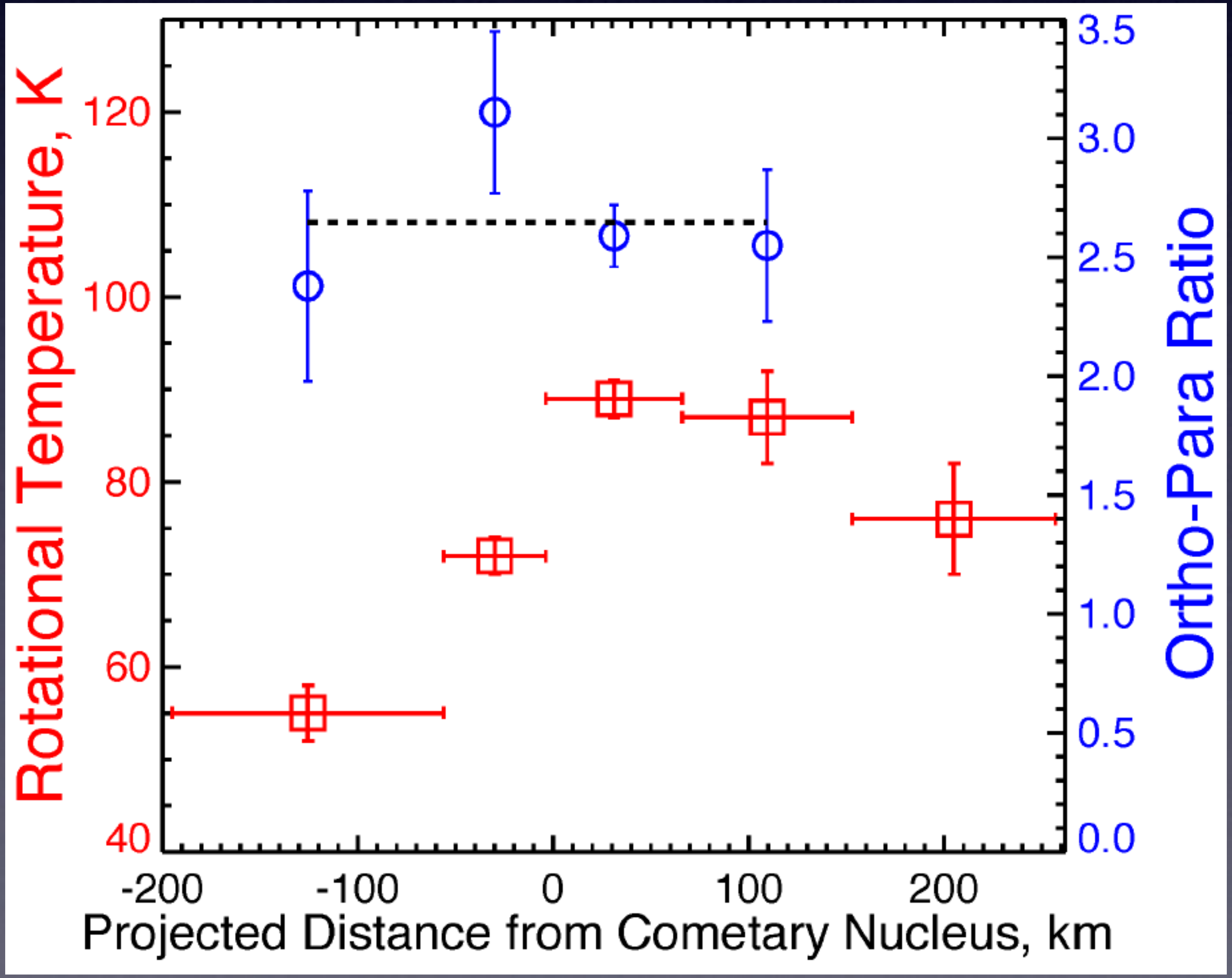




Hartley 2

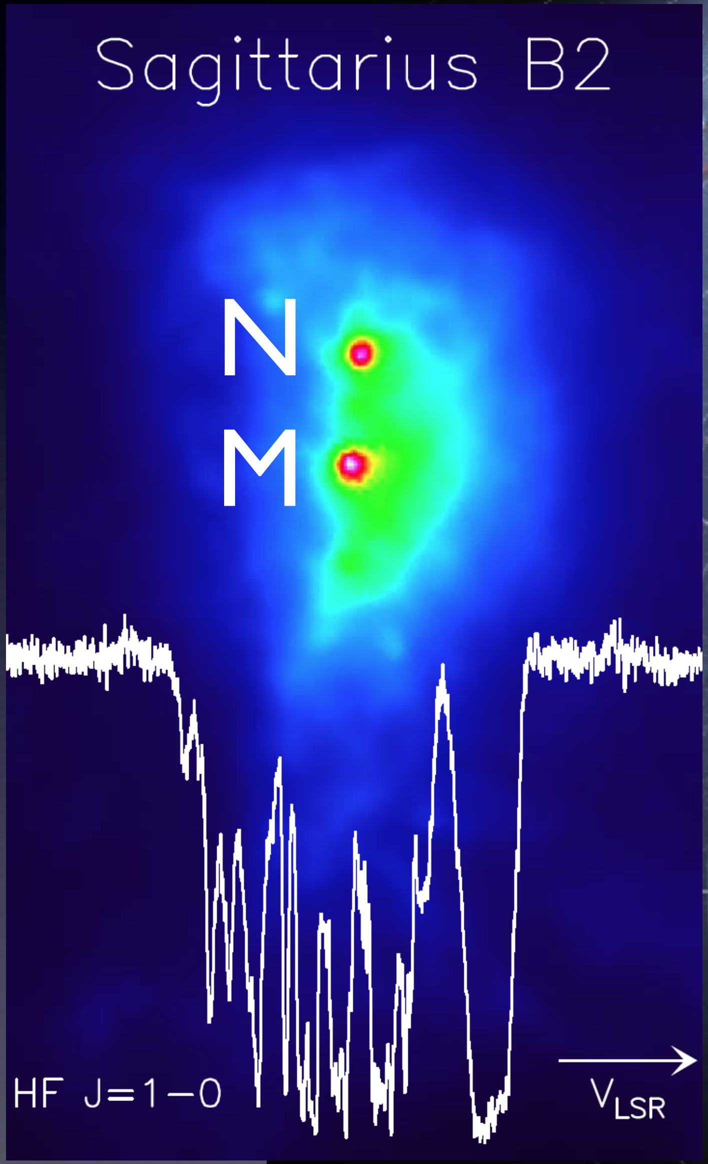
- Long-slit spectroscopy: measure OPR as a function of projected distance
- Most precise value 2.59±0.13, T_{spin} 31±3 K
- T_{rot} varies strongly with projected distance, but T_{spin} does not

