Molecular spectroscopy and NASA missions

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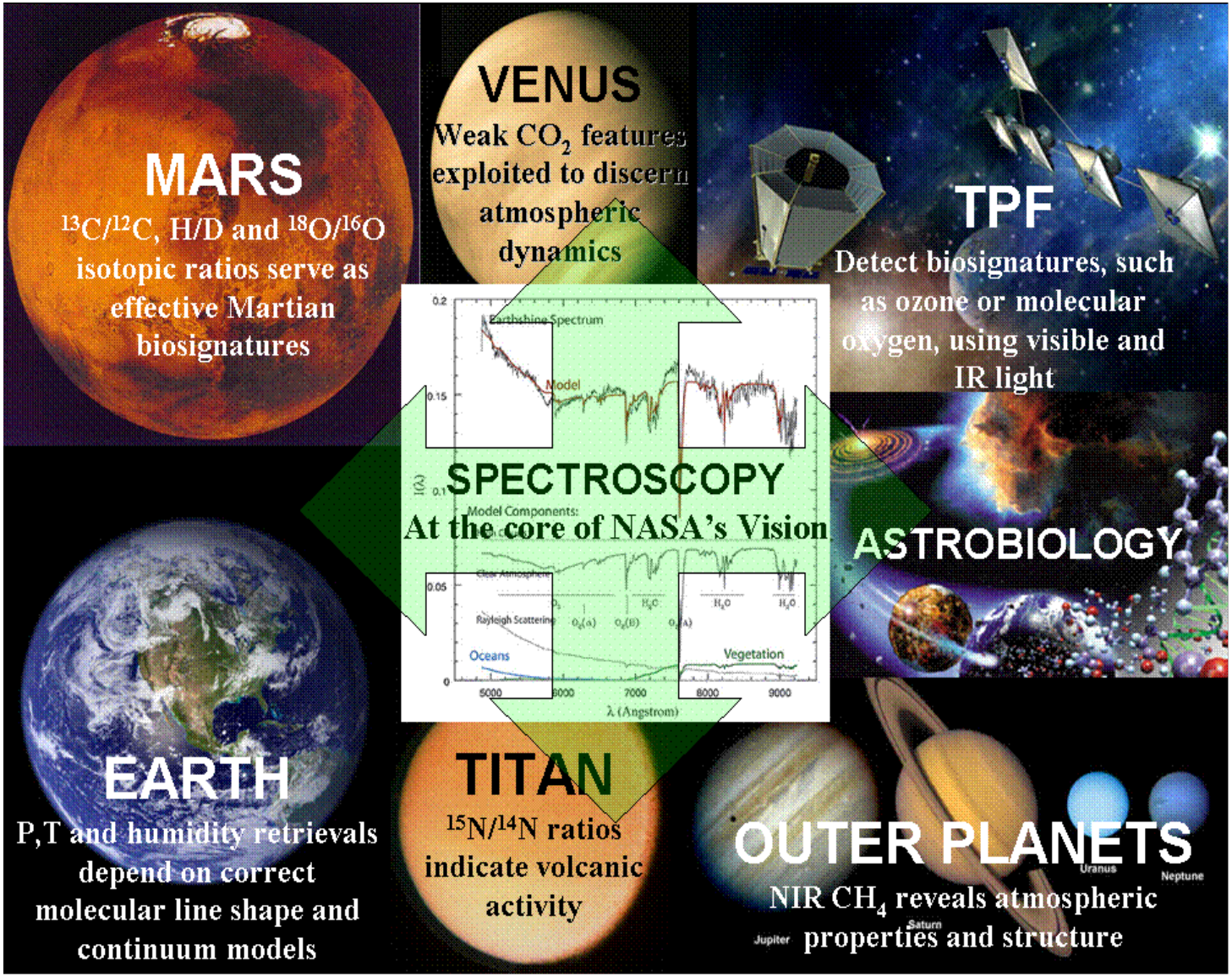
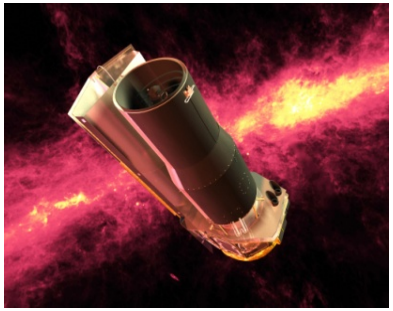
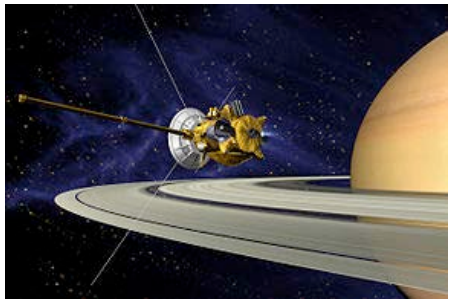
Astronomical remote sensing



Astrophysics missions involving spectroscopy

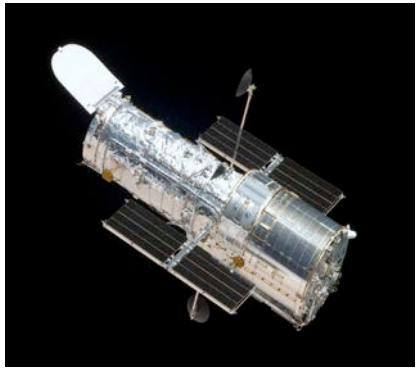


Spitzer (2003)
Infrared
$1b

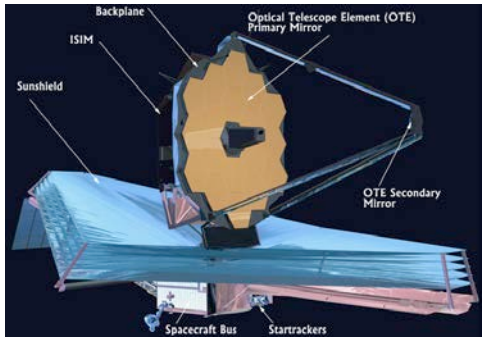


Cassini (2004)
UV to IR
$3.2b

Herschel (2009)
Far-IR
$1.5b



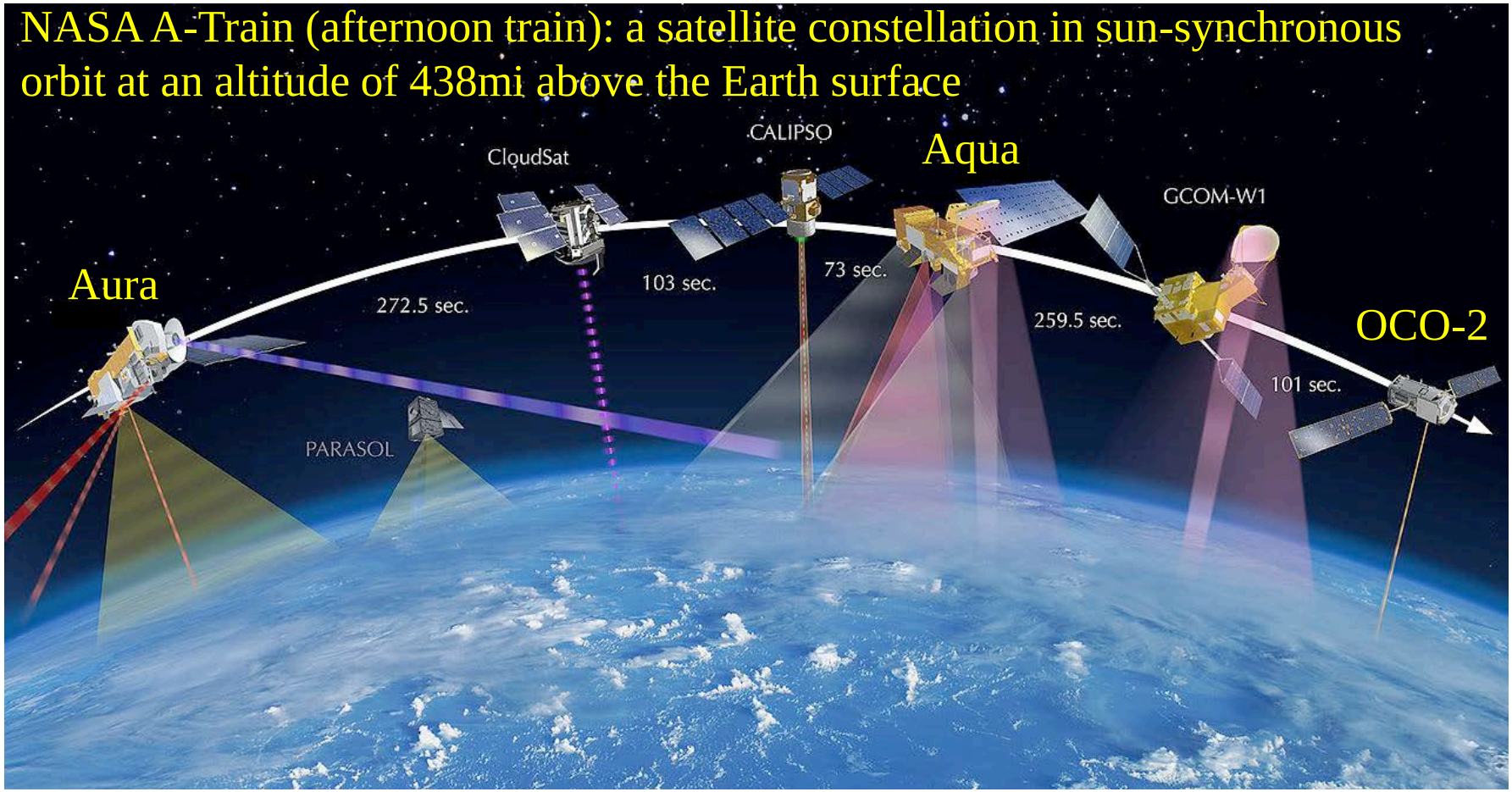
Hubble (1990)
UV to near-IR
$5b (inc servicing)



JWST (2018)
Visible to mid-IR
> $8b

WFIRST (2020s)
Visible to mid-IR
$1.6b

Earth observation satellites needing spectroscopy



Aura (2004-present)
air quality & O_3

Aqua (2002-present)
weather forecast

OCO-2 (2014-present)
climate change

Tasks our group does for NASA missions

- Maintain and update a millimeter and submillimeter spectral line catalog
- Provide spectroscopic line parameters contributing to HITRAN database
- Serve as instrument and science team members
- Instrument development

