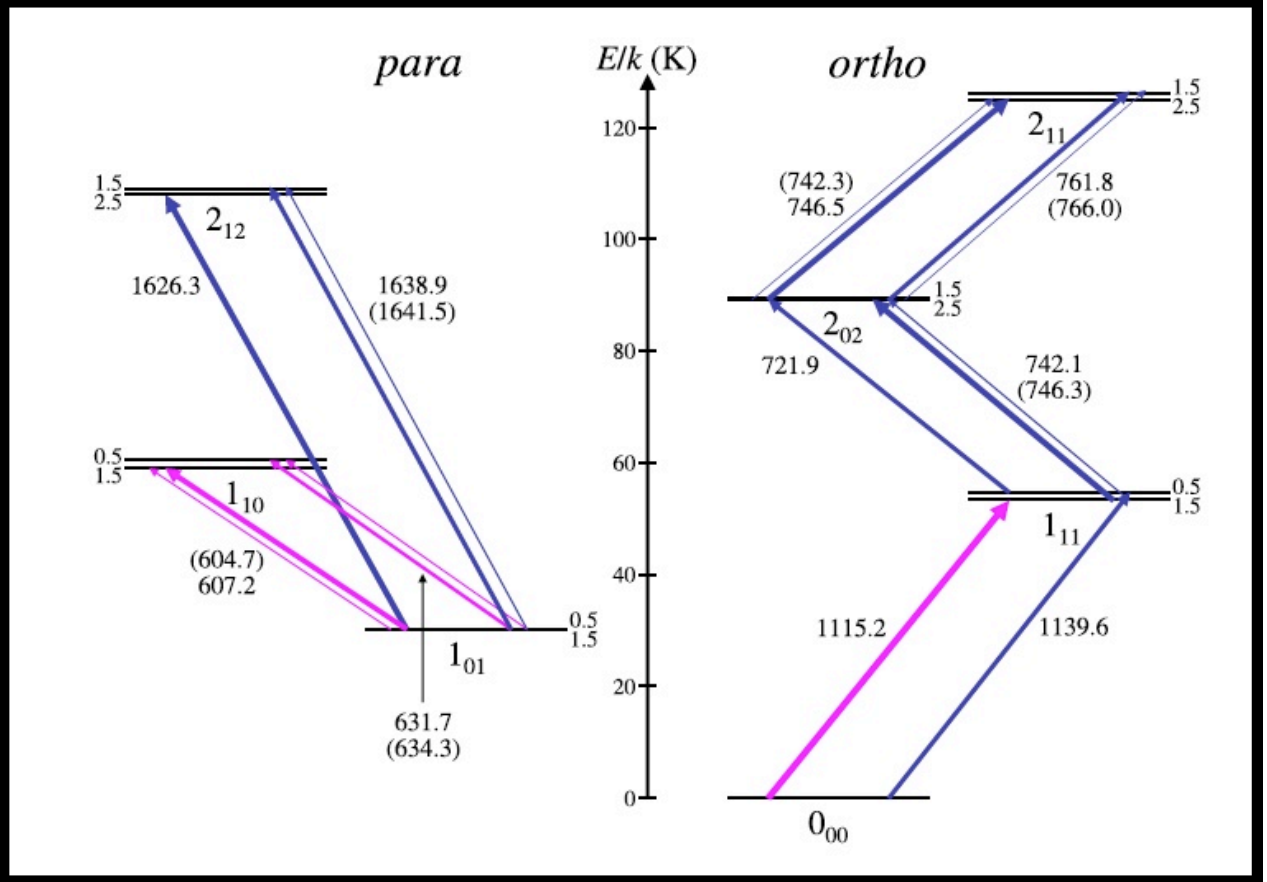
Vibrations and high-frequency rotations: Supporting NASA space missions in the laboratory

NASA LAW 2010

- recent successes: H_2O^+(*Herschel*), fullerenes (*Spitzer*)!
- Challenges: many and highly varied
  - Molecular targets: new species and improved measurements
  - Complementary studies: collisional studies, excitation, theory, other wavelengths, etc.
  - Improved methodologies: greater bandwidth, sensitivity, specificity, etc.
- Unexpected discoveries likely…

Early science with HIFI: H_2O^+ and the ortho/para ratio

- Discovery of H_2O^+ early achievement of HIFI; observed along numerous lines-of-sight
- ortho-H_2O^+ is the lower energy form
- o/p = 3 in high temp limit
- exceeds 3 if in equilibrium below 50 K.



Schilke et al. 2010

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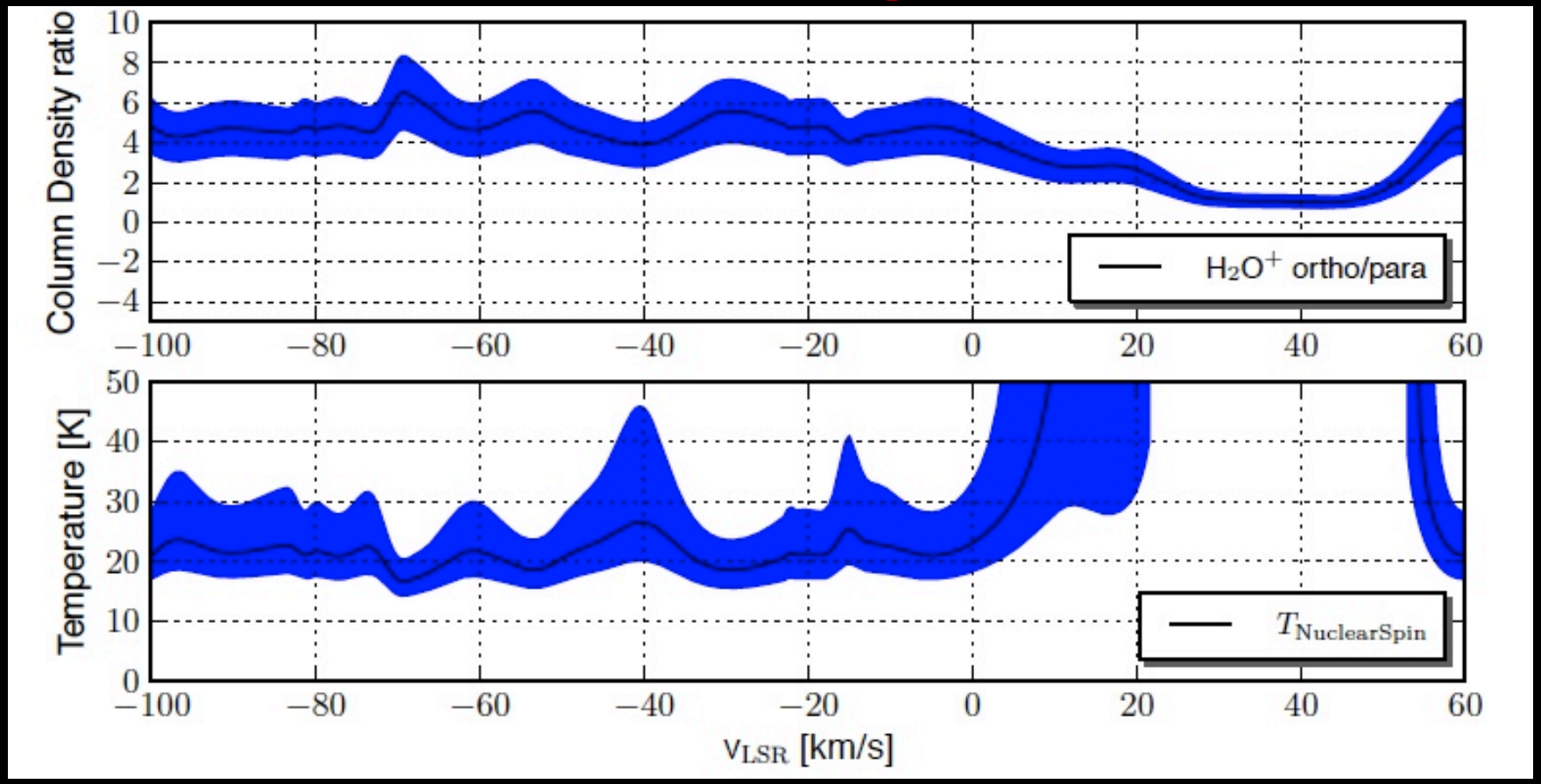
H_2O^+ ortho/para ratio



Schilke et al. 2010

- H_2O^+ ortho/para ratio finding comparable spin temperature to water at same velocities
- more work to be done - including understanding why