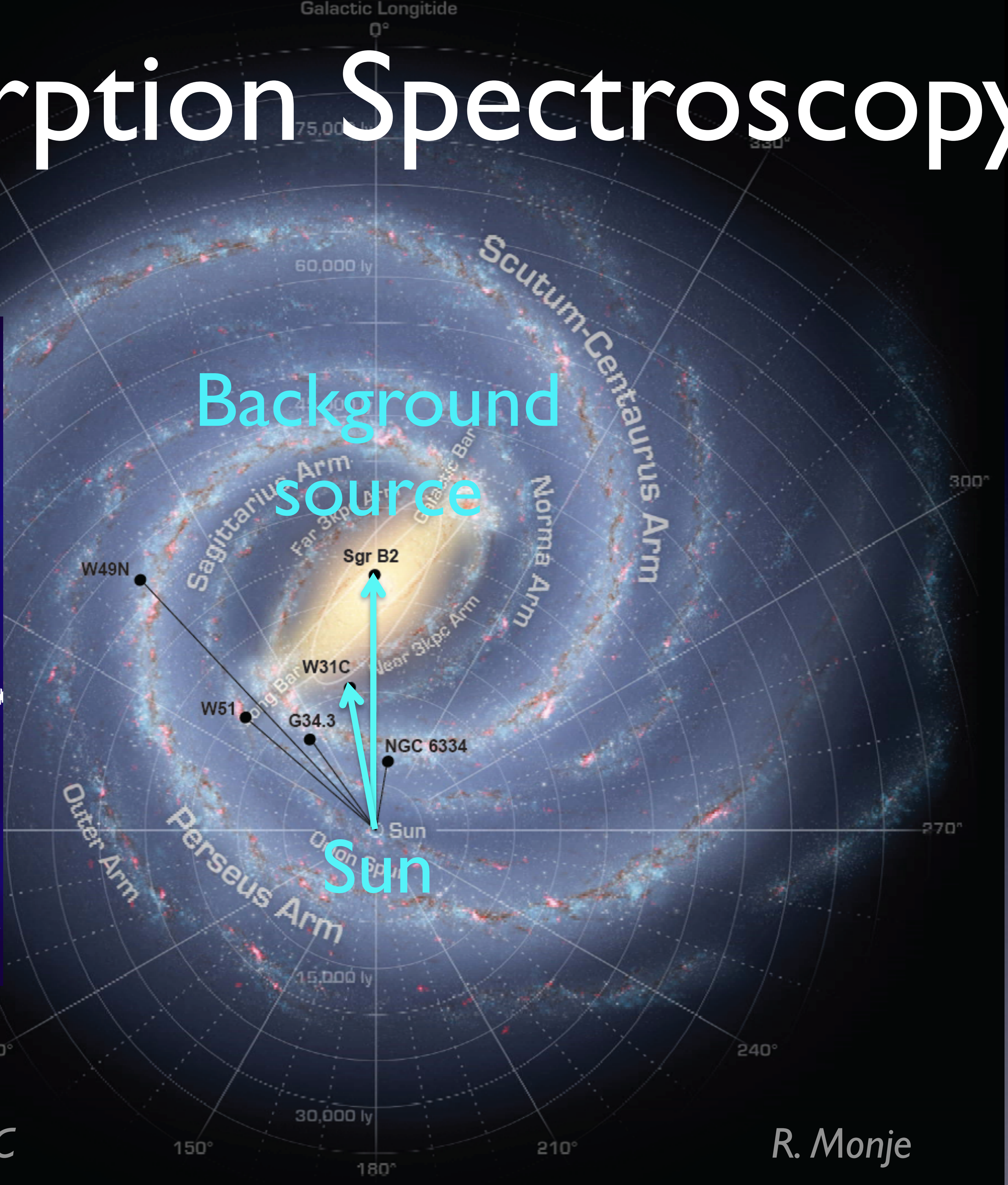
- Solar nebula vs. ISM materials?
- Molecular abundances, isotopic ratios—OPR may provide additional useful information