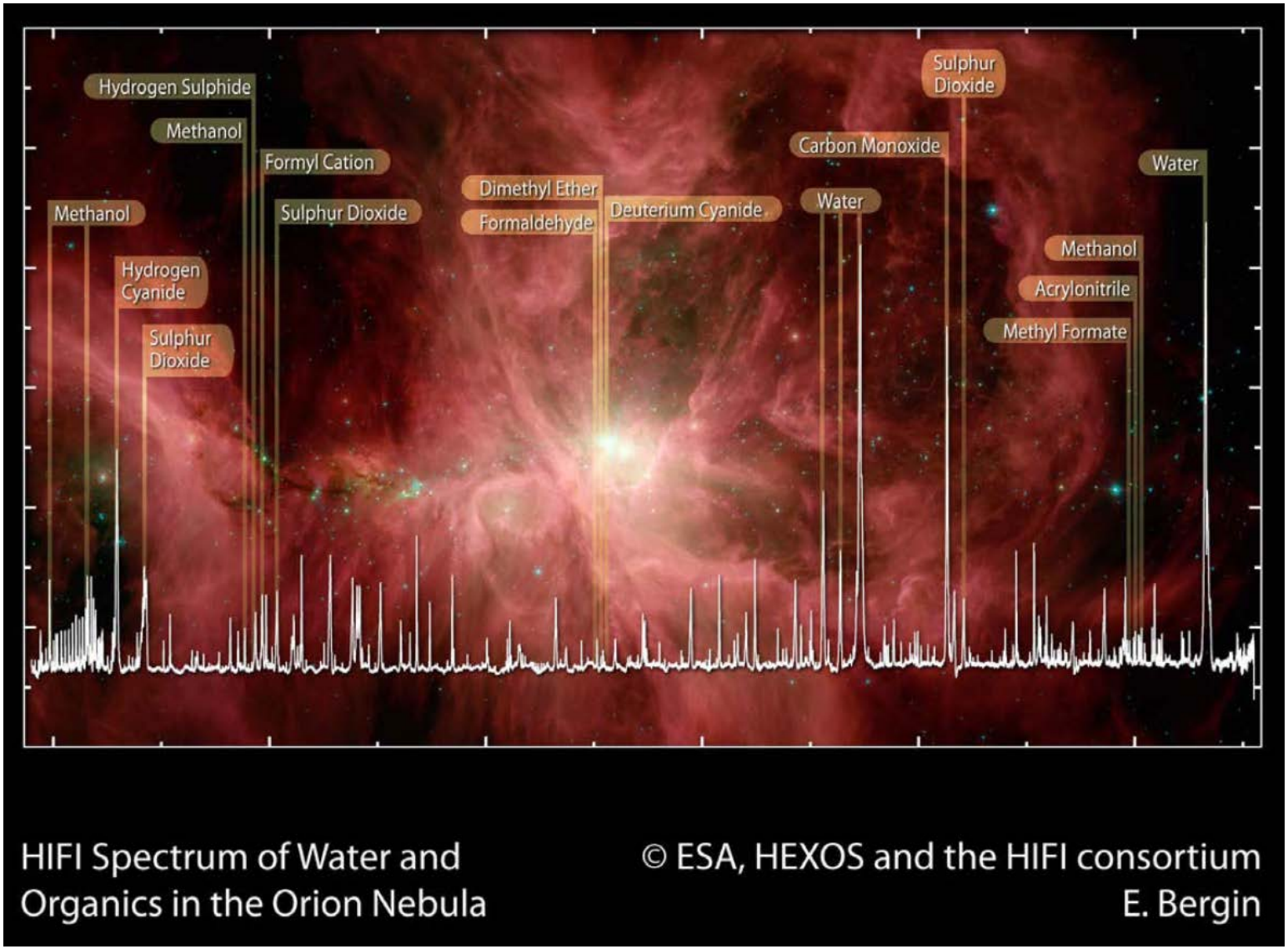
Spectroscopic data needed for space missions

- Line-by-line list of spectrum
  - Frequency and lower state energy
  - Line strength and lineshape
- Cross sections
- Collision-induced absorption (CIA) of N_2, H_2, He, CO_2, O_2, H_2O etc.
- State dependent collision excitation rates
- Quantum assignment for species found in non-thermal conditions

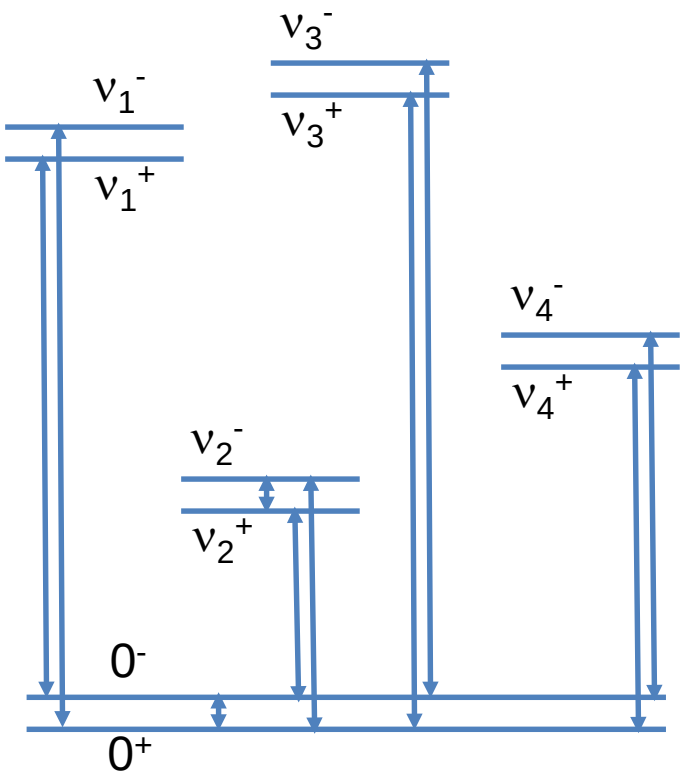
- Our studies supporting the **Herschel** mission
  - H_3O^+ in THz and IR
  - NH_3 in THz and Far-IR
  - CH_3OH in MW and THz
- Our studies supporting the **OCO-2** mission
  - O_2 in MW, THz, IR and UV

Our studies supporting the Herschel mission (1/11)

Herschel/HIFI spectrum at 1058-1115 GHz overlaid on Spitzer image



Our studies supporting the Herschel mission (2/11)



H_3O^+ vibrational levels in SPFIT (1114 transitions total; 8 THz transitions from this work)

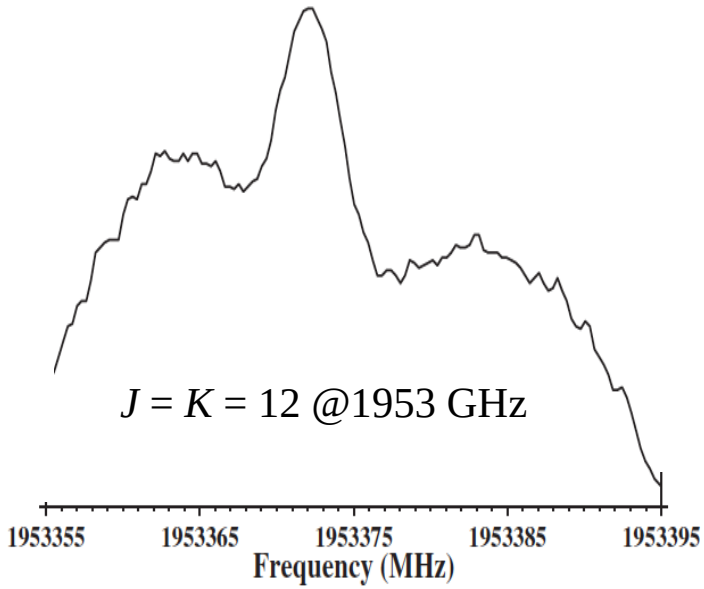
Motivation: ★ Strong Coriolis interactions between ν_1 (~3400 cm^{-1}) and ν_3 (~3500 cm^{-1}) prevented previous studies from fitting high-*J* data (J_{max}=16) to experimental accuracies (residuals up to 4.8 cm^{-1}).

Finding: ★ Adding the Coriolis and ΔK=3 interactions permitted all literature data to be fitted to experimental accuracy.

Significance: ★ In 2012, results enabled Herschel's surprising discovery of H_3O^+ high-*J* lines with *J*=*K* up to 12, revealing that the astrophysical H_3O^+ number density was previously underestimated by a factor up to 10 because the population in these high-*J* states was ignored.

Yu et al, *Terahertz spectroscopy and global analysis of H_3O^+*, APJSS 180, 119 (2009).

Our studies supporting the Herschel mission (3/11)



One of 47 H_3O^+ THz transitions measured in this work

(22 observed for the first time)

Motivation: ★ Interpolated high-*J* transition frequencies from successful analysis of IR data and limited THz data were too inaccurate to analyze the velocity-resolved observations by HIFI ★ Accurate lab rest frequencies with uncertainties of 1 MHz or better were required.

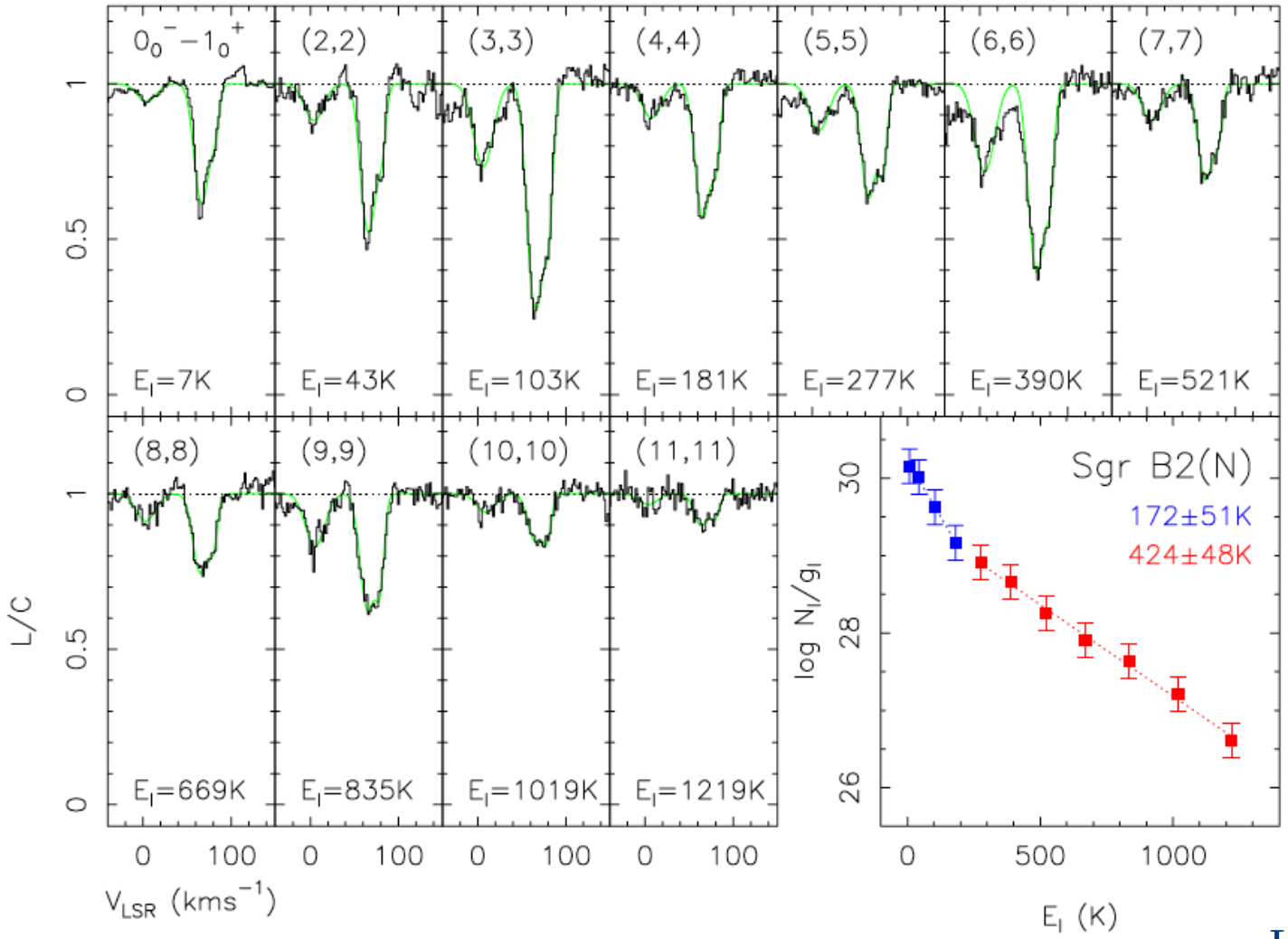
Finding: ★ 22 new ground state inversion transitions were detected in the 0.9 – 2.0 THz region with accuracy of 100 – 300 kHz and fitted with available literature data to within experimental accuracies.