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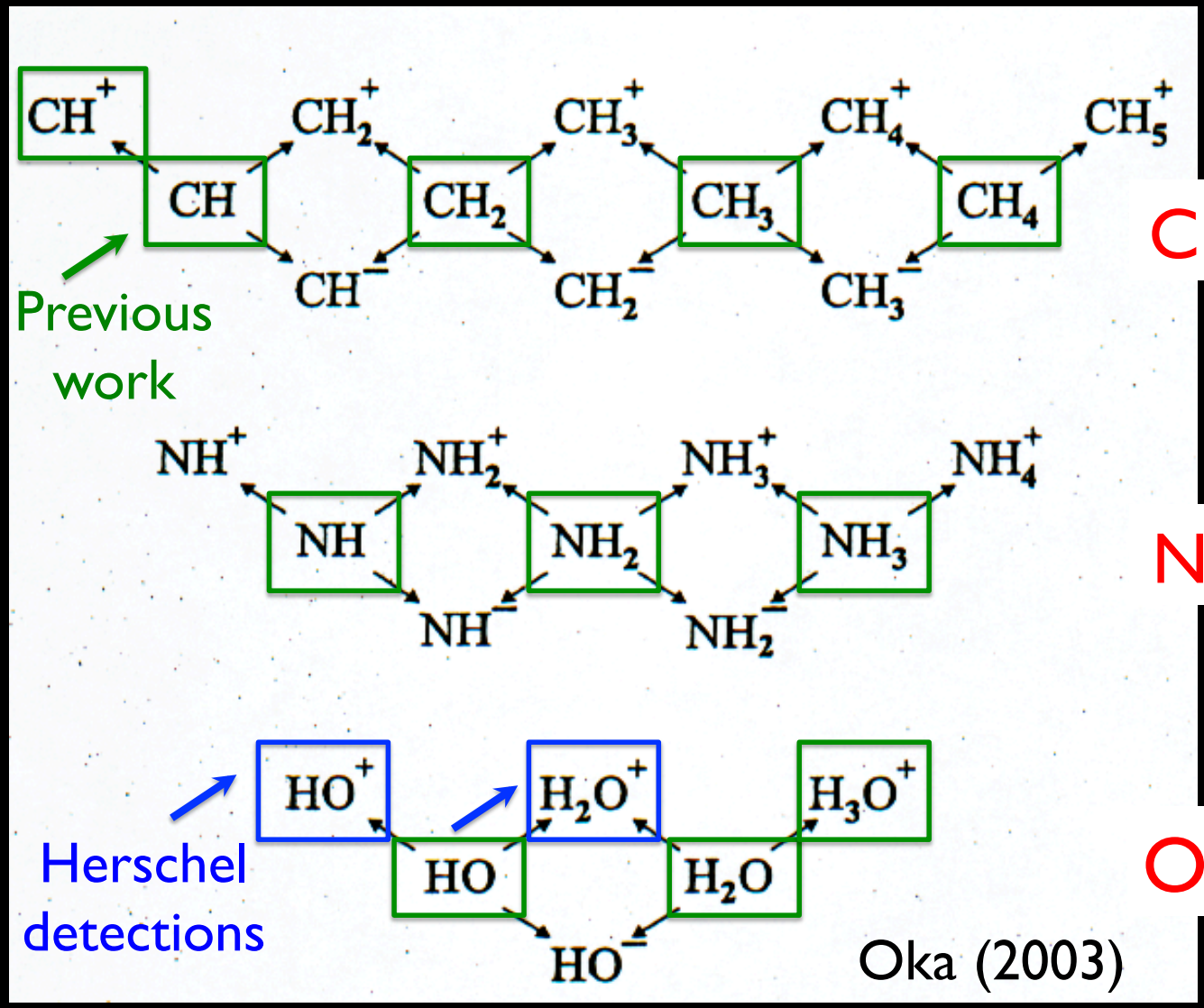
Radicals and Ions from H_2O, NH_3, & CH_4



C ⇒ Si

N ⇒ P

O ⇒ S

Emphasis on (ionic) hydrides

- Fundamental transition of OH^+ uncertain to ±1.5 MHz; H_2O^+ to about ±50-100 MHz
- FIR/THz spectroscopy of many light species incomplete or unknown
- Data on metal hydrides also desirable
- F and Cl chemistry, e.g. H_2Cl^+

  N(HF) / N(H_2O)~1 (assuming o/p=3)

Sonnentrucker et al. 2010, A&A

Small molecular anions

- Recent astronomical detection of CN^-
  - Isovalent to CO, highly stable
  - Anion abundance high wrt neutral, about 0.25%

    Agundez et al. 2010
  - Formation probably via larger anions, not e^- REA

    Eichelberger et al. 2007
- Detection in other sources seems likely
- Other small anions possible
  - e.g. OH^-, SiH^-

Need to improve/refine ion production and specificity

- Molecular beams
- Extended negative glow (DeLucia et al. 1983)
- Velocity modulation
- Light-induced reactions using cold ion traps (S. Schlemmer)

Complementary studies

- Collisional studies of many fundamental molecules still lacking

- Highly accurate ab initio studies of molecular properties needed [e.g., μ, IR intensities, E(J,v,..)]

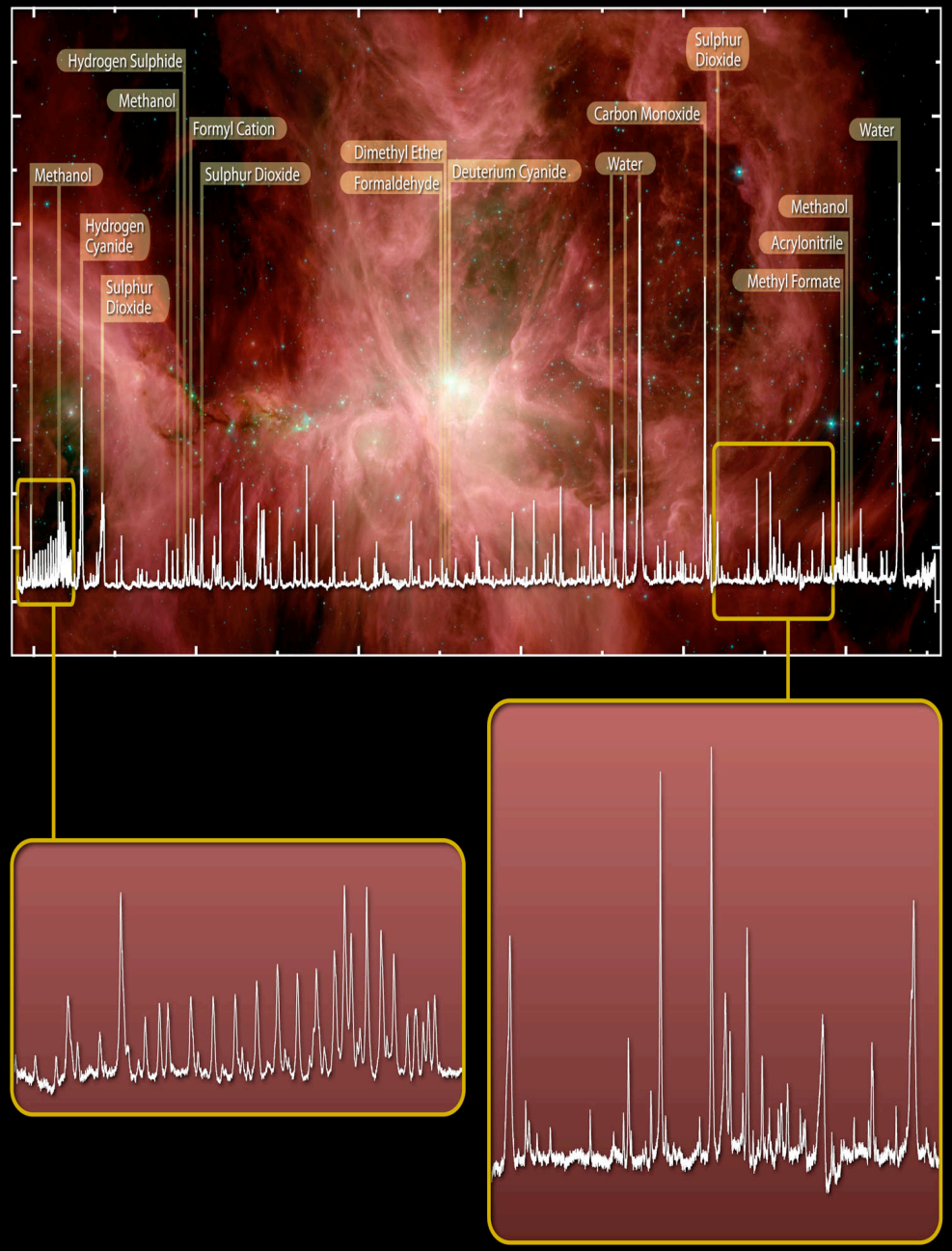
  some benchmark μ measurements probably needed

- Measurements of reaction rates

- Photodissociation cross sections (e.g., H_3O^+)

Unbiased line surveys with *Herschel*/HIFI

- Order of magnitude better sensitivity, and spectral and spatial resolution compared to previous studies
- HEXOS survey of the known chemically rich Orion Nebula shows large number of molecular lines, many (SO, H_2O, CH_3OH) identified with current line catalogs (JPL, CDMS)
- But many unassigned lines: new exciting unstable species or unassigned weeds?