Bonev et al. 2013, 2014

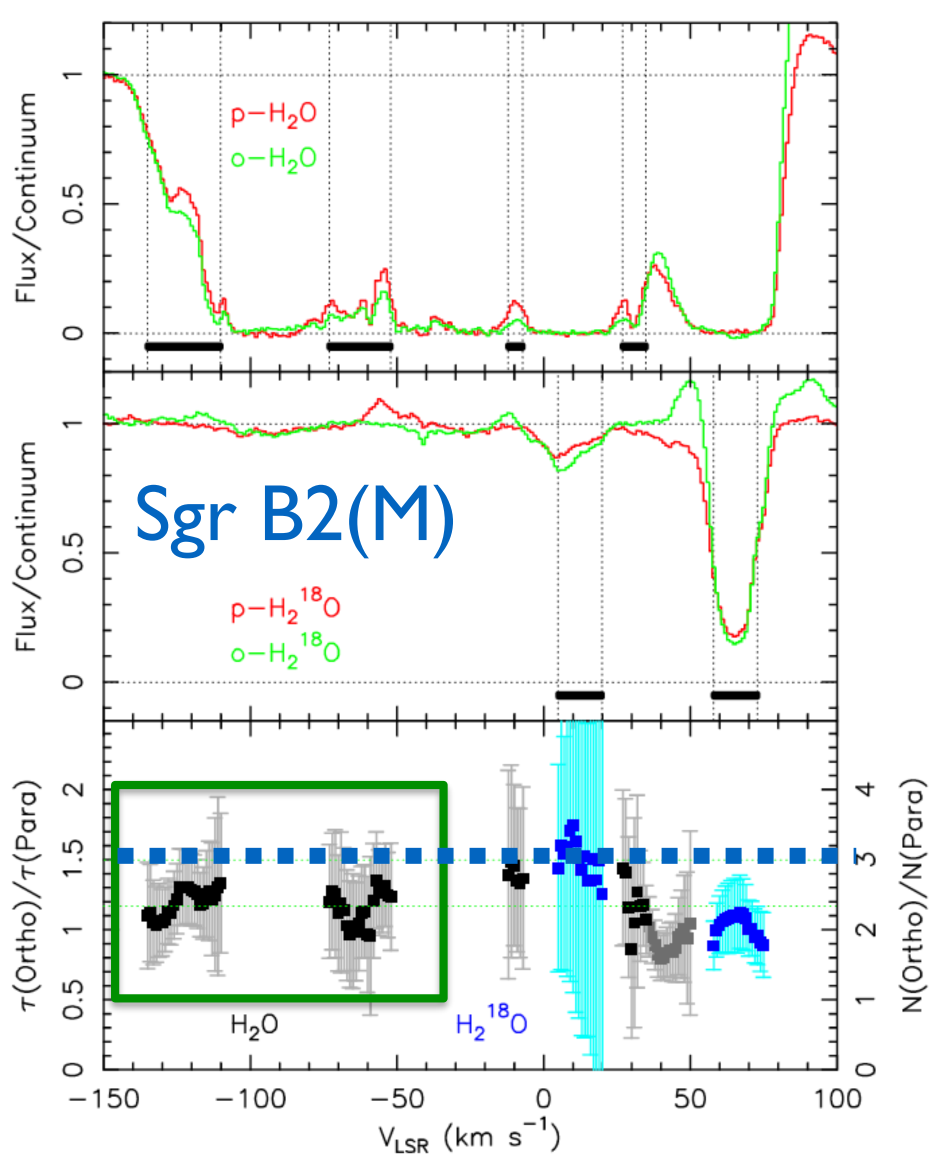
Absorption Spectroscopy

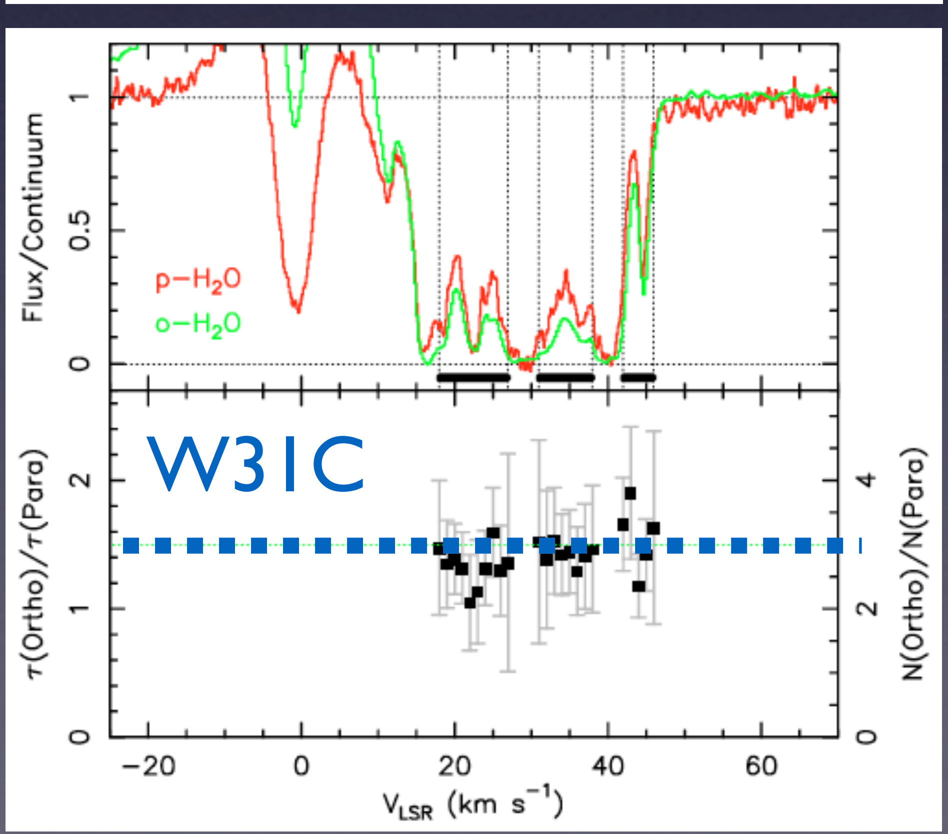




NASA/SSC

R. Monje





Early HIFI Observations

- $H_2{}^{16}O$ spectra nearly completely saturated
- $H_2{}^{18}O$ absorption typically not detected

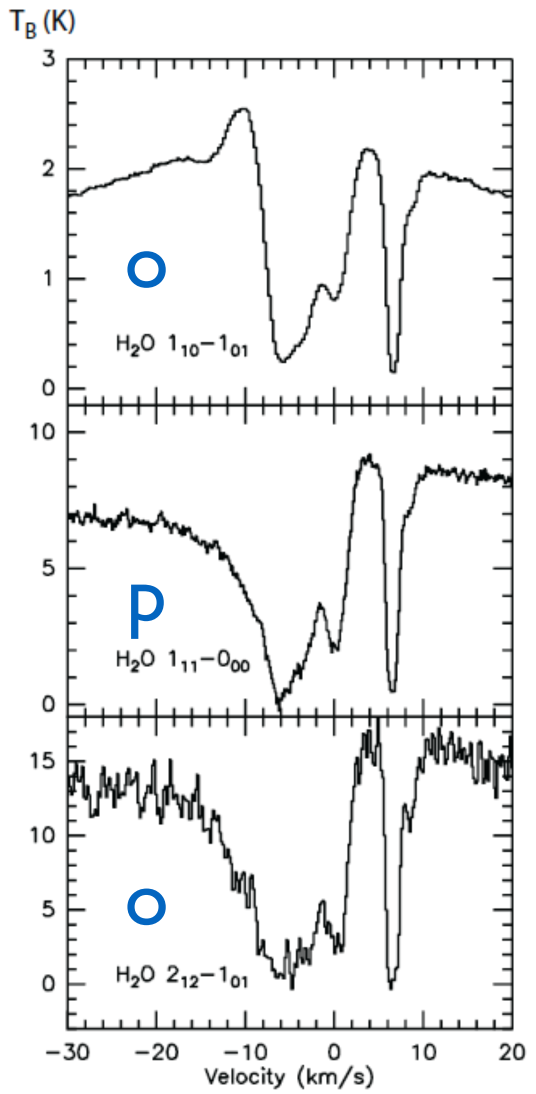
- Early results, based on the 557 and 1113 GHz data, showed that the OPR in most cases is consistent with the high-temperature limit
- Possible exception: negative velocities in Sgr B2, corresponding to "expanding molecular ring"

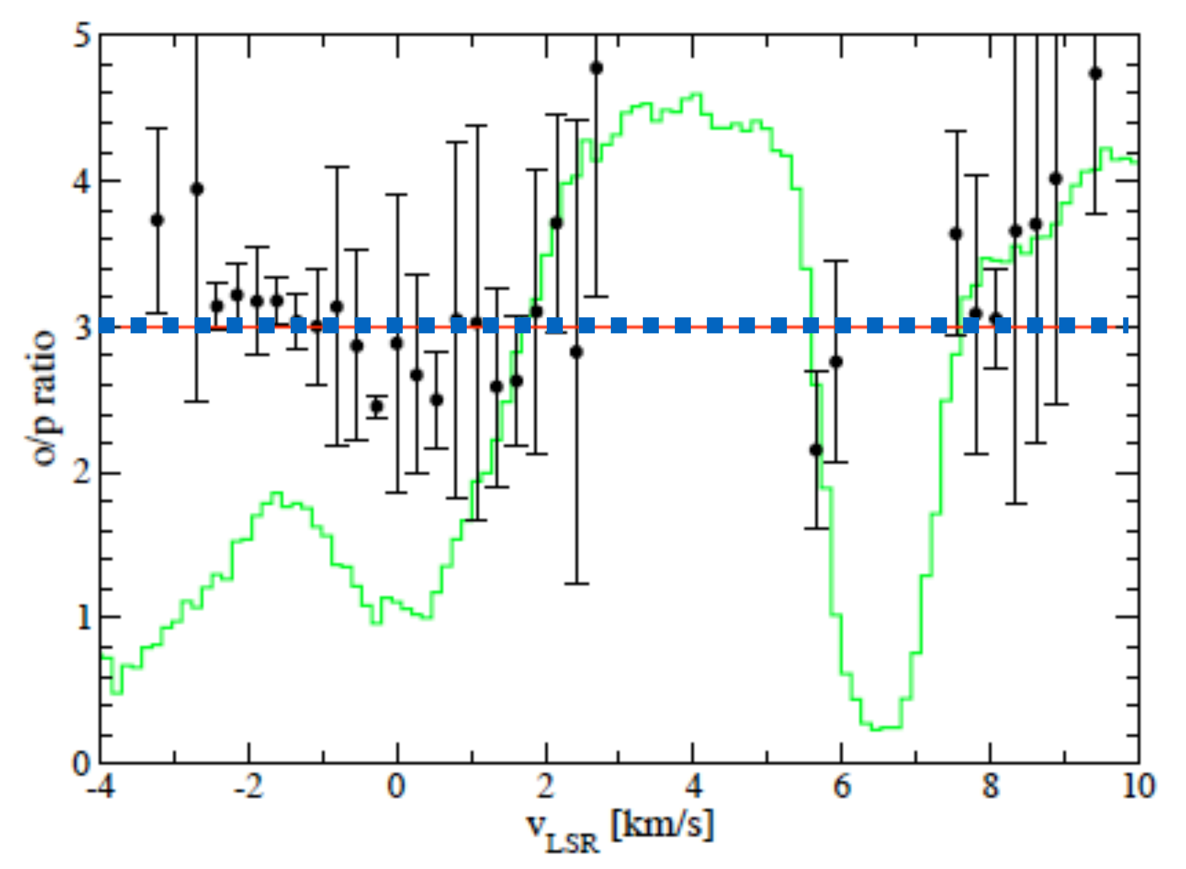
- OPR 2.35±0.35, T_{spin}~27 K, similar to values measured in cometary atmospheres

- *Difficult measurements*—have to get a good handle on *systematic effects* (e.g. baseline instabilities, sideband ratios), but also on *water excitation*