Significance: ★ These results enabled proper analysis of observations from Herschel/HIFI.

Yu and Pearson, *Terahertz measurements of the hot hydronium ion*, APJ 786, 133 (2014).

Our studies supporting the Herschel mission (4/11)

Herschel/HIFI's surprising observation of H_3O^+



Lis et al. 2014

Our studies supporting the Herschel mission (5/11)

- **These H_3O^+ detections revealed**
  - These highly excited H_3O^+ transitions already observed by ESO's Atacama Pathfinder Experiment telescope (APEX) a few years ago but classified as unidentified lines
  - H_3O^+ column densities previously underestimated by a factor up to 10 due to ignoring population in these metastable states
  - The inconsistent OH^+/H_2O and H_2O^+/H_3O^+ ratios (both give the H/H_2 ratio in the diffuse gas) in early Herschel results caused by non-observation of these transitions.
  - The following ISM chemistry needed (all highly exothermic and fast): $O^+ + H_2 \rightarrow OH^+ + H$ then $OH^+ + H_2 \rightarrow H_2O^+ + H$ and finally $H_2O^+ + H_2 \rightarrow H_3O^+$

Our studies supporting the Herschel mission (6/12)

- **Importance of NH_3**
  - One of most abundant nonlinear molecules in the universe
  - Exist in cold ISM and giant planets with temperatures from a few kelvin to a few thousand Kelvin
  - Provide reliable kinetic temperatures and physical densities for astrophysical sources
  - Large dipole moment compared to CO
  - Closely spaced lines compared to CS and HCN
- **Extremely difficult to model NH_3 spectrum using quantum mechanics**
  - Non-rigid due to large amplitude nature of the inversion motion
  - Excited inversion states couple strongly to other vibrational modes

Our studies supporting the Herschel mission (7/12)

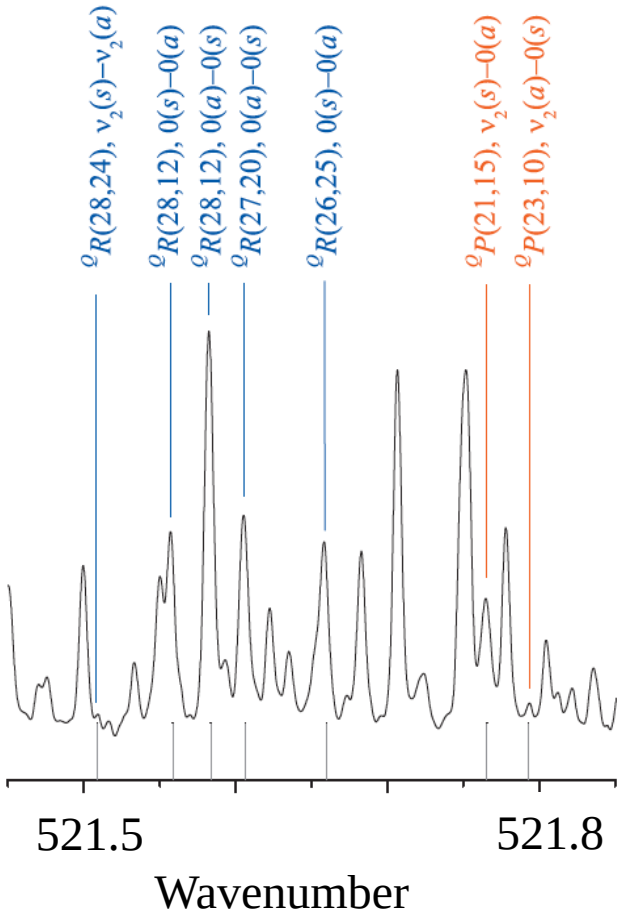
- Collaborations on NH_3
  - JPL lead terahertz measurements and data analyses
  - University of Toyama provided terahertz measurements
  - SOLEIL provided far-IR FTS measurements
  - University of Cologne provide data analysis support
  - Three papers resulted

Prof. K Kobayashi
Lead in Univ. of Toyama

Dr. O. Pirali
Lead in Synchrotron SOLEIL

Dr. C. Endres
Lead in Univ. of Cologne

Our studies supporting the Herschel mission (8/12)



Portion of FTS emission spectrum of NH_3 recorded at SOLEIL

Motivation: ★ Linelist with high-*J* transitions needed to model atmosphere of hot astronomical objects ★ Trusted GS energies needed for subsequent analysis of coupled vibrational states and predictions of hot bands

Finding: ★ 4394 data (~2000 new from this work, J_{max}**=35**) fitted to experimental accuracy ★ Effective Hamiltonian with ΔK=3 and 6 interactions sufficient ★ Significant shortcomings revealed in our understanding of the NH_3 dipole moment surface (ΔK=3 forbidden lines predicted ~100 times stronger than observed)

Significance: ★ Greatly improved our understanding of NH_3 molecular physics.

Yu et al, *Submillimeter/FIR spectroscopy of high-J transitions of NH_3*, JCP 133, 174317 (2010).

Our studies supporting the Herschel mission (9/12)

$2\nu_2$ S $\Delta K=0,6,..$	$\Delta K=3,9$ $\Delta\ell=0$	$\lvert K-\ell\rvert=3,9$ $\Delta\lvert\ell\rvert=1$	$\lvert K-\ell\rvert=3,9$ $\Delta\lvert\ell\rvert=1$	$\lvert K-\ell\rvert=0,6$ $\Delta\lvert\ell\rvert=1$	$\lvert K-\ell\rvert=0,6$ $\Delta\lvert\ell\rvert=1$
	$2\nu_2$ A $\Delta K=0,6,..$	$\lvert K-\ell\rvert=0,6$ $\Delta\lvert\ell\rvert=1$	$\lvert K-\ell\rvert=0,6$ $\Delta\lvert\ell\rvert=1$	$\lvert K-\ell\rvert=3,9$ $\Delta\lvert\ell\rvert=1$	$\lvert K-\ell\rvert=3,9$ $\Delta\lvert\ell\rvert=1$
		ν_4 S $\ell=1$ $\Delta K=0,6,..$	$\lvert K-\ell\rvert=0,6$ $\Delta\lvert\ell\rvert=2$	$\Delta K=3,9$ $\Delta\ell=0$	$\lvert K-\ell\rvert=3,9$ $\Delta\lvert\ell\rvert=2$
			ν_4 S $\ell=-1$ $\Delta K=0,6,..$	$\lvert K-\ell\rvert=3,9$ $\Delta\lvert\ell\rvert=2$	$\Delta K=3,9$ $\Delta\ell=0$
				ν_4 A $\ell=1$ $\Delta K=0,6,..$	$\lvert K-\ell\rvert=0,6$ $\Delta\lvert\ell\rvert=2$
					ν_4 A $\ell=-1$ $\Delta K=0,6,..$

Matrix elements for NH_3 $2\nu_2$ and ν_4

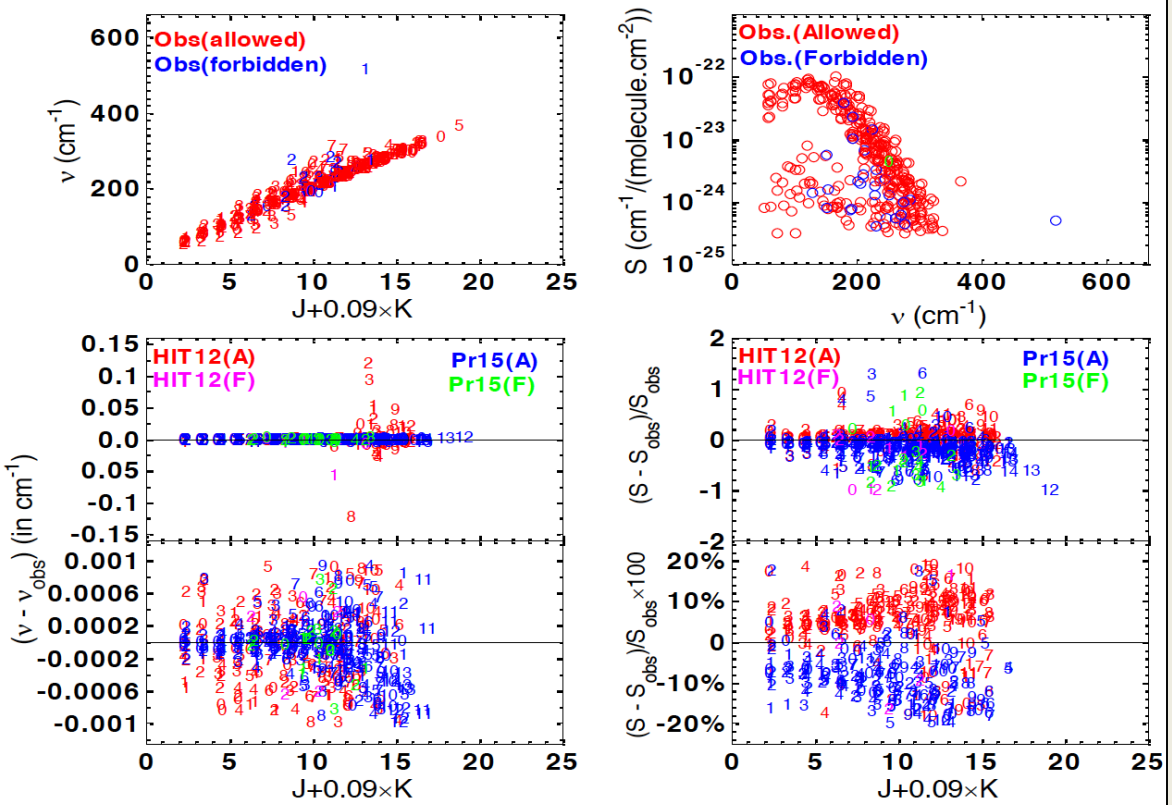
Motivation: ★ Spectrum defied analysis to experimental accuracy in all previous studies (**J_{max}=12** fitted to 10σ)

Finding: ★ 7565 (~3000 new from this work, **J_{max}=19**) fitted to 1.7σ
★ many interactions required for the fit

Significance: ★ Results will enable subsequent analysis of coupled states in inversion problems and predictions of hot bands.