HIFI Spectrum of Water and Organics in the Orion Nebula

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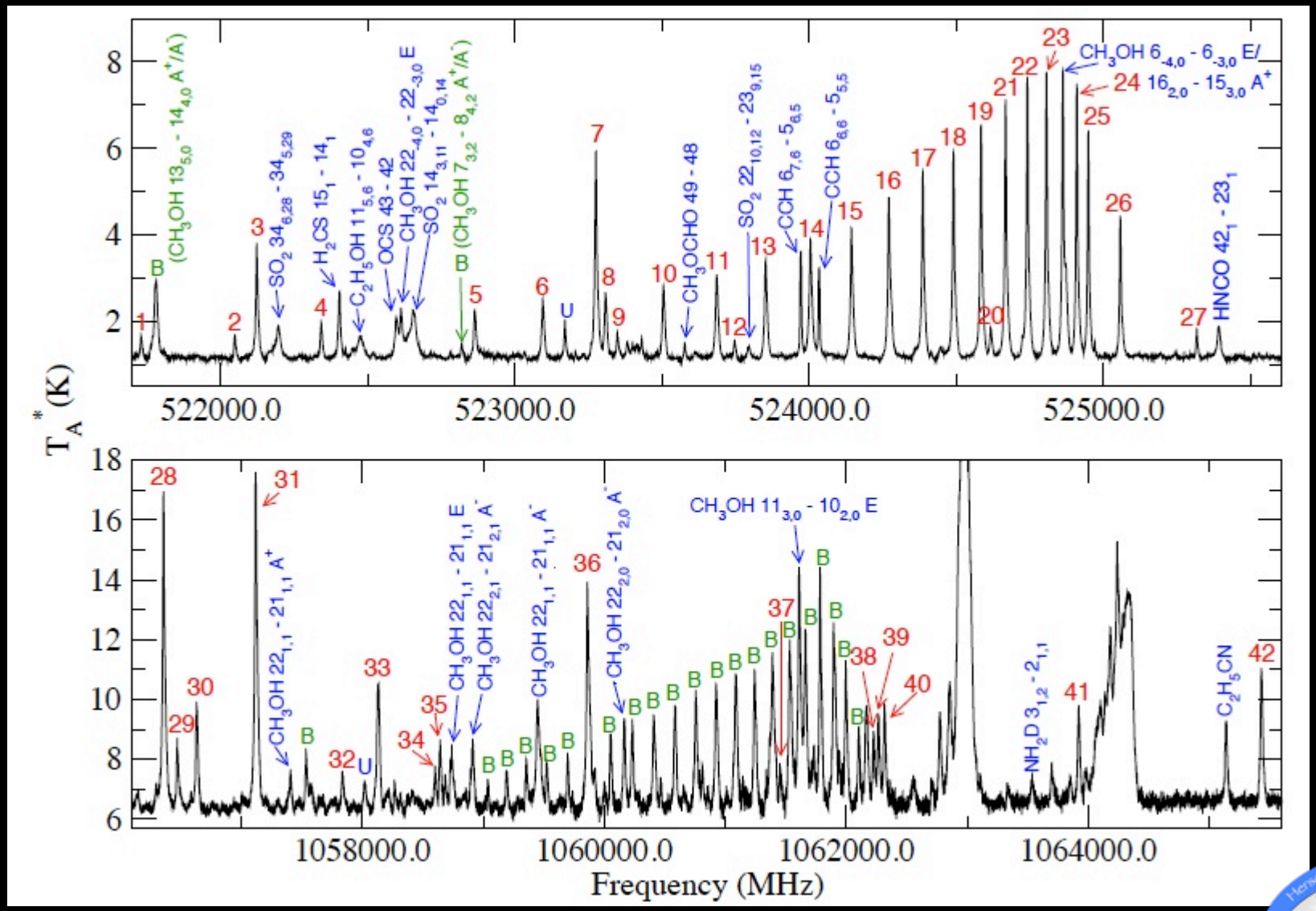
CH_3OH bands in Orion



Wang et al. (2010)

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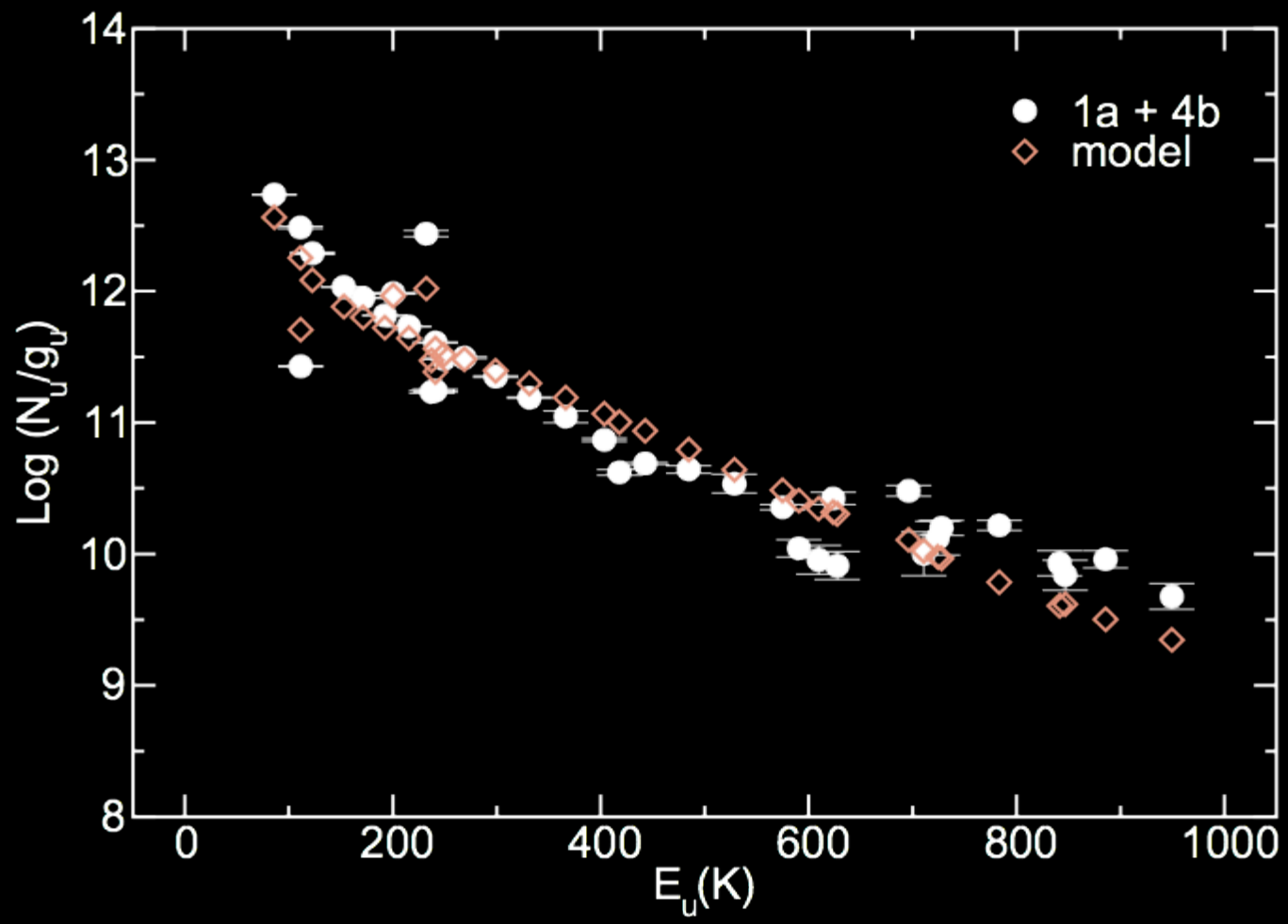
CH_3OH: Weed or Flower?

Bands probe wide range of E in small region of spectrum: direct probe of temperature structure!

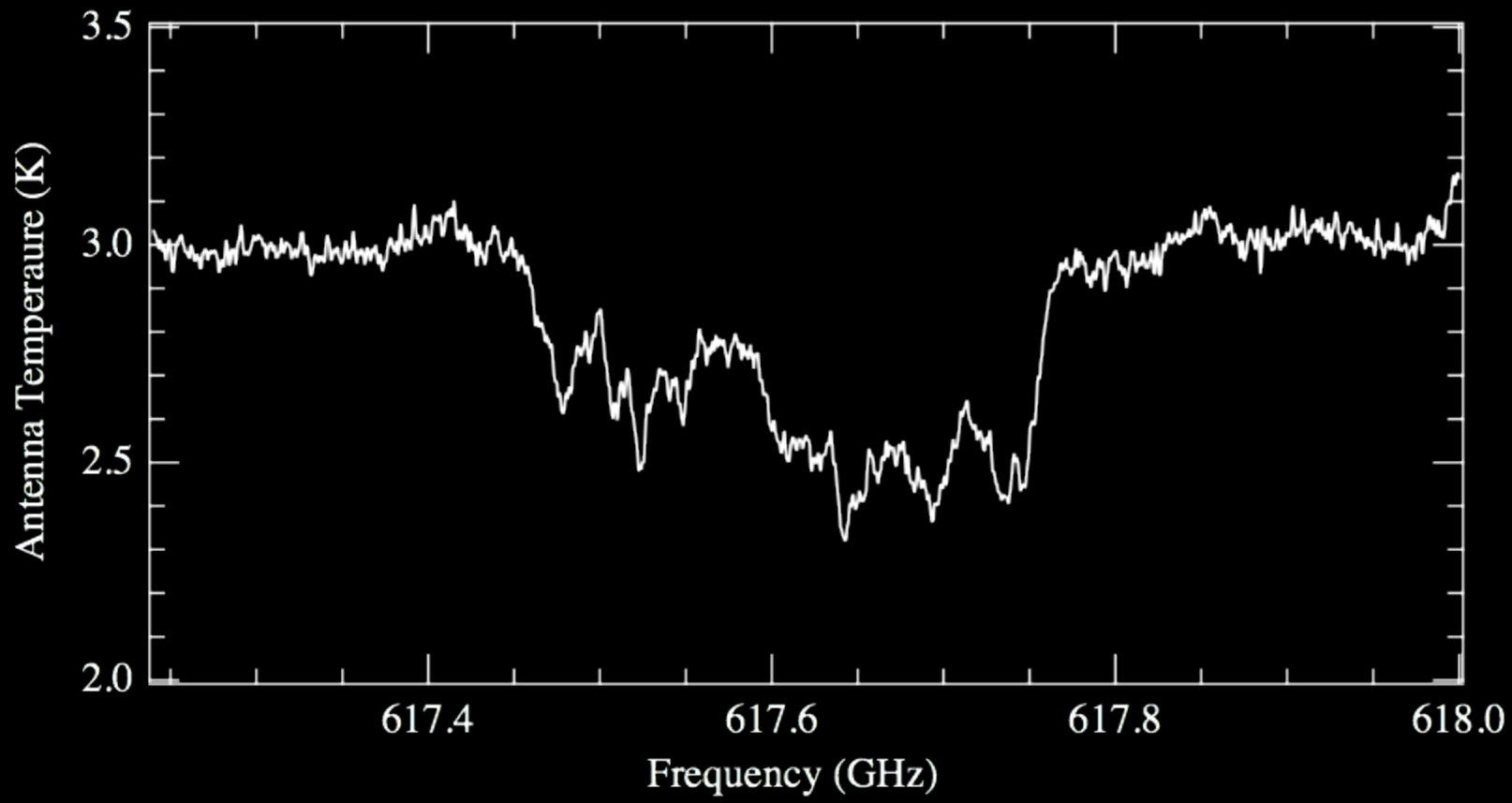
Plot shows model fit including a thermal gradient