Lis et al. 2010

Molecular Excitation

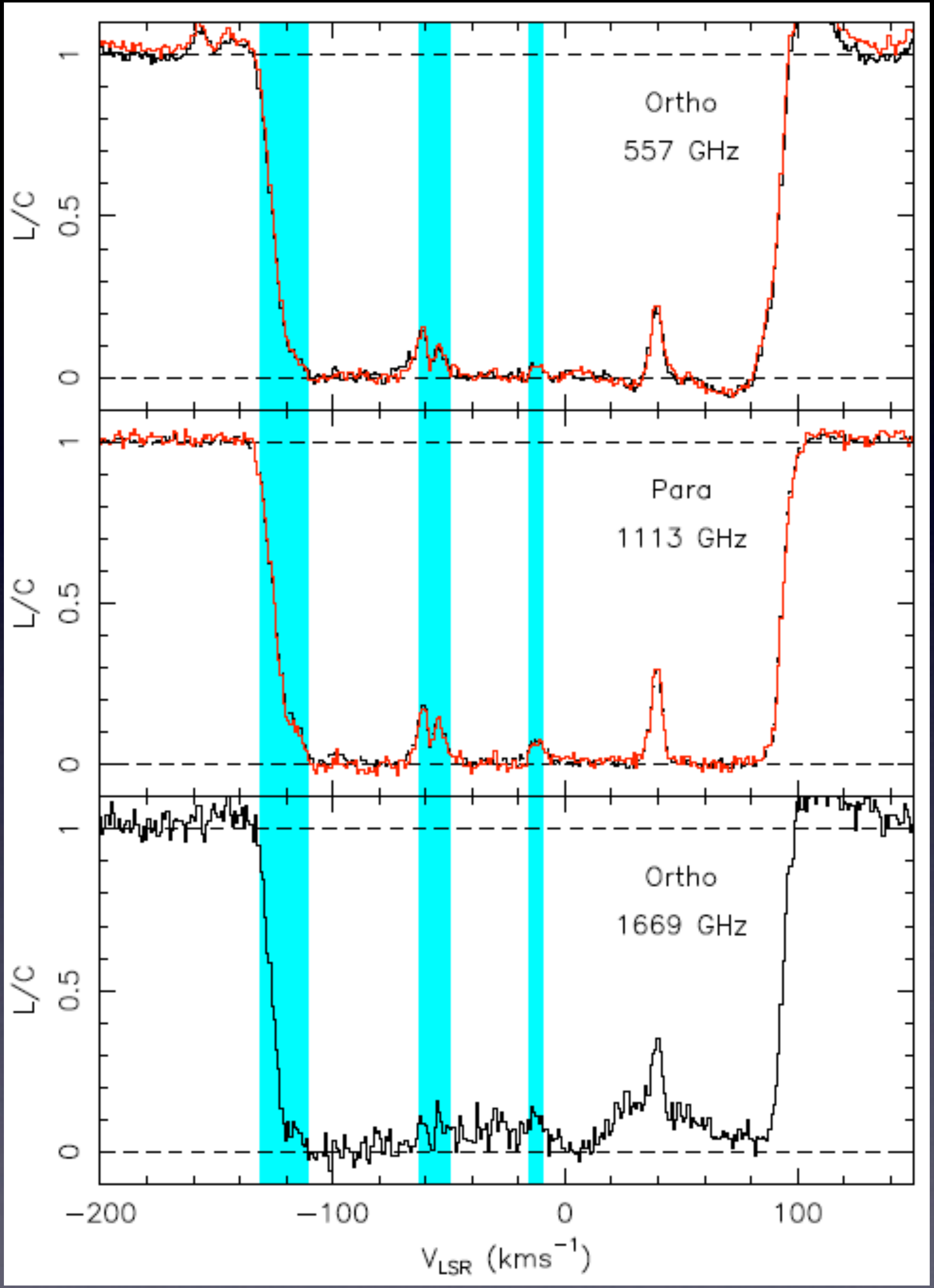




Emprechtinger et al. 2010, 2013

- Fundamental rotational transitions of light hydrides typically have very high critical densities
- Ortho-H_2O, 557 GHz, $n_{crit}=6\times10^7$ cm^{-3}
- Assume all population in the ground rotational state in diffuse ISM
- NGC6334I: OPR 1.6±1in the cold, quiescent gas, 2.5±0.8 in the outflow
- Addition of the 1669 GHz ortho-H_2O line allows *direct determination* of the excitation temperature
- NGC6334I: T_{ex}=6.5 K
- High for diffuse clouds, but absorption also seen in the ground state para-NH_3 line (tracer of dense gas)
- Revised OPR consistent with the high-temperature limit of 3

Sagittarius B2(N)



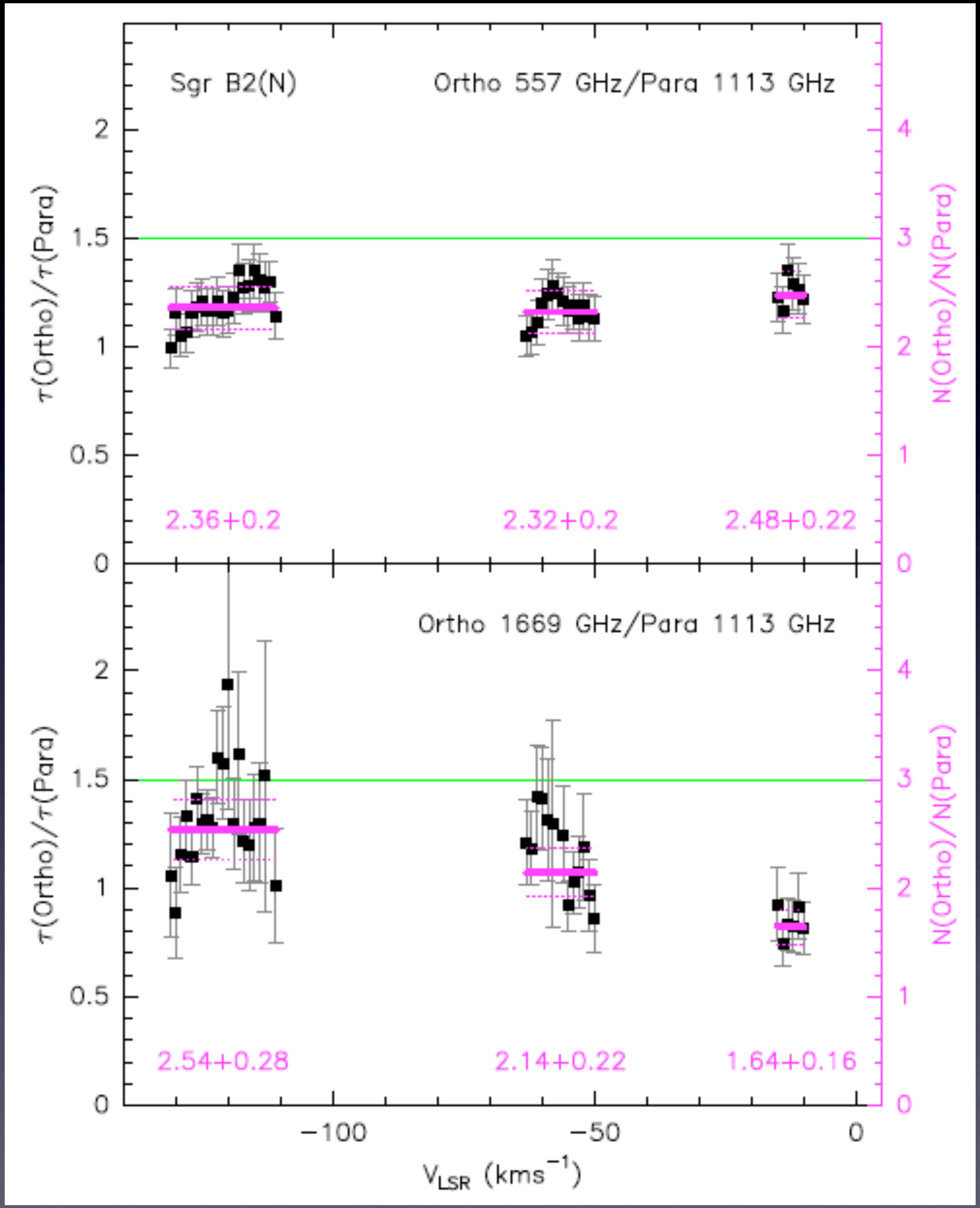
Lis et al. 2013

- Revisit Sagittarius B2
- Different line of sight, but nearby to Sgr B2(M) (tracing the same foreground gas)
- Independent measurement
- Better data reduction
- Redundant data set
- For the 557 and 1113 GHz lines: two independent measurements, using the HIFI mixer bands 1a/1b and 4b/5a
- Expect completely different systematics in terms of standing waves, sideband ratios etc.