Pearson et al., *Modeling NH3 $2\nu_2$ and $\nu_{\square}$ states to experimental accuracy* (submitted to JCP)

Our studies supporting the Herschel mission (10/12)



Distribution of ν_4 inversion and comparison to Pearson et al. (2016) and HITRAN 2012

Motivation: ★ Fix the line intensity problem revealed in our previous study ★ Validate ab initio linelist

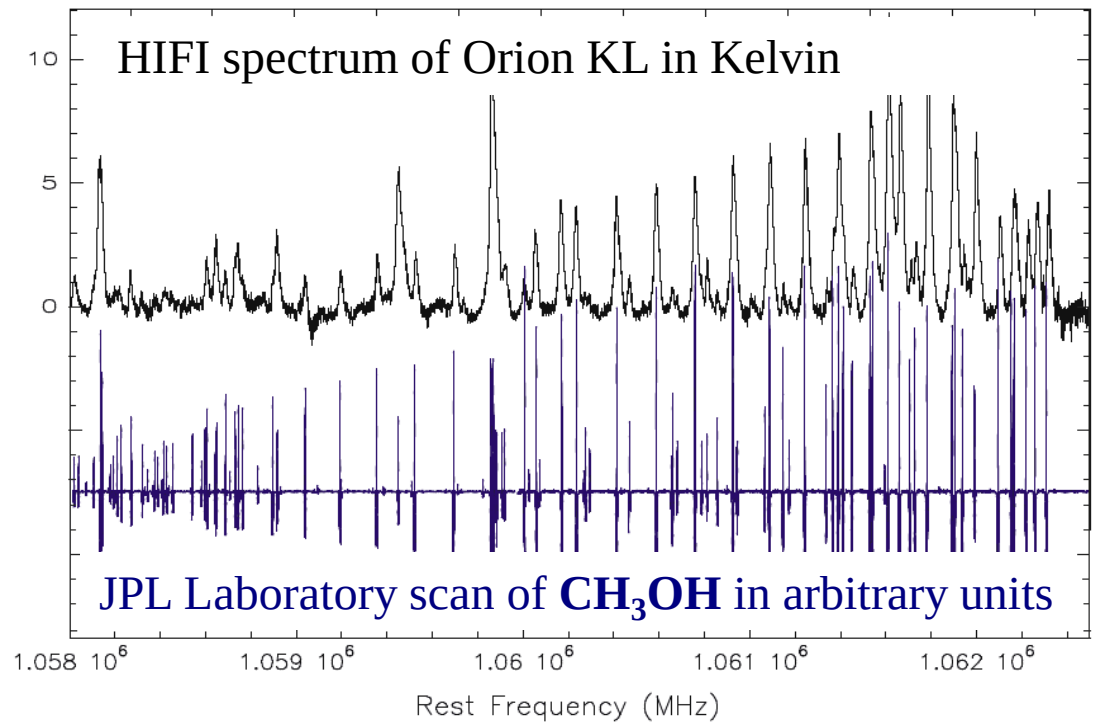
Finding: ★ Empirical positions from Yu2010 and Pearson2016 are good ★ Problems in HITRAN12 high *J* positions ★ Line intensity problems in all previous work

Significance: ★ Results provide critical insights on how to fix NH_3 intensity problems

Sung et al., *Far –IR $^{14}NH_3$ line positions and intensities* (submitted to JMS)

Our studies supporting the Herschel mission (11/12)

- Interstellar weeds: high abundance; dense spectrum; spectrum difficult to predict
- Four most prominent (Class I) weeds defined in the 2006 workshop of laboratory spectroscopy in support of Herschel, Sofia and ALMA:
  - methanol (CH_3OH)
  - methyl formate ($HCOOCH_3$)
  - dimethyl ether (CH_3OCH_3)
  - ethyl cyanide (CH_3CH_2CN)
  - the isotopologues
- We recorded their spectra in
  - 0.3 – 1.2 THz
  - 1.3 – 2.0 THz
  - 2.4 – 2.7 THz
- For data analyses, we led some and collaborated with many groups, publishing ~20 papers
- Half of the laboratory spectra still remain to be analyzed.



Our studies supporting the Herschel mission (12/12)

Many collaborations on methanol and other Class I species

Prof. Z. Kisiel
Polish Academy of Sciences

Prof. V. Ilyushin
Radioastrono. Ins. Ukraine

Dr. H.S.P. Mueller
Univ. of Cologne, Germany

Dr. C. Endres
Univ. of Cologne, Germany

Prof. M. Carvajal
Univ. de Huelva, Spain

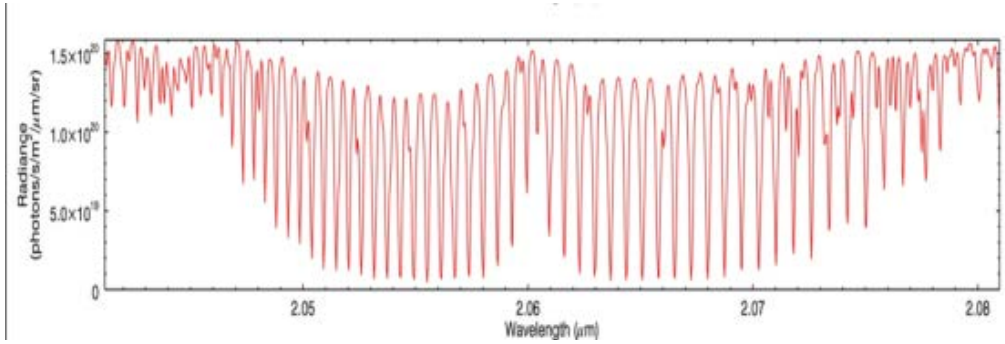
Prof. I Kleiner
Lisa, France

Prof. L.-H. Xu
Univ. of New Brunswick, Canada

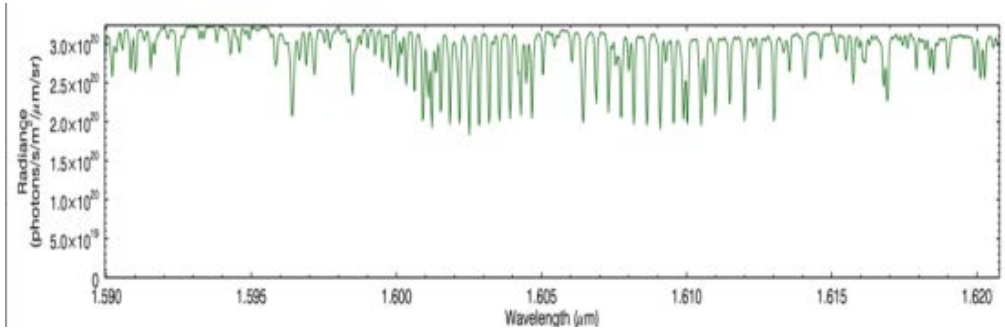
Prof. L. Margules
Univ. Lille, France

Our studies supporting the OCO-2 mission (1/5)

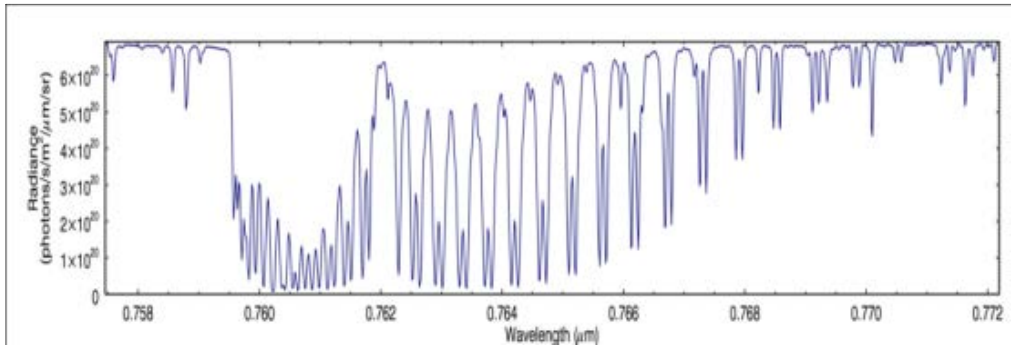
OCO-2 observes two CO_2 bands and one O_2 band in the infrared



CO_2 @ 2.06 μm

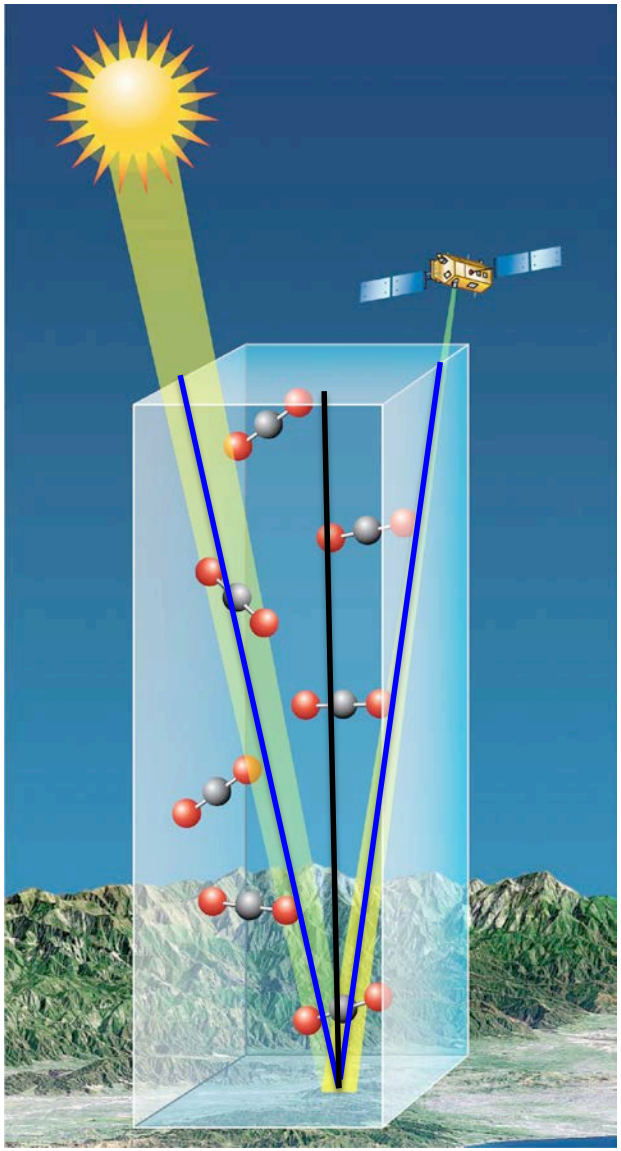


CO_2 @ 1.6 μm



O_2 A-band @ 0.76 μm for air mass (path length) calibration

Our studies supporting the OCO-2 mission (2/5)