Wang et al. 2010

E. Bergin

U617.6



Molecule present in *all* spiral arm clouds between us and the galactic center; reminiscent of c-C_3H_2

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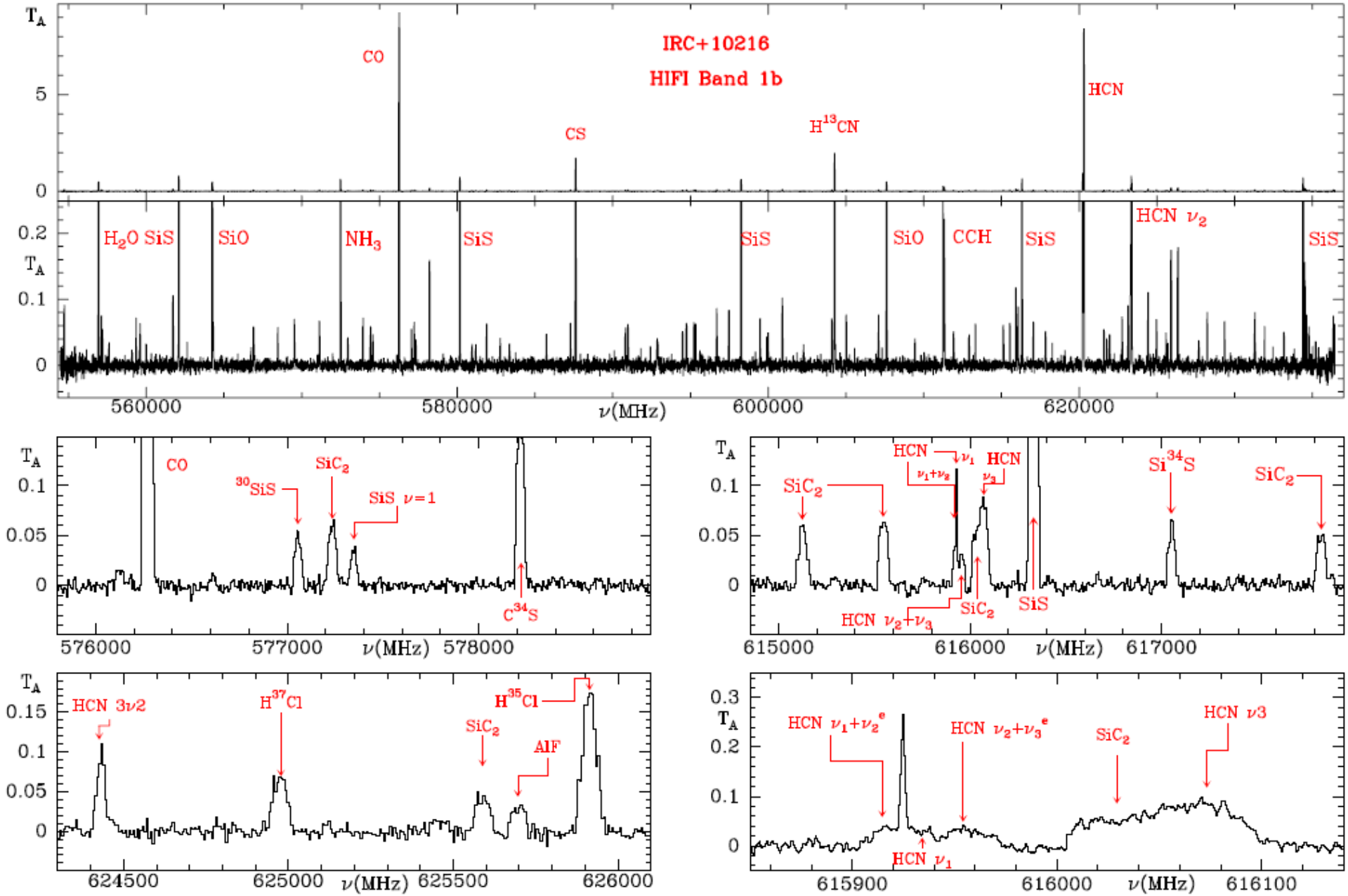


Fig. 1. Spectra of IRC +10216 observed with HIFI band 1b. The two upper panels present the complete spectrum on two different intensity scales. The panels below show different 3 GHz wide ranges of the survey. All data have been smoothed to a spectral resolution of 2.8 km s^{-1} except for the right bottom panel, which shows the spectrum around several vibrational lines of HCN with the nominal WBS resolution (1.1 MHz, ≃0.5 km s^{-1}).

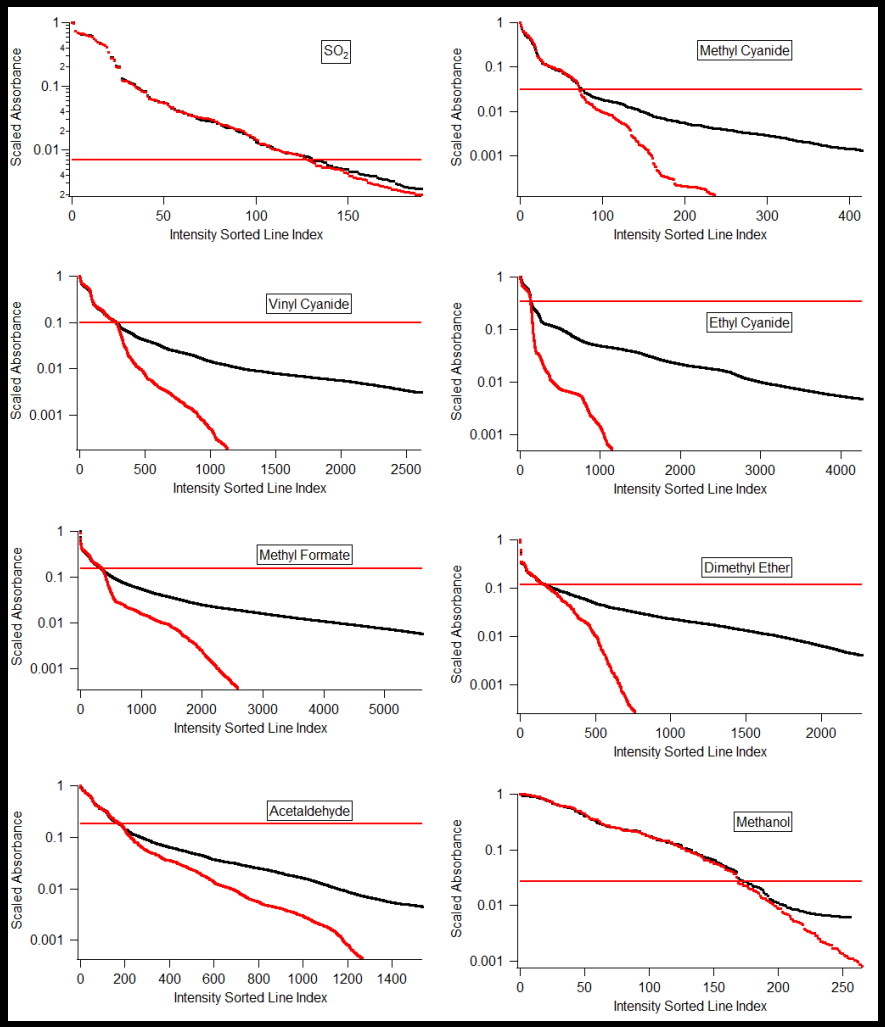
Cernicharo et al., 2010, A&A, 521, L8

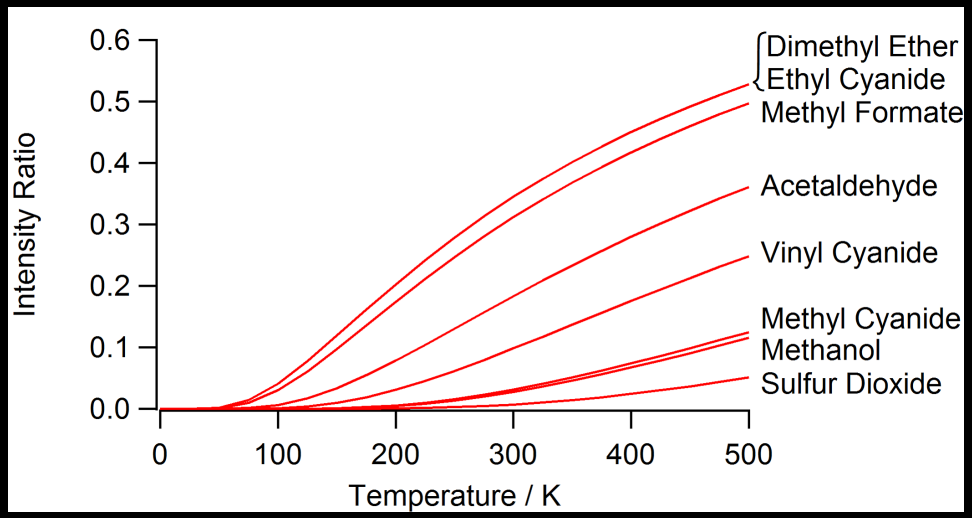
HCl has been detected with PACS/SPIRE (Cernicharo et al., 2010, A&A, 518, L136)

Broad program in laboratory rotational spectroscopy needed

- Continued emphasis on commonly observed astronomical molecules over a wide range of frequency, abundance, and temperature (!)
  - hot cores: e.g., CH_3OH, class 2 weeds
  - stellar: e.g., HCN, SiC_2, NaNC
- Unstable species (radicals, ions, etc.) and prebiotic/biogenic intermediates
  - $CH_3OH_2^+$, $C_2H_4O_2H^+$, carbonic acid (H_2CO_3), etc.