Errorbars, Errorbars, Errorbars!

- The two independent spectra of the 557 and 113 GHz lines are in *very good* agreement, confirming excellent stability and calibration of HIFI
- Quantitatively, you can compute the difference between the two spectra and the corresponding rms in the velocity intervals of interest
- That gives you the uncertainty in individual 1 km/s wide velocity bins
- How do you compute the uncertainty of the average—individual measurements may not be independent (correlated noise)
- Resample the spectra to 5 and 10 km/s velocity resolution and investigate how the noise varies with spectral resolution
- For 1113 and 1669 GHz lines, the rms goes down by factor of 0.67 and 0.60 (instead of 0.45 and 0.32, as expected for uncorrelated measurements)
- For the 557 GHz line the rms only goes down by a factor of 0.9 (essentially completely correlated noise)

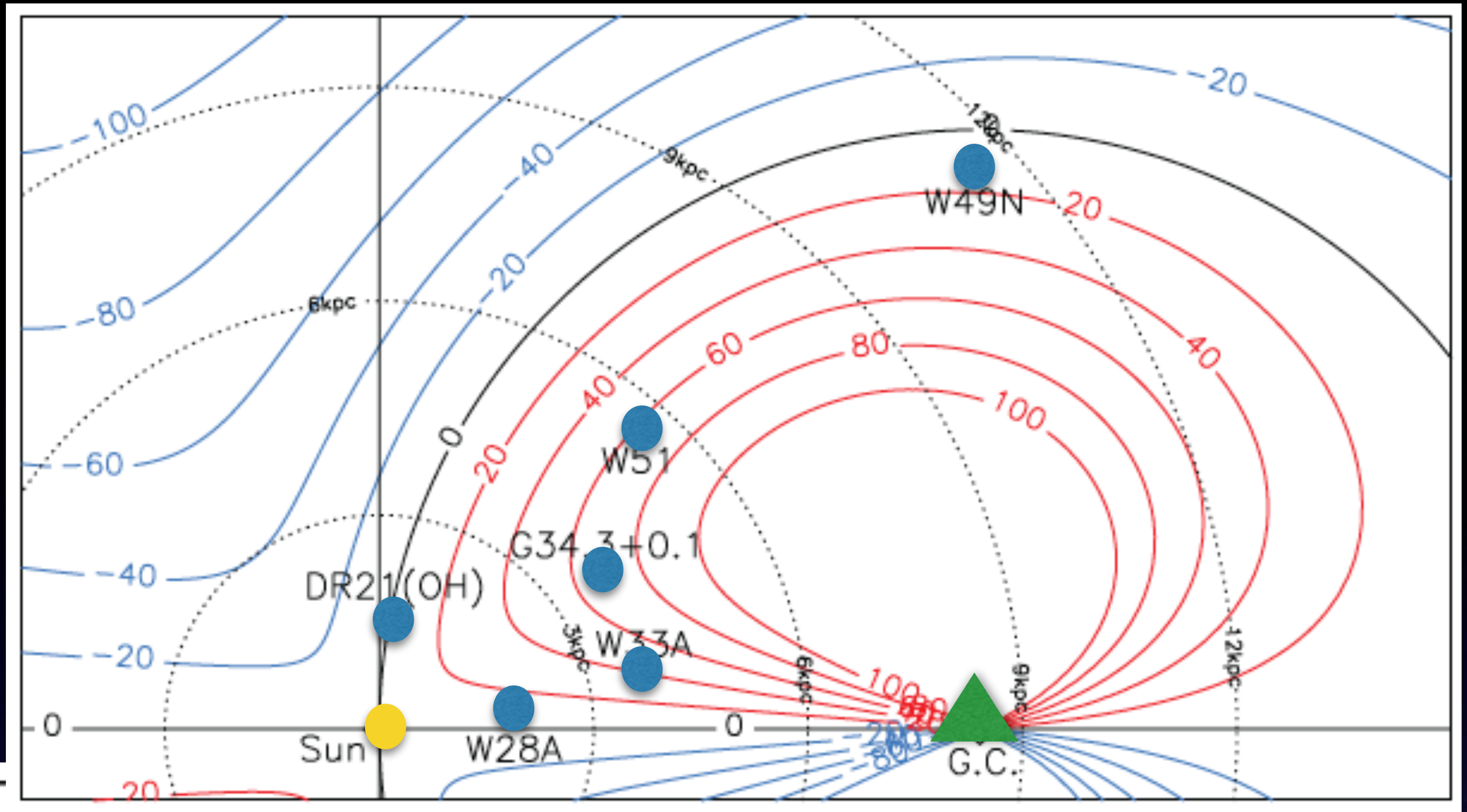