O_2 - important tool in Earth observation missions

- Calibrate air mass (path length)
- Determine surface pressure

Slant column density from spectra

Vertical column density as final products of Earth observation missions

Sunlight also scattered by aerosols in the air (path length calibration needed)

O_2 spectroscopic accuracy required: 0.1%

(The state-of-art was 1% before OCO-2)

- Frequency and lower state energy accurate to a few MHz at 13000 cm^{-1}
- Intensity, lineshape including line mixing, CIA studied at pressures, temperatures and path lengths comparable to the atmosphere

http://oco.jpl.nasa.gov/images/ocov2/OCO_column.jpg

Our studies supporting the OCO-2 mission (3/5)

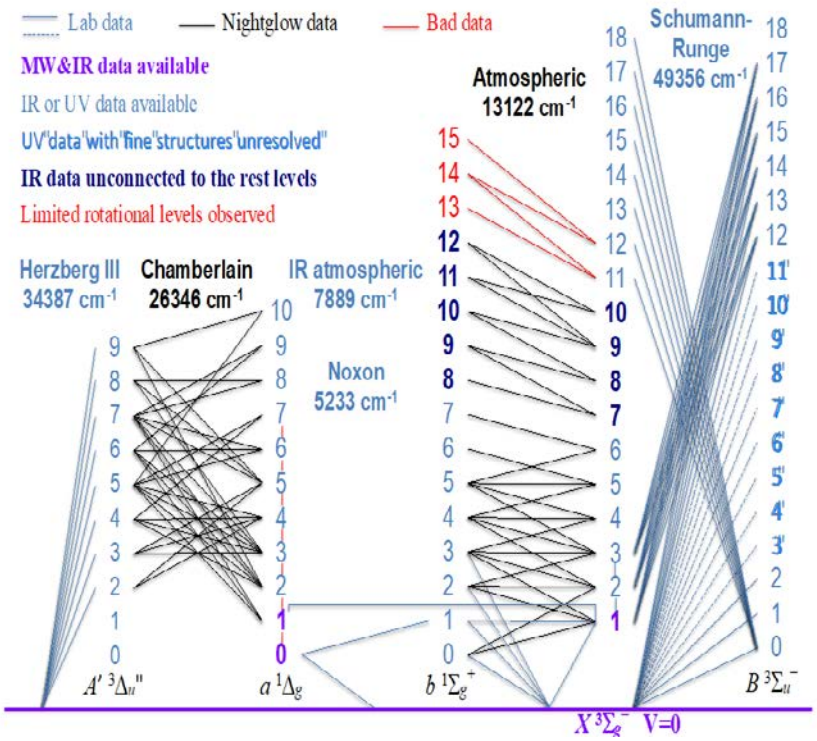
Our series papers on spectral analysis of oxygen

1. S. Yu et al., JCP 2012, **Paper I** on "isotopically invariant dunham fit for the $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ states"
2. Drouin et al., JCP 2012, **Paper II** on "rotational spectra of $a^1\Delta_g$ O_2 isotopologues"
3. Drouin et al., JCP 2013, **Paper III** on "Laboratory investigation of the airglow bands"
4. Yu et al., JCP 2014, **Paper IV** "Energy levels, partition sums, band constants, RKR potentials, Franck-Condon factors involving the $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$ states"

Dr. C.E. Miller,
Co-author, JPL

Dr. H.S.P. Mueller
Co-author, Univ. of Cologne

Our studies supporting the OCO-2 mission (4/5)



Vibrational levels of $^{16}O_2$ in SPFIT (11944 transitions total)

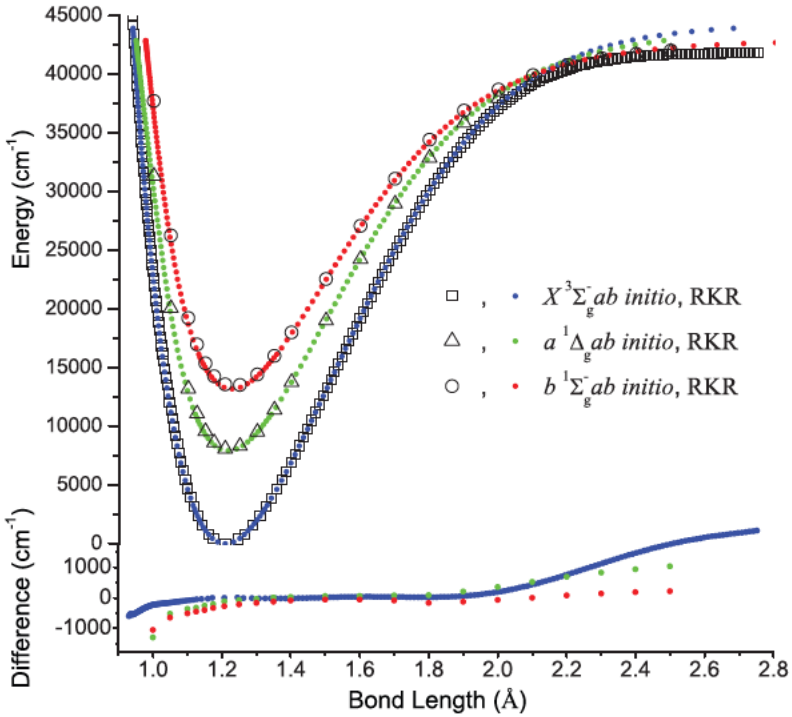
Motivation: ★ 0.1% spectroscopic accuracy at 1 ATM required by **OCO-2** ★ Complete linelist involving high vib-states required to analyze the Earth's airglow spectra.

Finding: ★ 11944 literature data of $^{16}O^{16}O$, $^{16}O^{17}O$, $^{16}O^{18}O$, $^{17}O^{17}O$, $^{17}O^{18}O$ and $^{18}O^{18}O$ fitted to experimental accuracies. ★ Model predictions of line positions support **OCO-2** and other missions.

Significance: ★ Better of accurate intensity and lineshape parameters for the A-band ★ Will improve geophysical measurements of P and T.

Yu et al, Isotopically invariant Dunham fit of O_2 frequencies, JCP 137, 024304 (2012).

Our studies supporting the OCO-2 mission (5/5)



Derived RKR potentials and their differences from ab initio calculation

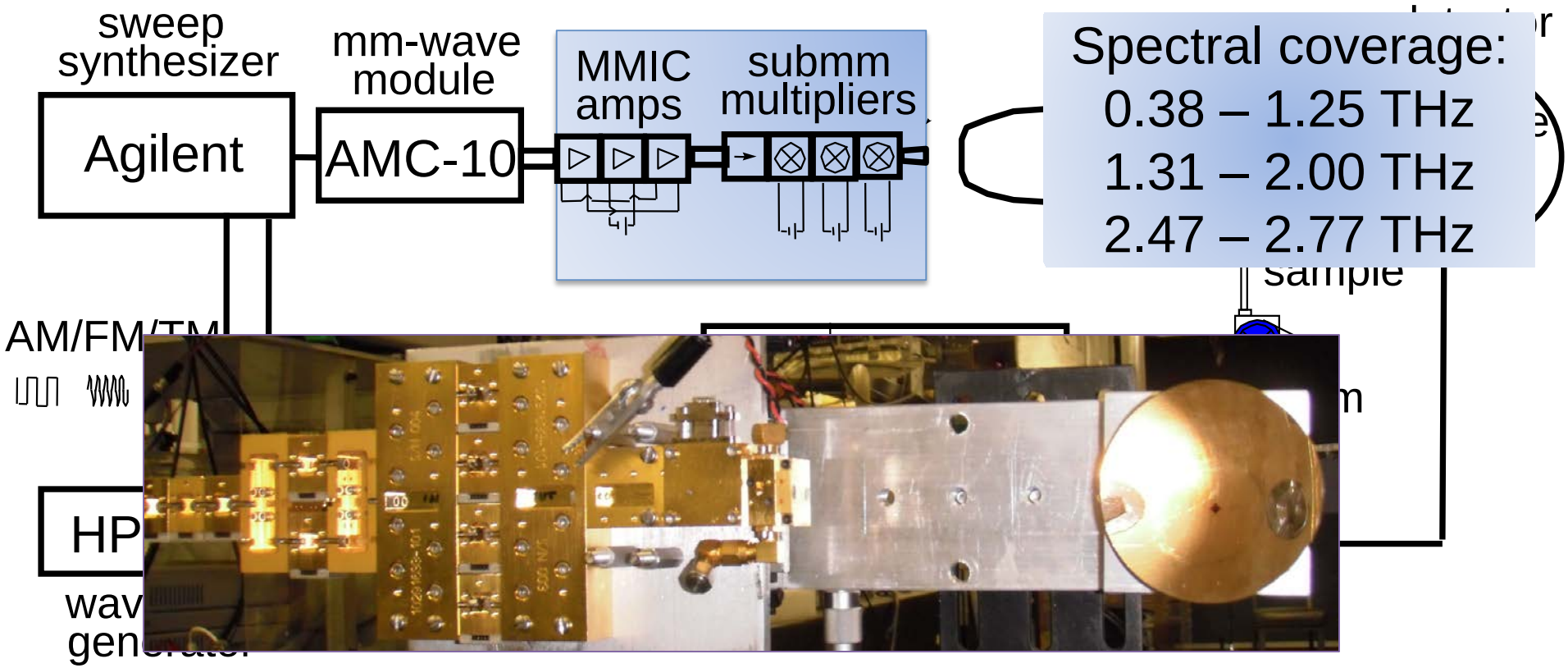
Motivation: ★ Partitions & Franck-Condon factors necessary to provide consistent calculations of intensities for all vibronic transitions involving the *X*, *a* and *b* states of O_2

Finding: ★ Partitions & F-C factors successfully obtained ★ Minor error found in TIPS partitions for $^{16}O^{17}O$ and $^{16}O^{18}O$ introducing systematic errors of 1%.

Significance: ★ Results will enable consistent calculation of intensities for vibronic transitions.