Importance of Databases and Catalogs



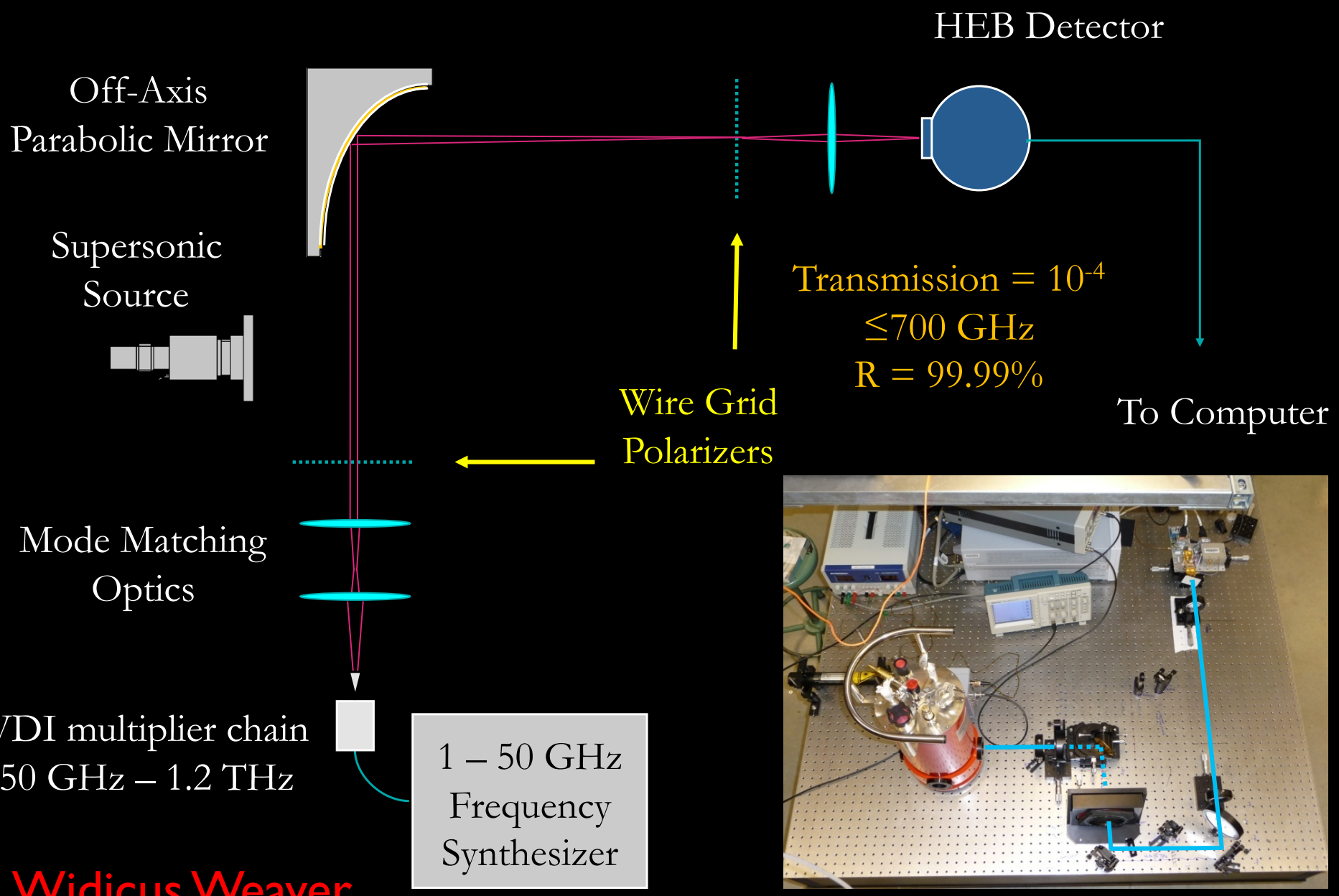


Current catalogs are incomplete!

210-270 GHz window

F. DeLucia

New laboratory tools: THz-CRDS spectroscopy



S. Widicus Weaver

Broadband mmw-THz spectroscopy and library free detection

- Frequency extension of chirped FT microwave spectroscopy (Pate)
- Variant of frequency comb spectroscopy
- Technique (still unproven) may allow acquisition of a spectrum with ~100 GHz of bandwidth in less than 1 ms
- Rotational spectrum «—» molecular structure relation, implies that new identifications may be possible using the right combination of experiment and theory

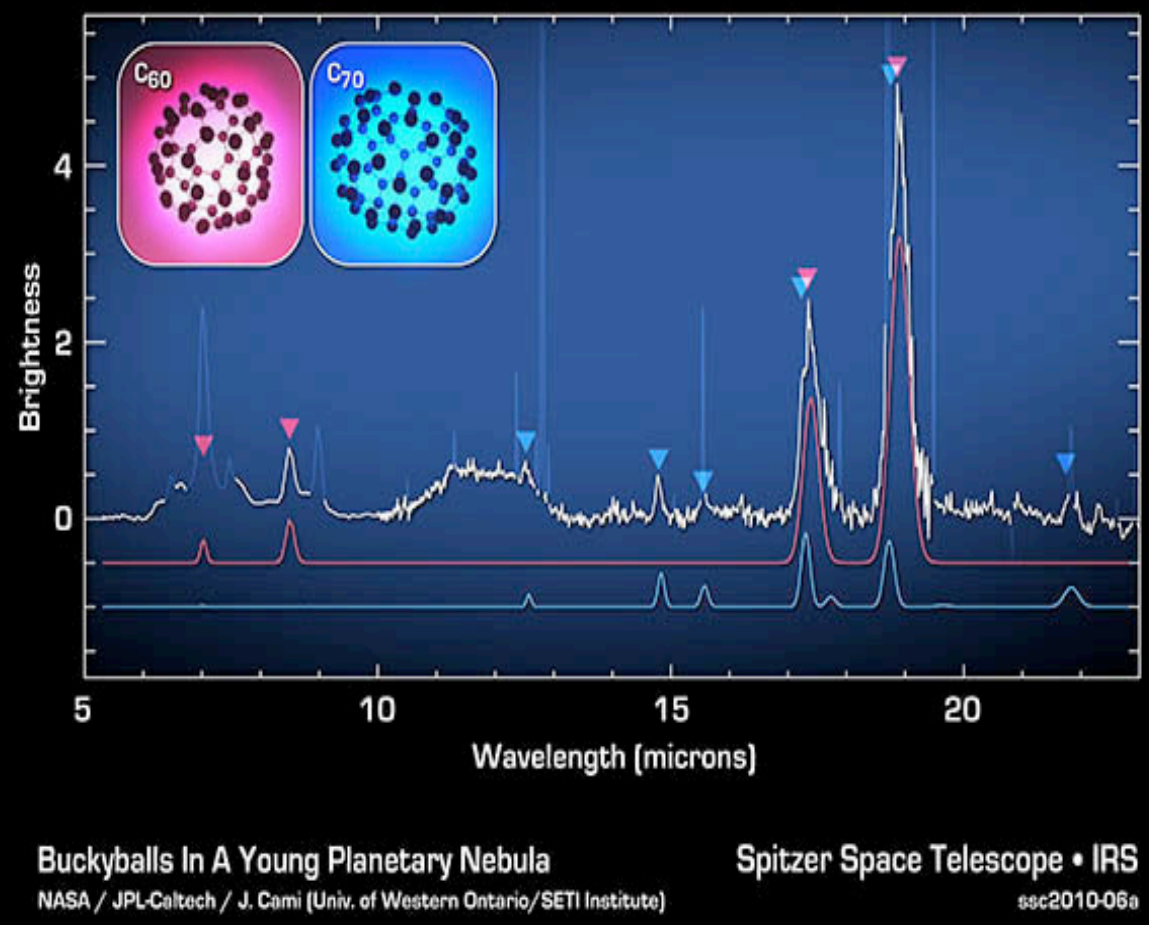
Pate, Lehmann (UVa)

First "buckyball" identifications in space

(archived Spitzer data)