Sgr B2(N) Results

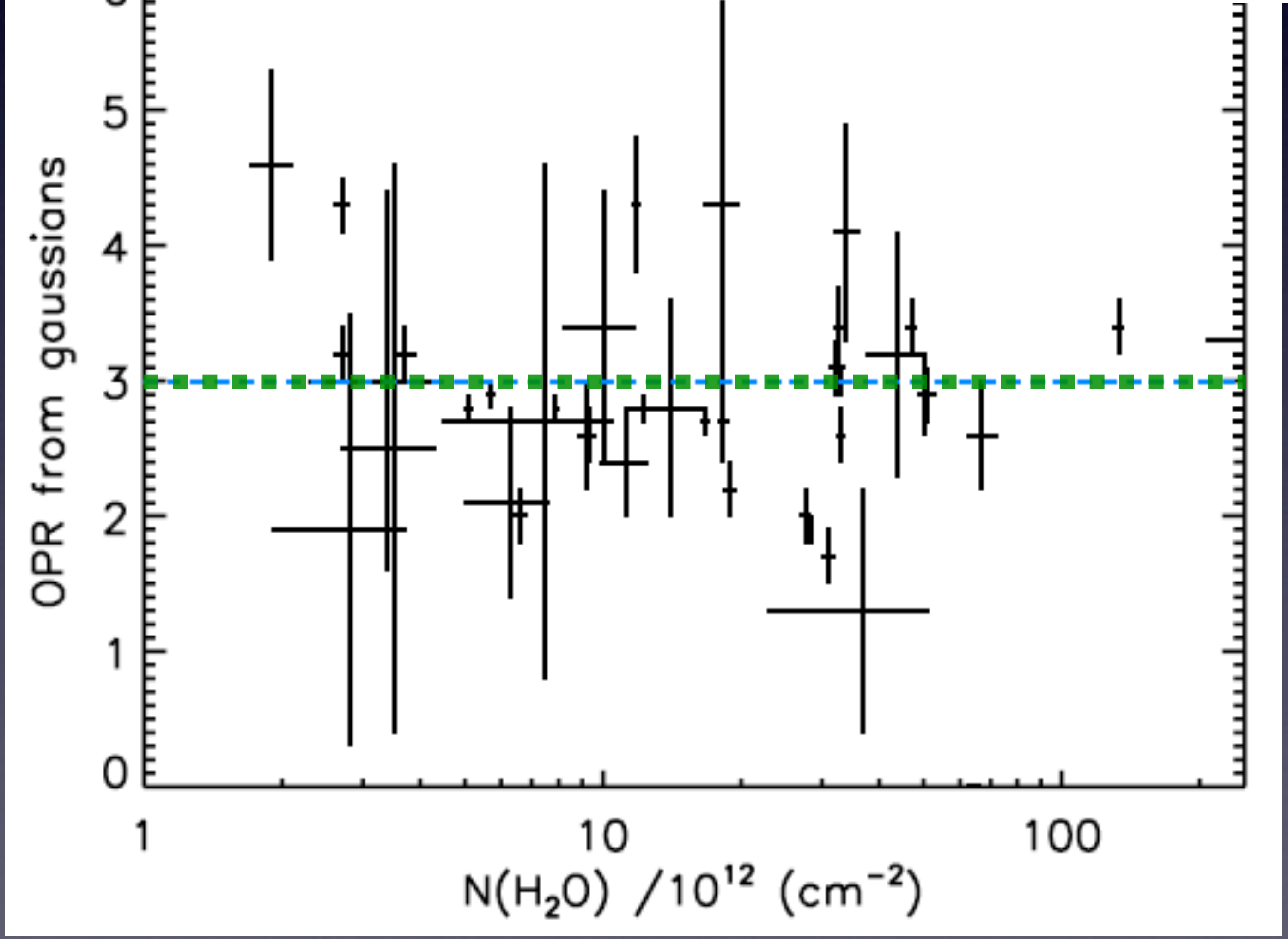


Lis et al. 2013

- With a good understanding of the correlated noise, we can derive accurate estimates of the uncertainties of the OPR in the three velocity intervals (2σ)
- Confirms the earlier results that the OPR in water at negative velocities corresponding to the gas in the "x2" orbits is lower than 3
- Same OPR based on observations of the 557 at 1669 GHz ortho-H_2O lines—assumption of low Tex justified for this line of sight
- Final value 2.34±0.35 (2σ)
- Spin temperature 24–32 K

Galactic Disk Sources

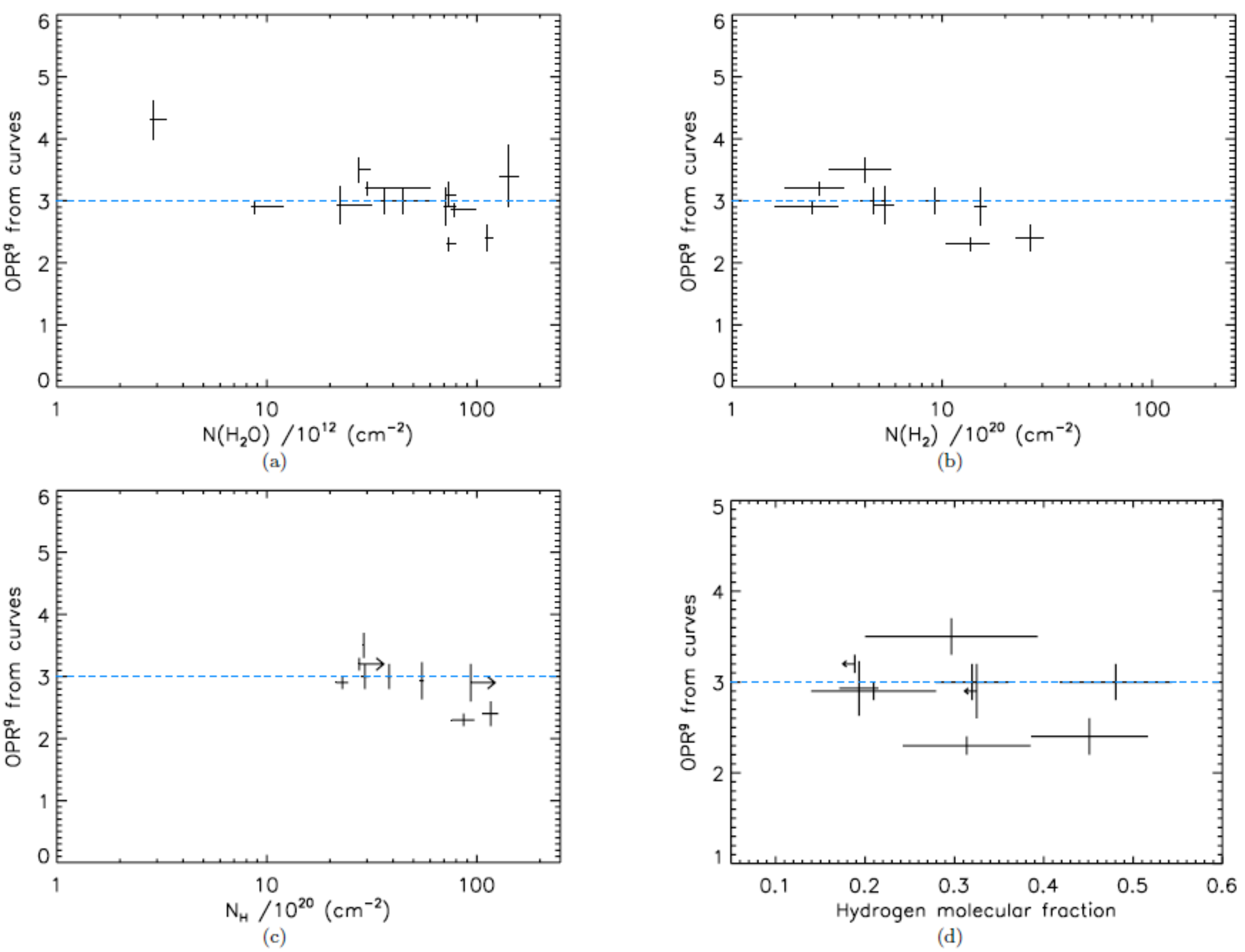




- Extensive compilations of PRISMAS observations of sources in the Galactic disk
- Different galactocentric distances, probe gas in different spiral arms
- H_2O/H_2 ~ 5 10^{-8} in diffuse clouds
- OPR generally consistent with 3, possibly with the exception of some components toward W49N