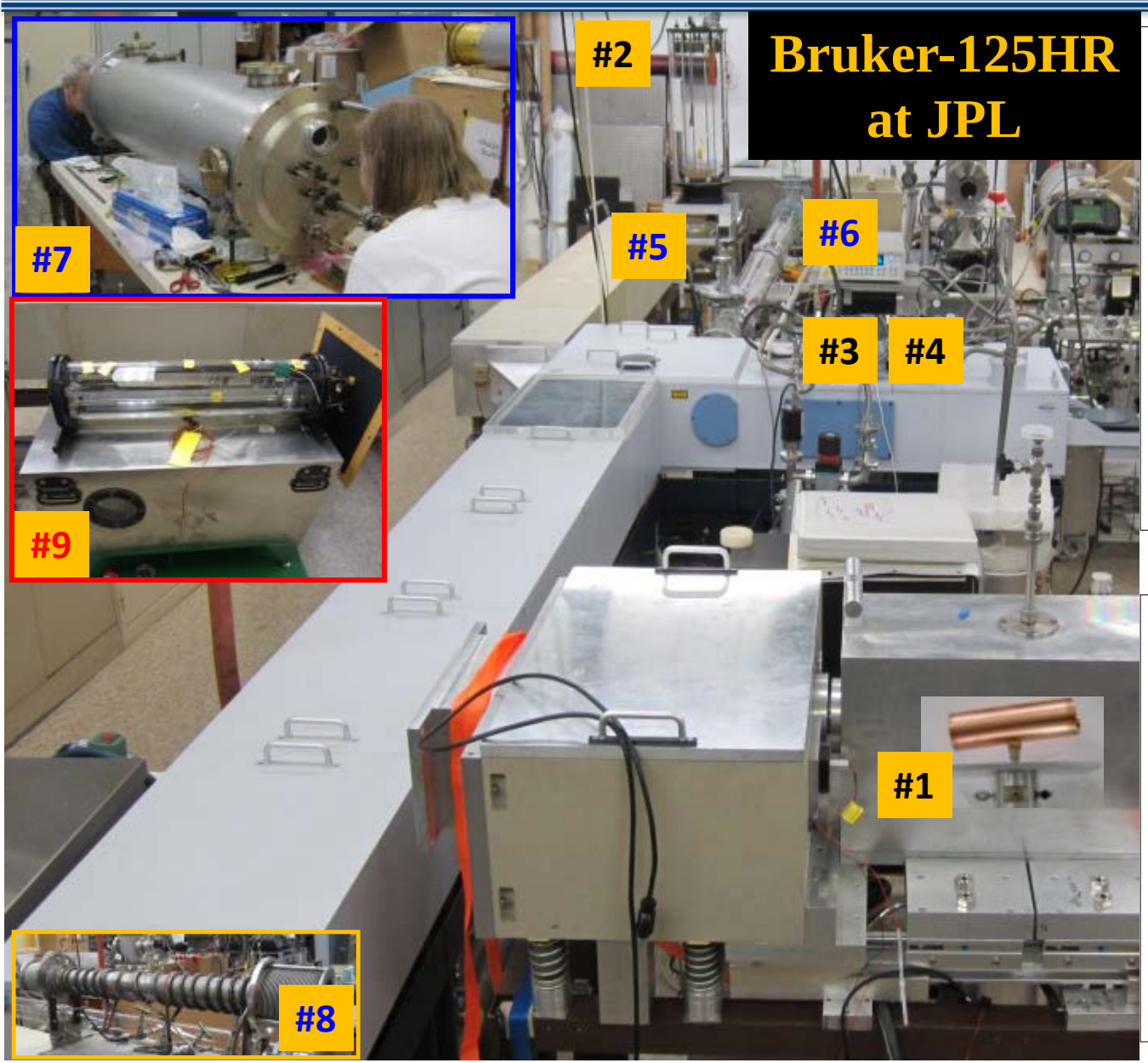
Yu et al, Energies, partitions, RKR and F-C factors of O_2, JCP 141, 174302 (2014).

JPL Frequency Multiplication Submillimeter Spectrometer



- ✓ Power comparable to BWOS (thanks to advanced JPL technology)
- ✓ Scanning speed 200 times faster than BWOs (crucial to study weeds)

High-Resolution Infrared Spectroscopy Lab (JPL)



(a) FT-IR

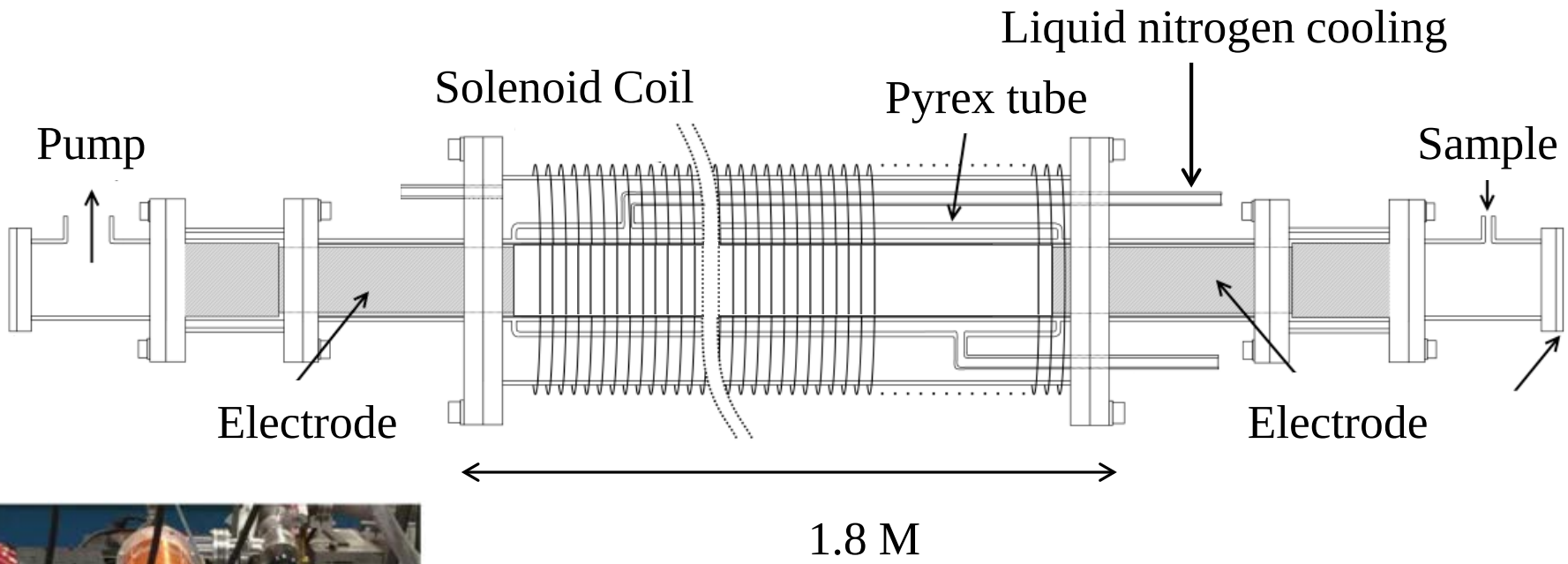
- **Beam splitters**
  Mylars/KBr/CaF2/Quartz
- **Detectors**
  Bolo/MCT/InSb/SiDi
- **Spectral coverage**
  20 – 15000 cm^{-1}
- **Max. resolution**
  0.0011 cm^{-1}

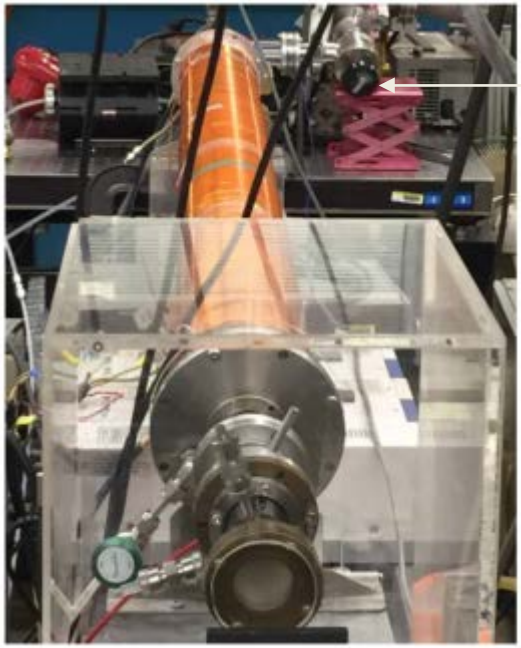
(b) Gas cells

- **Cold/Hot cells**
  (80 – 400 K)
- **Single/multipass cells**
  L = 0.2 cm – 151 m

(c) Extension chamber
housing additional cell

Extended negative glow discharge cell at JPL

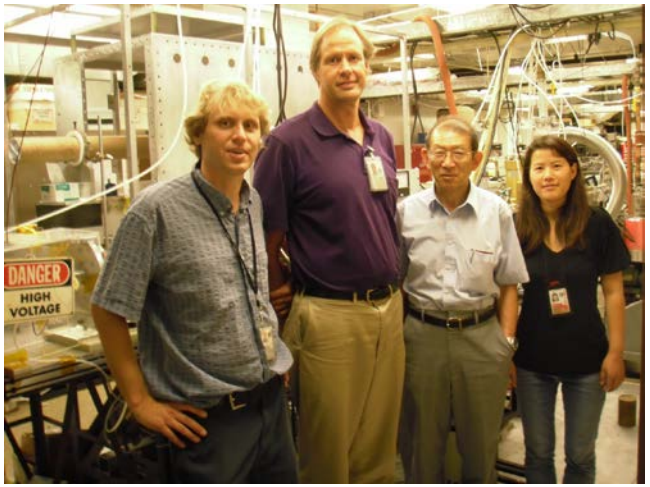




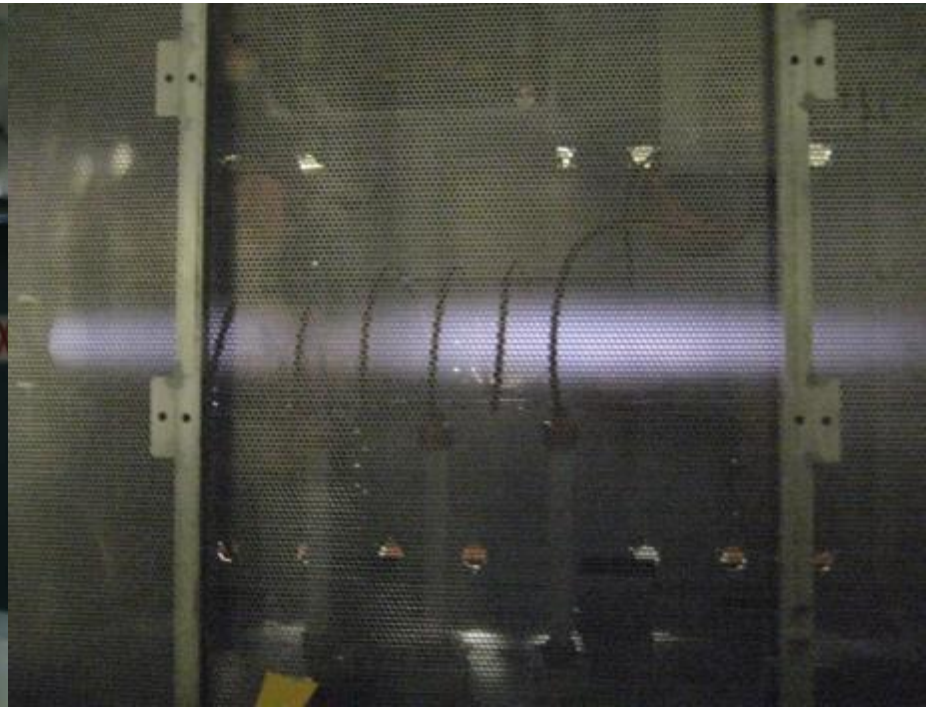
Cell temperature: 77 K

Magnetic field: 120 Gauss

DC discharge: 15 mA, 4 kV



Radio frequency discharge (KJPL)