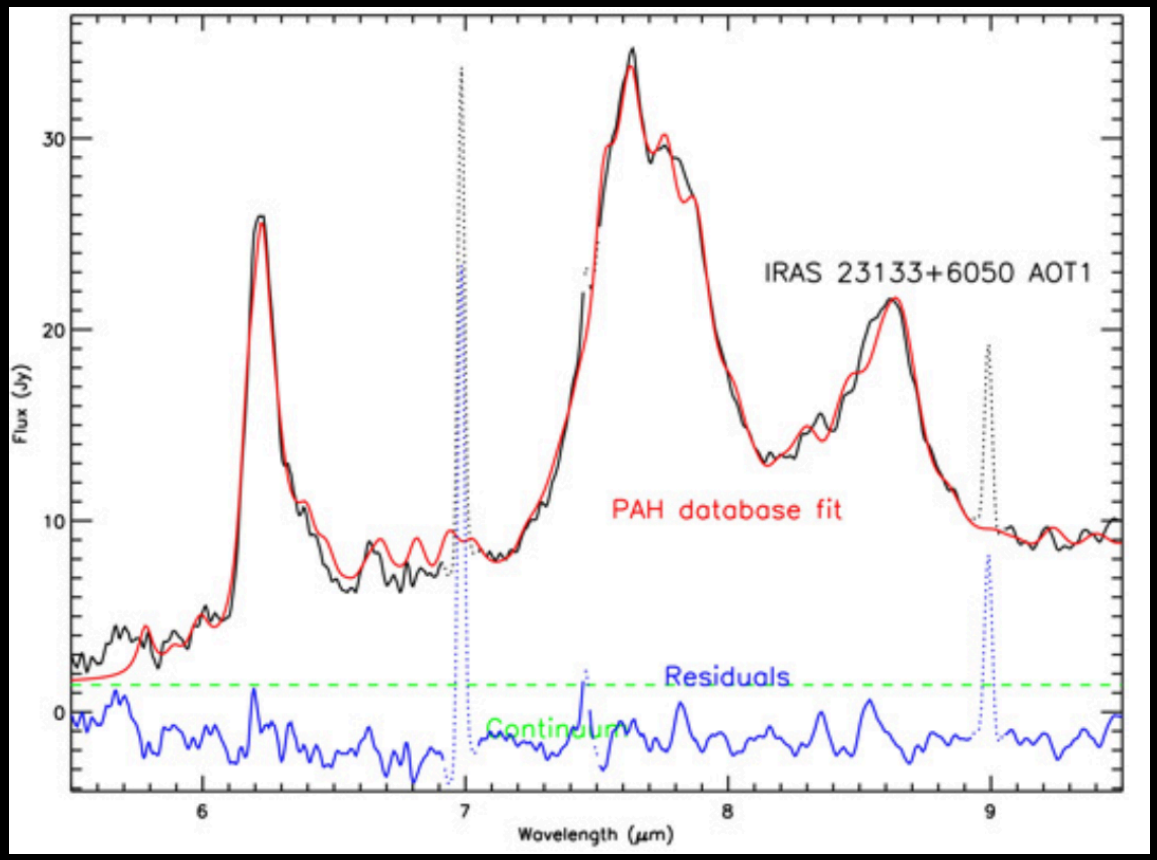
demonstrates that molecules of considerable size and complexity exist in space

- Line coincidences toward one H-poor source; four new sources now reported
- Need laboratory spectroscopy on gas-phase C_{60} and C_{70}
- Need more astrophysical spectra: SOFIA & JWST



J. Cami

IR emission bands and large organic molecules (PAHs)



LSR fit of ISO SWS data to Ames database

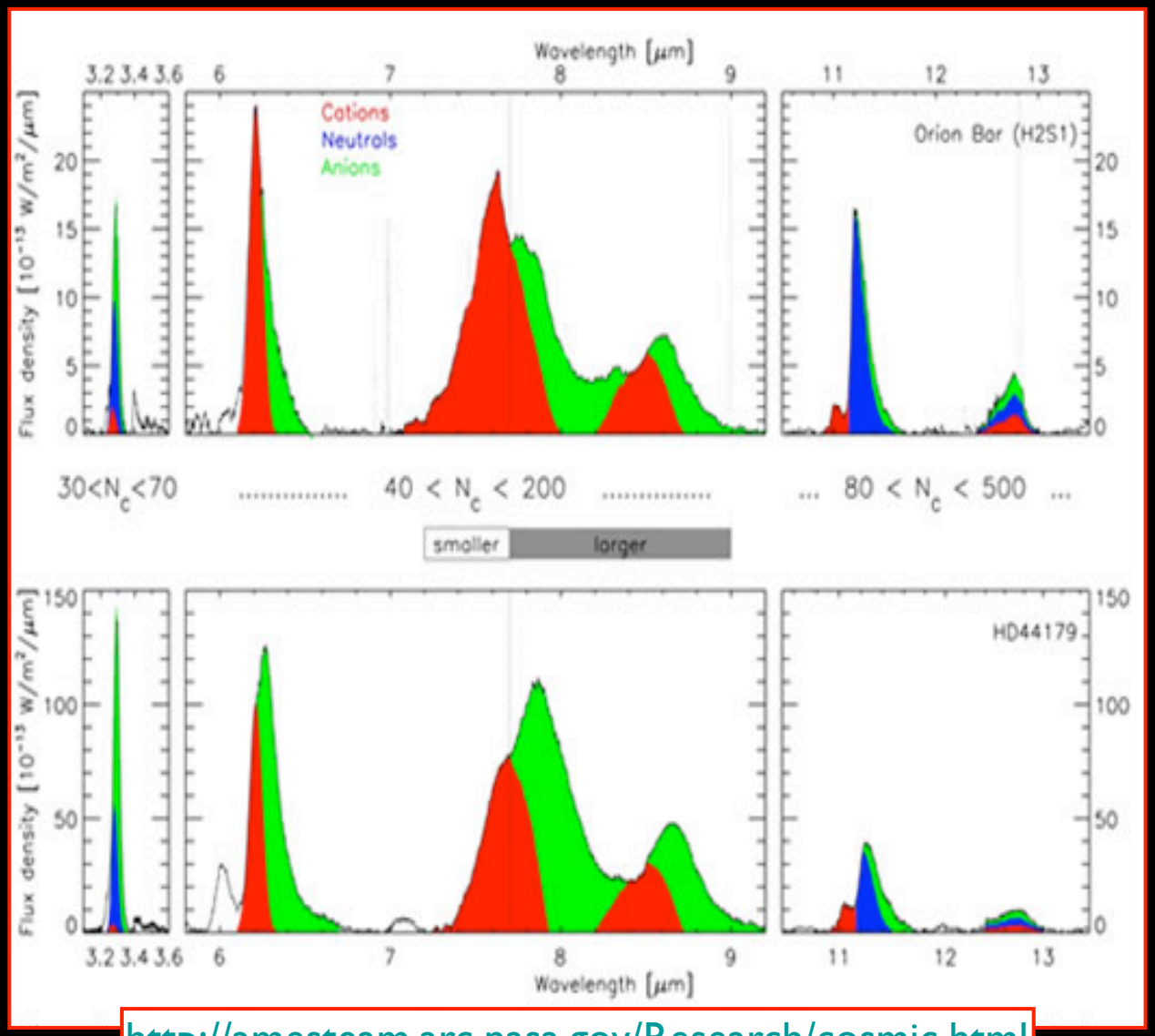
Database is a combination of matrix, jet-cooled, and theoretical intensities

widely used to interpret *Spitzer* and *ISO* data

NUV-NIR (Salama et al.) includes MIRFIR (Allamandola)

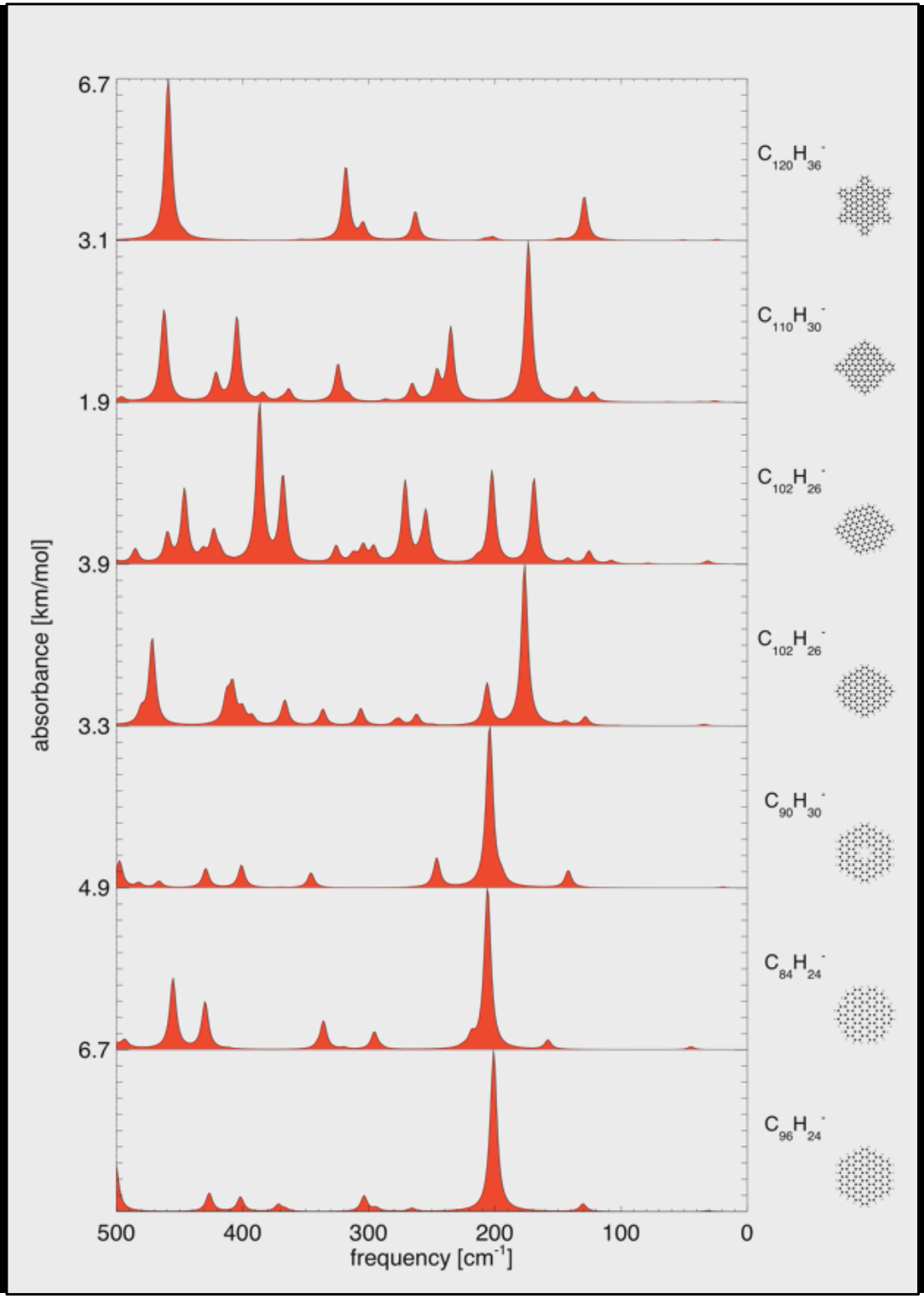
Polyaromatic hydrocarbons (PAHs) and Spitzer