Flagey et al. 2013

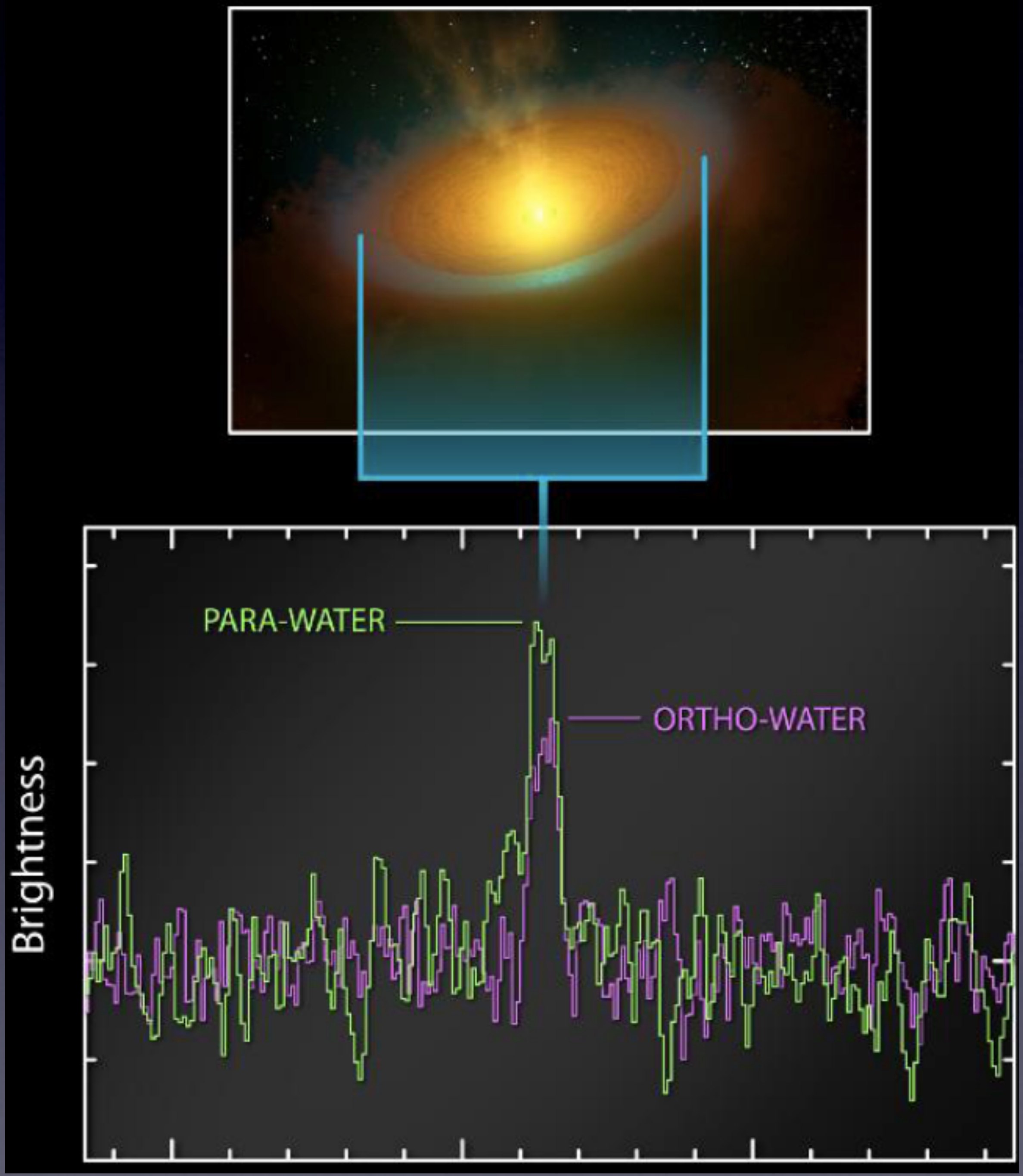
No Apparent Trends



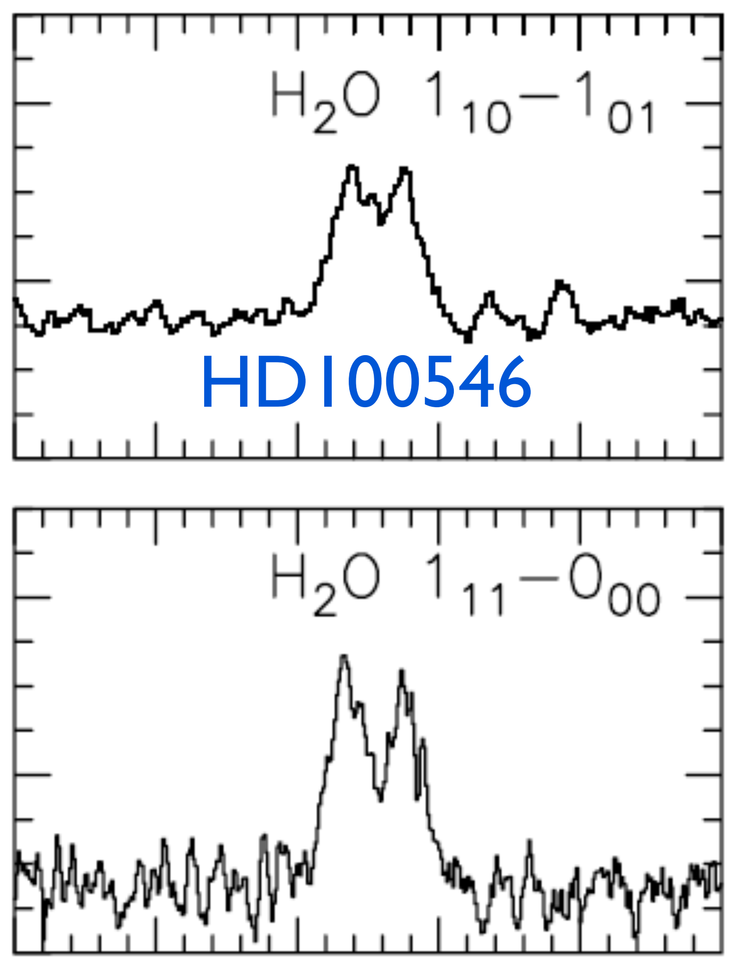
Flagey et al. 2013

Water in Disks

TW Hya



Hogerheijde et al. 2011 and in prep.



- Lines of ortho and para water detected for the first time with Herschel/HIFI in TW Hydrae
- 10 mln years old T Tauri star, 0.6 $M_\odot$ at 54 pc
- Lines seen in emission
- OPR 0.77+0.07 (1σ); T_{spin}=13.5 K
- Lower than the cometary values—but very model dependent

Observational Summary

- There is a range of OPR values in water in the diffuse ISM
- Most values are consistent with the high-temperature limit of 3, given the uncertainties
- There are some exceptions, e.g., gas on the “x2” orbits toward Sagittarius B2, where T_{spin}~24–32 K (2σ); also some velocity components toward W49N
- There are no very low OPR values
- No trends seen in the OPR with the H_2O, H_2, H column density, galactocentric distance, or molecular fraction

- All these conclusions are consistent with the latest cometary measurements
- What does it mean?

Well, It’s Complicated!

- Gas phase: water forms with OPR=3
- Nuclear spin conversion (through proton exchange reactions with H^+, H_3^+) is slow, dependent on the local ionization rate and gas density (3×10^5 yr for 10^4 cm^{-3}, abundance of protonated ions 10^{-8})
- Alternative: water formation via grain-surface processes

- What happens to water molecules in the ice?
- If they can no longer rotate freely, does it still make sense to talk about ortho and para spin states?
- Do the molecules loose their identity?

- Even if the OPR in the ice can be defined, we still need a mechanisms that releases water molecules into the gas phase

Photo-Desorption of Water Ice

- Molecular dynamic calculations of water photo-desorption
  - photodissociation followed by recombination of H and OH and subsequent desorption of recombined H_2O molecules
  - "kick-out" of another H_2O molecule by the energetic H atom released from photodissociation
  - 60% H+OH, 20% of H_2O recombined, 20% of H_2O "kicked-out" from the surface
- Only "kicked-out" molecules *would preserve the OPR* acquired in the ice
- This may explain why we never see very low OPR values