- Couple high RF power into gas and study the molecular physics
- Study new transient molecules that will be relevant to astrophysics and heliophysics

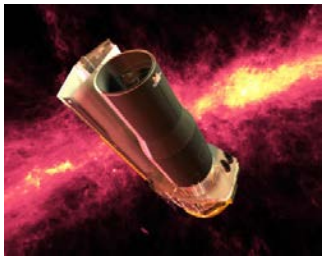
Acknowledgements

- Colleagues
  - Dr. Herb Pickett and his SPFIT/SPCAT programs
  - Prof. Takayoshi Amano (Now JPL Visiting Independent Advisor)
  - Drs. Linda Brown, Ed Cohen and Chip Miller, Mr. Tim Crawford
  - Many collaborators…
- Funding Sources
  - The NASA Herschel science center
  - NASA's Astrophysics Research and Analysis Program (APRA)
  - NASA's Atmospheric Composition: Laboratory Research Program (ACLR)
  - The OCO-2 mission

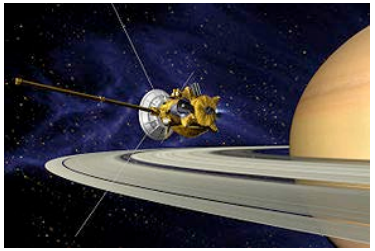
- Part of this research was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

Backup slides

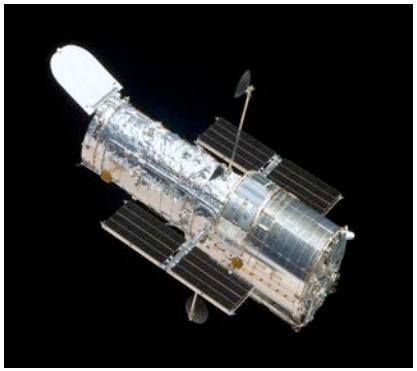
Astrophysics missions involving spectroscopy



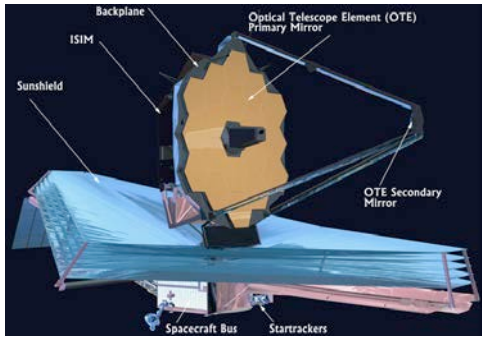
Spitzer (LEO-353mi)
Launch: 2003
Infrared
$1b



Cassini
Launch: 2004
UV to IR
$3.2b



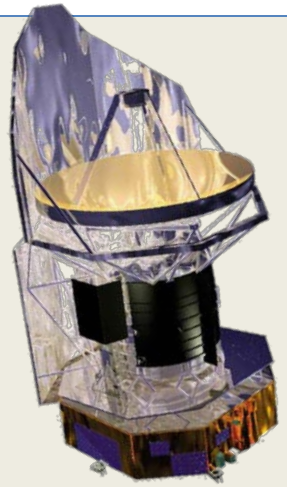
Hubble (LEO-370mi)
Launch: 1990
UV to near-IR
$5b (inc servicing)



JWST (L2)
Launch: 2018
Visible to mid-IR
> $8b

WFIRST (L2)
Launch: mid 2020s
Visible to mid-IR
$1.6b

Herschel Space Observatory



- Budget: $1.5b
- ESA and NASA joint mission
- The only space facility dedicated to the terahertz region
- Launched May 2009, observations ended April 2013 (4yrs)
- Orbit: L2 (0.93 million miles away from Earth)
- Telescope: 3.5 meter diameter, <100 K temperature
- Objective: how the first galaxies formed and how they evolved to give rise to present day galaxies

- Three instruments:
  - **PACS**, a camera and medium-resolution grating spectrometer (60-210 μm)
  - **SPIRE**, a camera and low-resolution FTS spectrometer (200-670 μm).
  - **HIFI**, a very high resolution heterodyne spectrometer sensitive in 480-1250 and 1410-1910 GHz (157-625 μm)

The Orbiting Carbon Observatory (OCO-2) Mission

- Launched: July 2014
- Grating spectrometer for 3 bands
  - CO_2 at 4850 cm^{-1} (2.06 micron)
  - CO_2 at 6220 cm^{-1} (1.6 micron)
  - O_2 at 13120 cm^{-1} (0.76 micron)

- Objective: dry air mole fraction (X_{CO2}) in the Earth' atmosphere
  - To quantify CO_2 sources and sinks
- High accuracy requirements for X_{CO2}
  - Goal ~ 0.25% (1 ppm out of 400)
- Goal for spectroscopic accuracy: 0.1%
  - Positions, intensities and lineshapes required

Earth observation satellites involving spectroscopy (II)

- **Aura** (air quality and stratospheric O_3)
  - **HIRDLS** 6-18 μm (limb sounder): O_3, H_2O, CH_4, N_2O, NO_2, HNO_3, N_2O_5, CFC11, CFC12, $ClONO_2$
  - **MLS** 112-3000 μm (limb sounder): O_2, H_2O, HNO_3, HCN, N_2O, O_3, CO, HCl, ClO, HOCl, HO_2, BrO, volcanic SO_2, OH
  - OMI 350-500 nm (Ozone Monitor): O_3
  - **TES** 3.2-15.4 μm (FTS): H_2O, O_3, CH_4, CO, HDO, HNO_3, NH_3, CO_2, N_2O, CHOOH, CH_3OH
- **Aqua** Launch 2002 (weather forecasting)
  - **AIRS** 3.7-15.4 μm (Flux & Grating spectrometer): H_2O, O_3, CO, CO_2 and CH_4
  - ***AMSR-E*** Microwave radiometry
  - **AMSU**-Microwave sounding (atmospheric temperature)
  - **CERES** 0.3-100 μm radiometer
  - **HSB**-Millimeter wave humidity sounder

Stratospheric Observatory For Infrared Astronomy ($2 B)

- NASA and German Aerospace Center joint mission
- The largest airborne observatory in the world
- Operation: 2010 (20 years lifetime)
- Orbit: The stratosphere at altitudes of about 12 km
- Telescope: 2.5 meter diameter, 240 K temperature
- Objective: identify complex molecules in space, star birth and death etc.
- Seven first generation instruments:

THz spectroscopy: a new era for the cool Universe

1 terahertz = 10^{12} Hz = 300 μm = 33.3 cm^{-1}

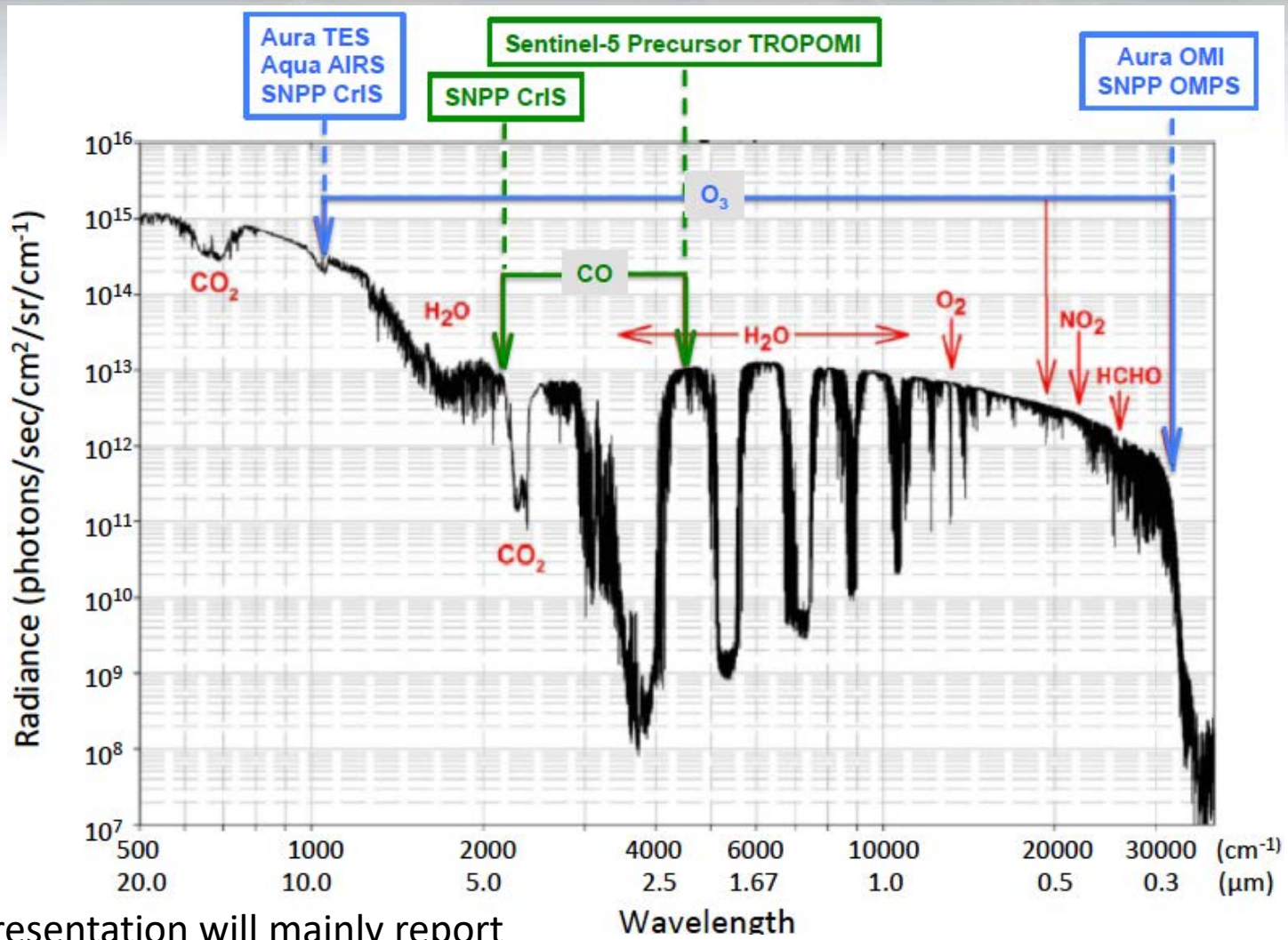
Terahertz

	Cosmic Rays	γ-Rays	X-Rays	UV	Visible	Infrared	Microwave	Radio
ν(Hz)	3.00×10^{20}	3.00×10^{18}	3.00×10^{16}	$(7.89\text{-}3.84)\times10^{14}$		1.00×10^{12}		3.00×10^{8}
λ(μm)	1.00×10^{-6}	1.00×10^{-4}	1.00×10^{-3}	$(3.80\text{-}7.80)\times10^{-1}$		3.00×10^{2}		1.00×10^{6}
ν(cm^{-1})	1.00×10^{10}	1.00×10^{8}	1.00×10^{6}	$(2.63\text{-}1.28)\times10^{4}$		3.33×10		1.00×10^{-2}