- Comparison with laboratory (and calculated) spectra of PAHs has resulted in UIR assignments with PAH families...
- and estimates of importance of different families (size, charge) in different lines of sight.
- No individual assignments - the far-IR and sub-mm may be the key



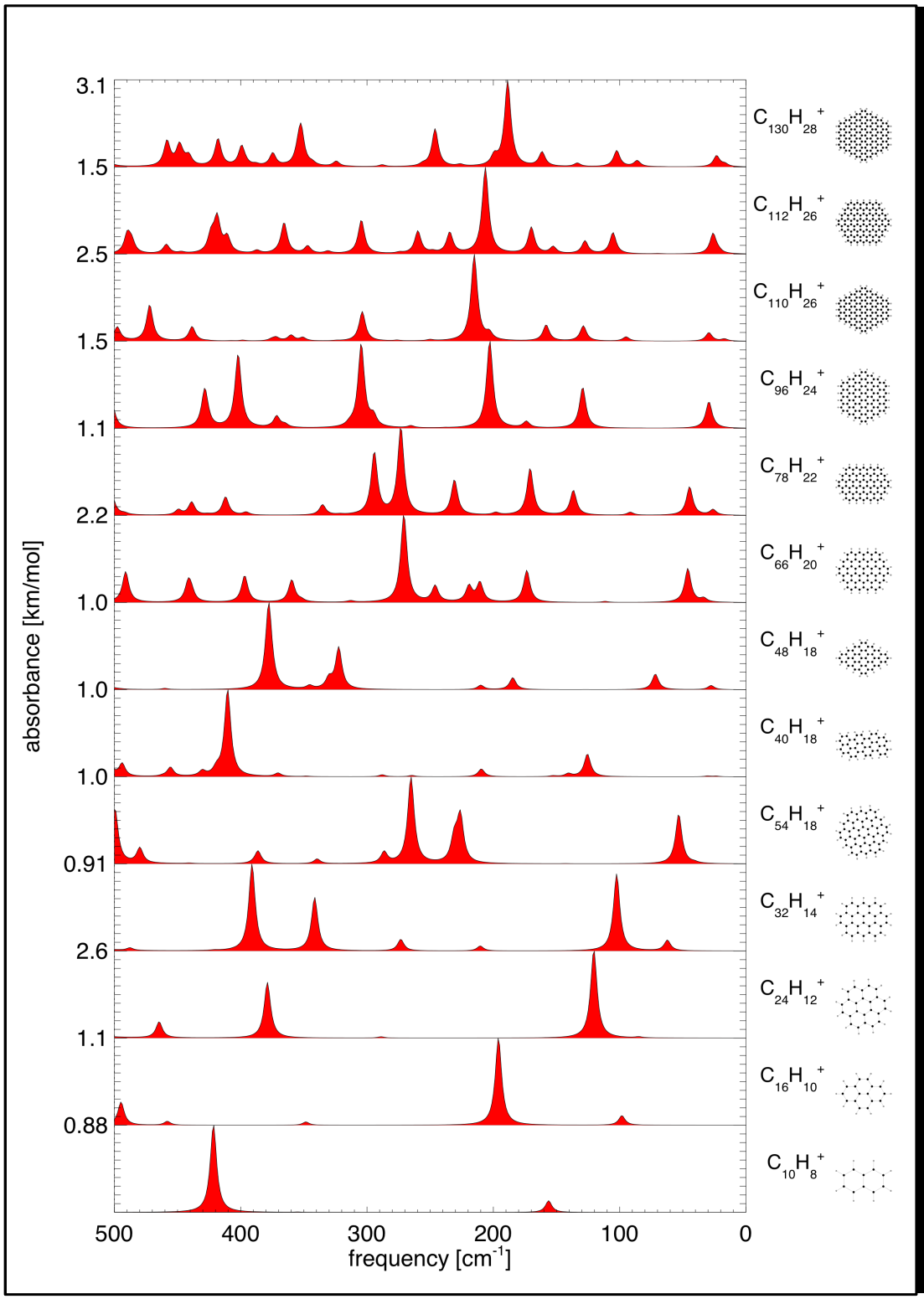
http://amesteam.arc.nasa.gov/Research/cosmic.html

Need laboratory data at far-IR wavelengths!



PAH FIR Spectra are molecule dependent

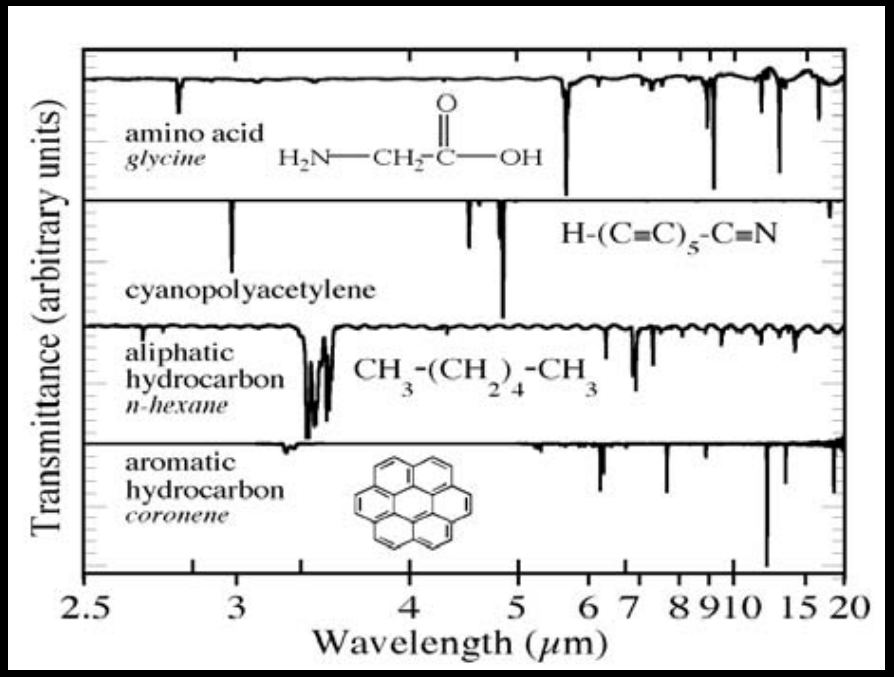
Boersma et al. ApJ submitted



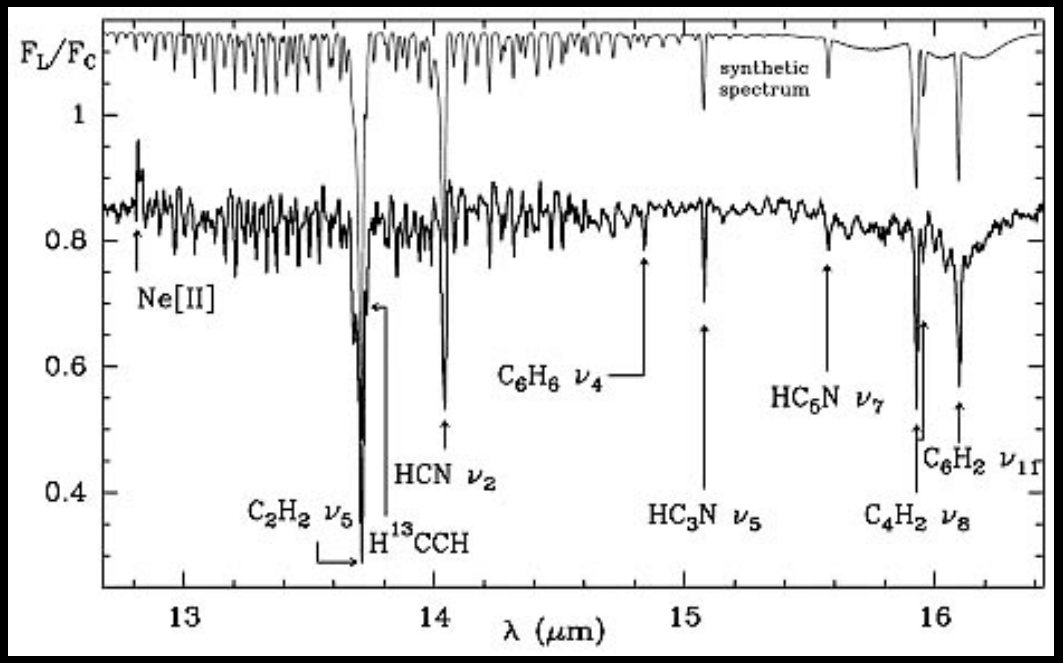
FIR Spectral complexity depends on PAH size and 'shape'.