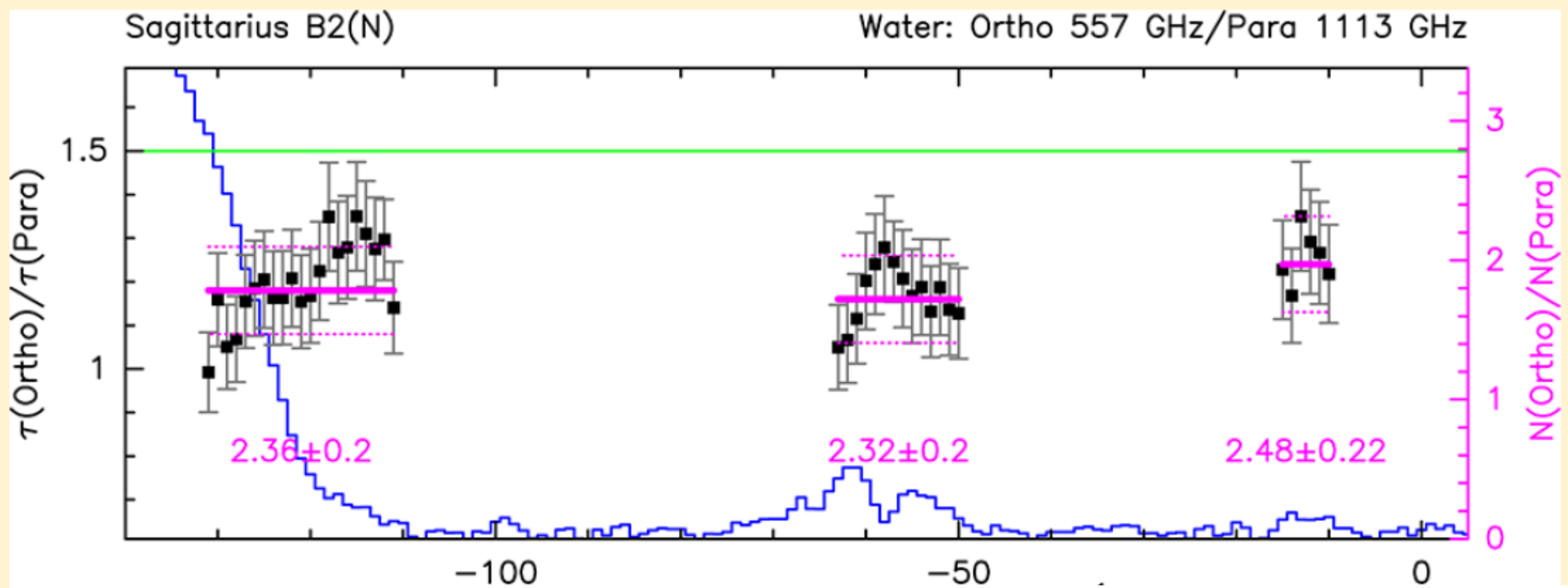
- Other mechanisms proposed—in general *no one-to-one correspondence* between the H_2O molecules on the surface and in the gas phase

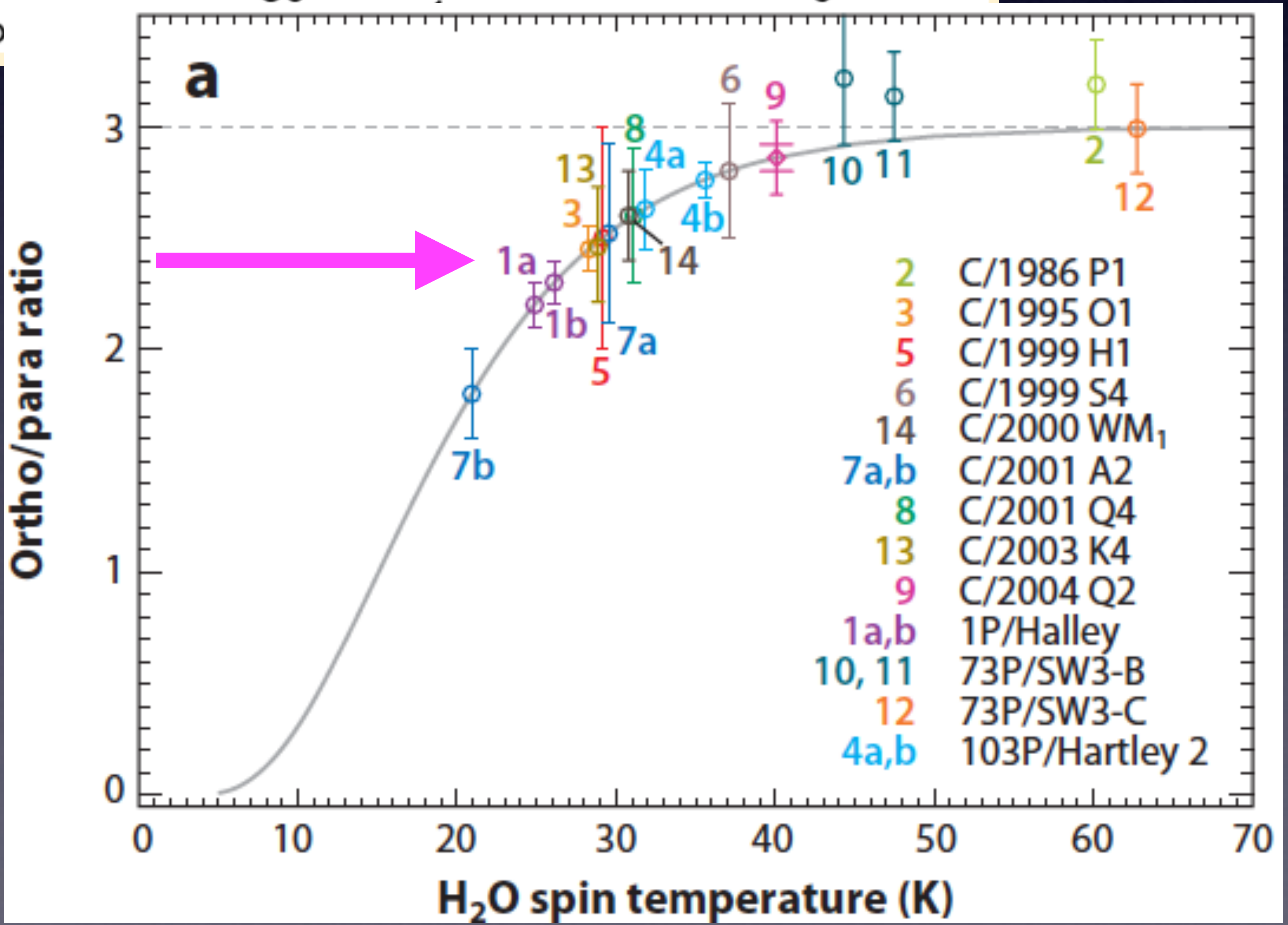
Andersson & van Dishoeck 2008

Thermal Desorption of Water Ice

- Laboratory measurements of water vapor above ice heated to 260 K, initially prepared as pure para-H_2O, show thermal OPR
- *"…long time stability of para-water molecules in ices at higher temperatures seems unlikely, and the conclusion that cometary formation temperatures can be probed using the OPR ratios is in doubt."*
- Spectra of desorbed molecules from ASW measured at 150 K, deposited at 8 K, show thermal OPR=3
- OP conversion does not occur in ASW at 8 K, or re-equilibration during TPD
- Nuclear spin temperatures of gas phase H_2O molecules thermally desorbed from ice do not necessarily reflect the surface temperature at which H_2O formed or condensed
- These measurements may not precisely reproduce the conditions in the ISM, but are very important and should ultimately lead to a generally accepted interpretation of the OPR values measured in the ISM and cometary atmospheres

Sliter et al. 2011 and Hama, Watanabi et al. 2011


Sagittarius B2(N)
Water: Ortho 557 GHz/Para 1113 GHz
τ(Ortho)/τ(Para)
N(Ortho)/N(Para)
1.5
1
3
2
1
0
2.36±0.2
2.32±0.2
2.48±0.22
−100
−50
0
Local Standard o


a
Ortho/para ratio
H₂O spin temperature (K)
0
1
2
3
0
10
20
30
40
50
60
70
1a
1b
2
3
4a
4b
5
6
7a
7b
8
9
10
11
12
13
14
2 C/1986 P1
3 C/1995 O1
5 C/1999 H1
6 C/1999 S4
14 C/2000 WM₁
7a,b C/2001 A2
8 C/2001 Q4
13 C/2003 K4
9 C/2004 Q2
1a,b 1P/Halley
10, 11 73P/SW3-B
12 73P/SW3-C
4a,b 103P/Hartley 2

Thank you!