Boersma et al. ApJ submitted

Spectral signatures in the IR



Spectral variations of different organic molecules



CRL 618 (Cernicharo et al. 2001)

High-resolution spectroscopic needs in the IR:

Emphasis on spectra at high T: correlation between interstellar conditions for start/planet formation and chemistry of Earth

- Those blocked by Earth's atmosphere
  - abundant species such as H_2O, CH_4, NH_3

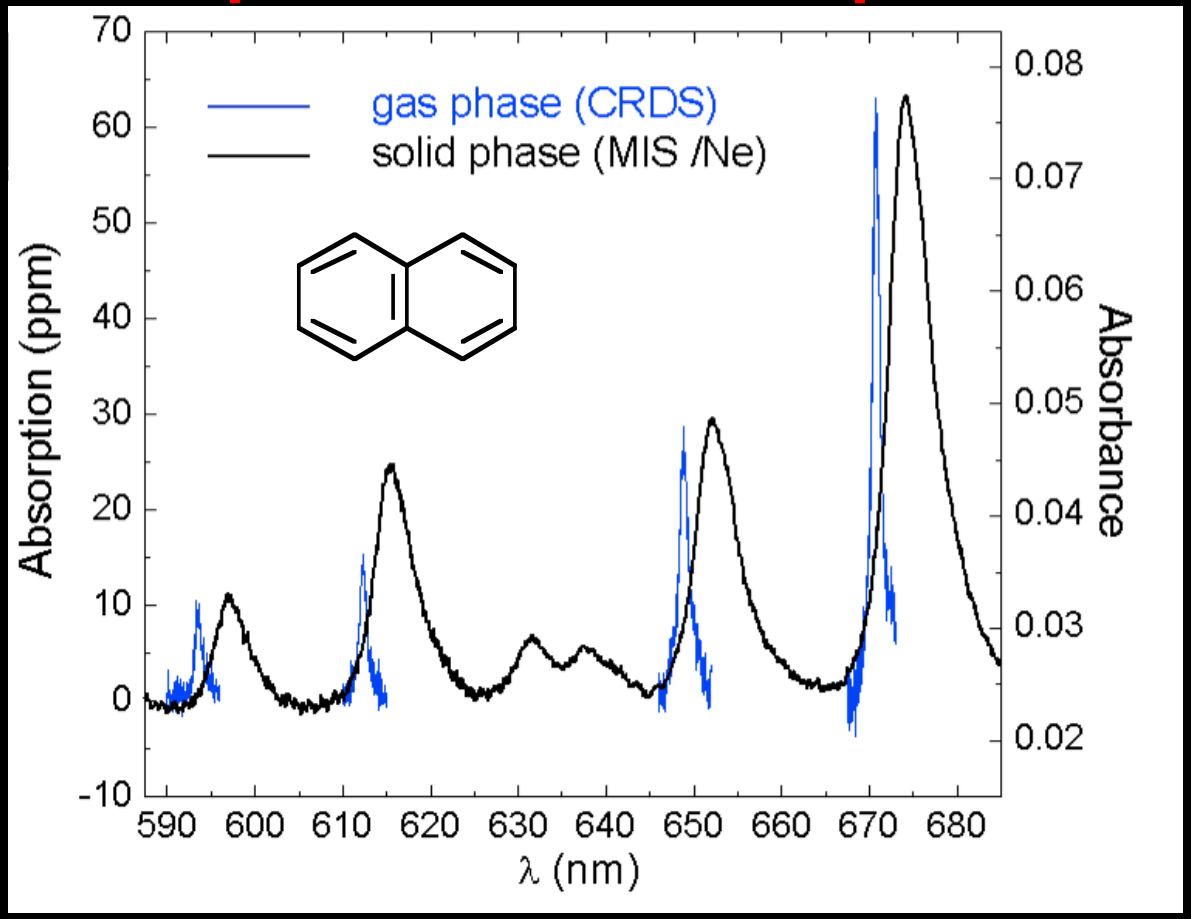
- Nonpolar molecules or those with unfavorable *Q*
  - large OM and their precursors over a wide range of size and structures; ionized: PAHs, smaller rings, and fullerenes
  - hydrocarbon and carbon chains such as $HC_{2n}H$, C_n
  - exotic species such as $C_3H_3^+$, H_5^+, CH_5^+

- Molecules containing main functional groups
  - Ten or so: e.g. R—OH, R—NH_2, etc.

Related studies

- Optical spectroscopy:
  - relaxation processes into IR, mid-IR, and far-IR
  - often provides clearer evidence for specific carriers
- High z universe:
  - strongest IR emitters may be detectable at z=1 and beyond
- Theory and chemical modeling

New laboratory capabilities in the IR and optical: CRDS Spectra of PAH Ions



Bandwidths:

MIS: 120 cm^{-1}

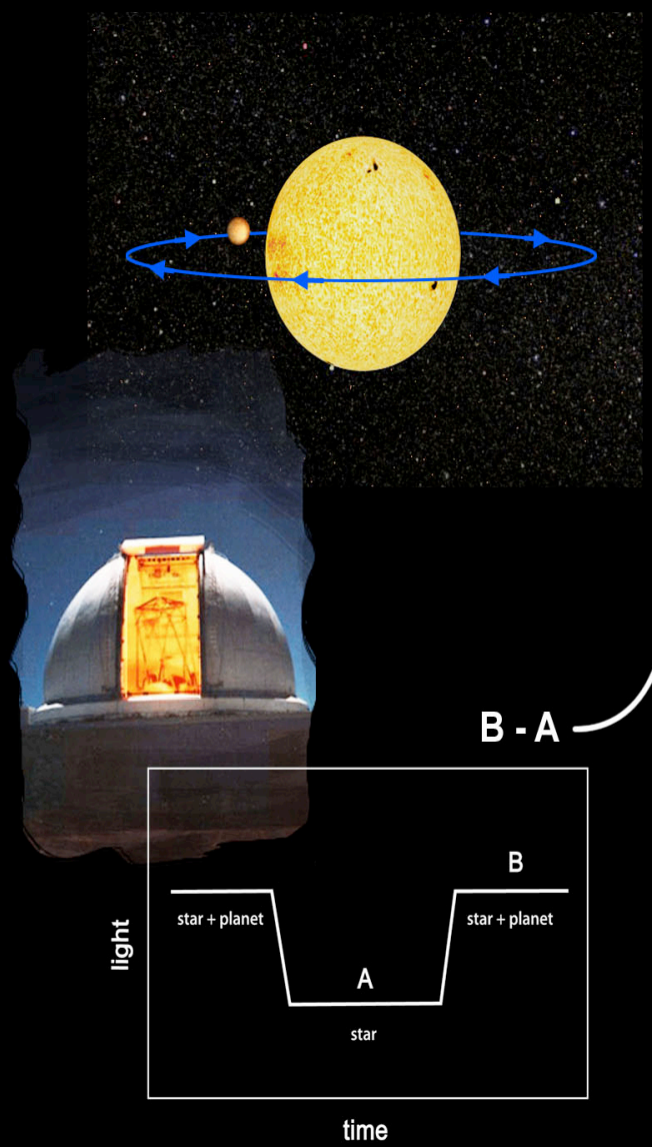
Gas: 25 cm^{-1}

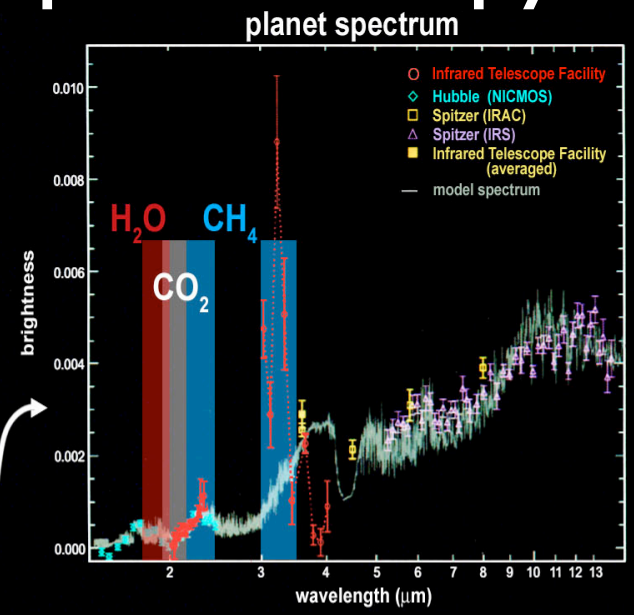
Biennier et al., JCP 2003

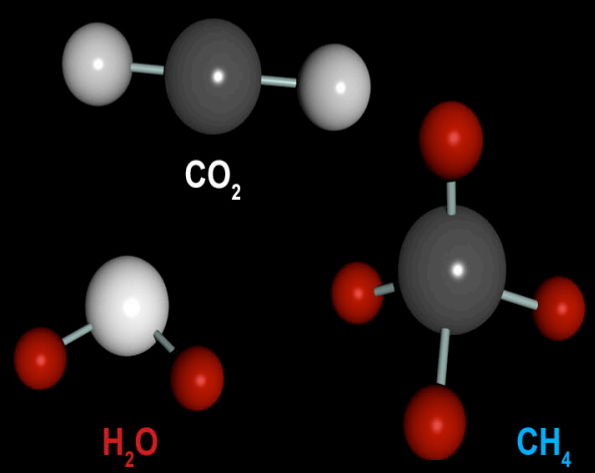
Intrinsic band profiles and peak positions can now be measured in the laboratory to search for specific PAHs (neutrals and/or ions) in space

F. Salama

Spitzer, HST, JWST and exoplanet spectroscopy







- Emission from small molecules detected with low-resolution spectroscopy
- Need higher resolution/sensitivity observations in the near and mid IR: JWST
- But also better model input: atmospheric models, laboratory data, and molecular opacities
- Figure of HD 189733b, credit NASA/JPL-Caltech

Acknowledgements

- Edwin Bergin
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