The electromagnetic spectrum

- Terahertz spectroscopy has historically been a technique challenge: limited radiation sources and detectors
- Recent technical advances in terahertz sources and mixers have led to the development of powerful terahertz systems for astrophysics

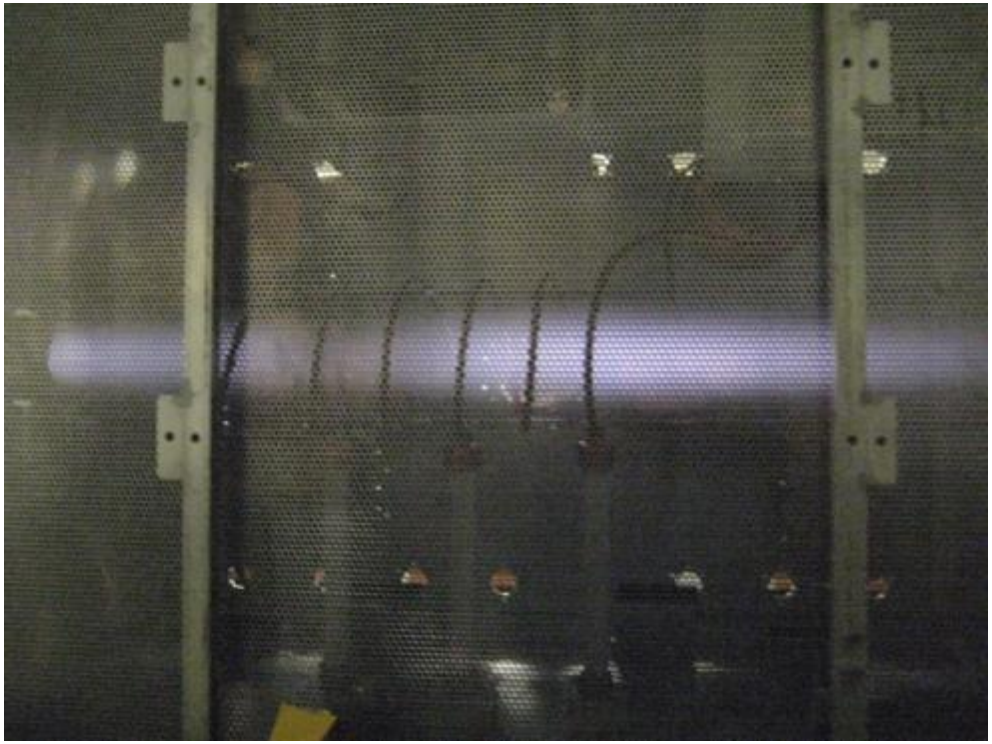
Spectral Regions Used in Joint Retrievals



This presentation will mainly report

- Joint AIRS/OMI ozone profile retrievals
- Joint CrIS/TROPOMI carbon monoxide profile retrievals

RF plasma system for open-shell ions



1.4 m

Plasma with 24 mTorr Ar at 10 W

Setup with 10 kW in progress

- ✓ Simulate interstellar cosmic rays and photo ionization chemical mechanism
- ✓ Generate open-shell ions or radicals by **stripping electrons off molecules or breaking chemical bonds** like HO^+, H_2O^+, NH^+ and NH_2^+ etc
- ✓ Generate highly excited neutral species like H_2O and HCN etc

DC glow discharge

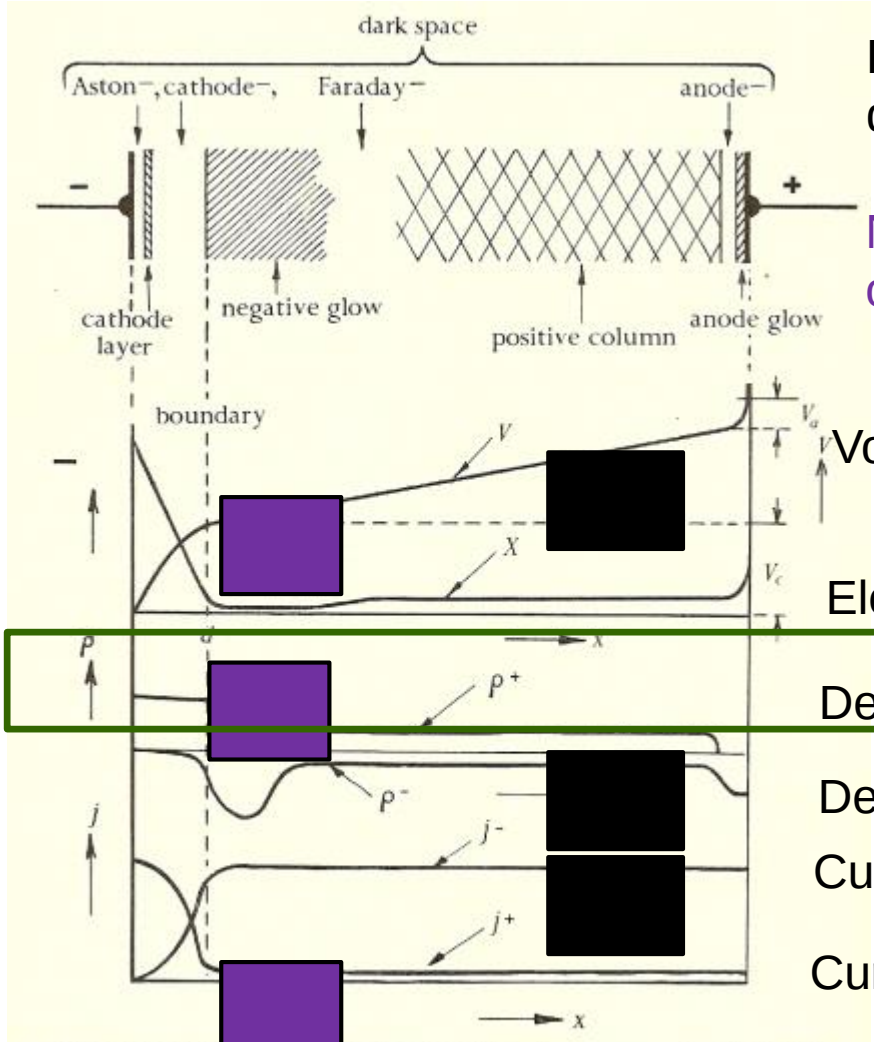


FIG. 113. Spatial distribution of dark and luminous zones, electric field X, space-charge densities ρ^+ and ρ^-, and current densities j^+ and j^- in a glow discharge (schematically).

Positive column: high voltage, high density of negative charges, high current

Negative glow: high voltage, high density of positive charges, low current

Voltage

Electric field

Densities of positive charges

Densities of negative charges

Current densities of negative charges

Current densities of positive charges

A.V. Engel, Ionized Gases, 1965

The following parameters can be calculated based on our fitting results:

- ν: the line position
- E_l: the lower state energy
- E_u: the upper state energy
- The partition function

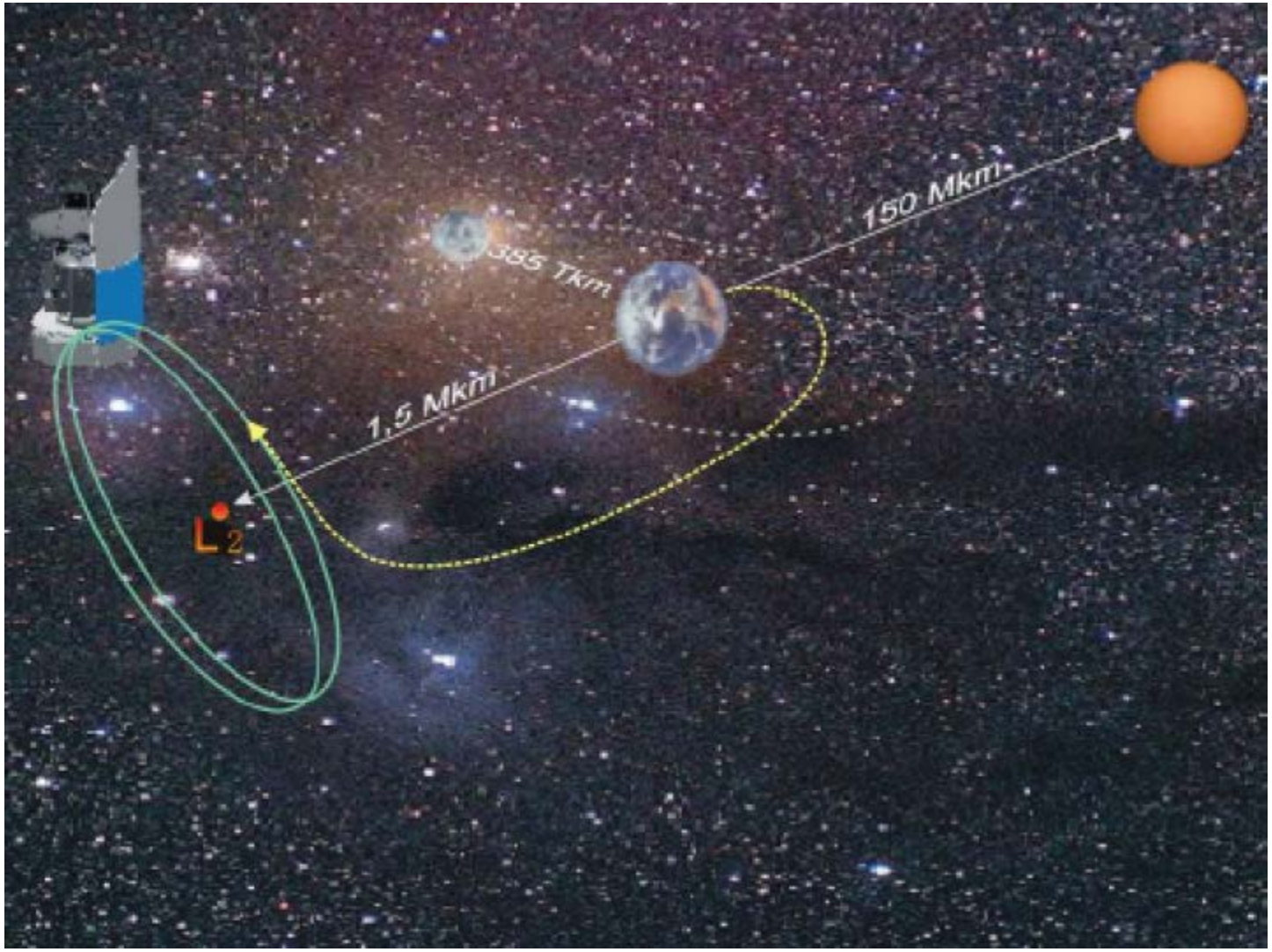
Which can be used to calculate line strength:

$$S'(T) = \nu \frac{8\pi^3}{3hc} \sum_{i=x,y,z} |\mu_i|^2 \frac{g_a e^{-E_l/KT} - g_b e^{-E_u/KT}}{\sum_{n=0}^{\infty} g_n e^{-E_n/KT}}$$

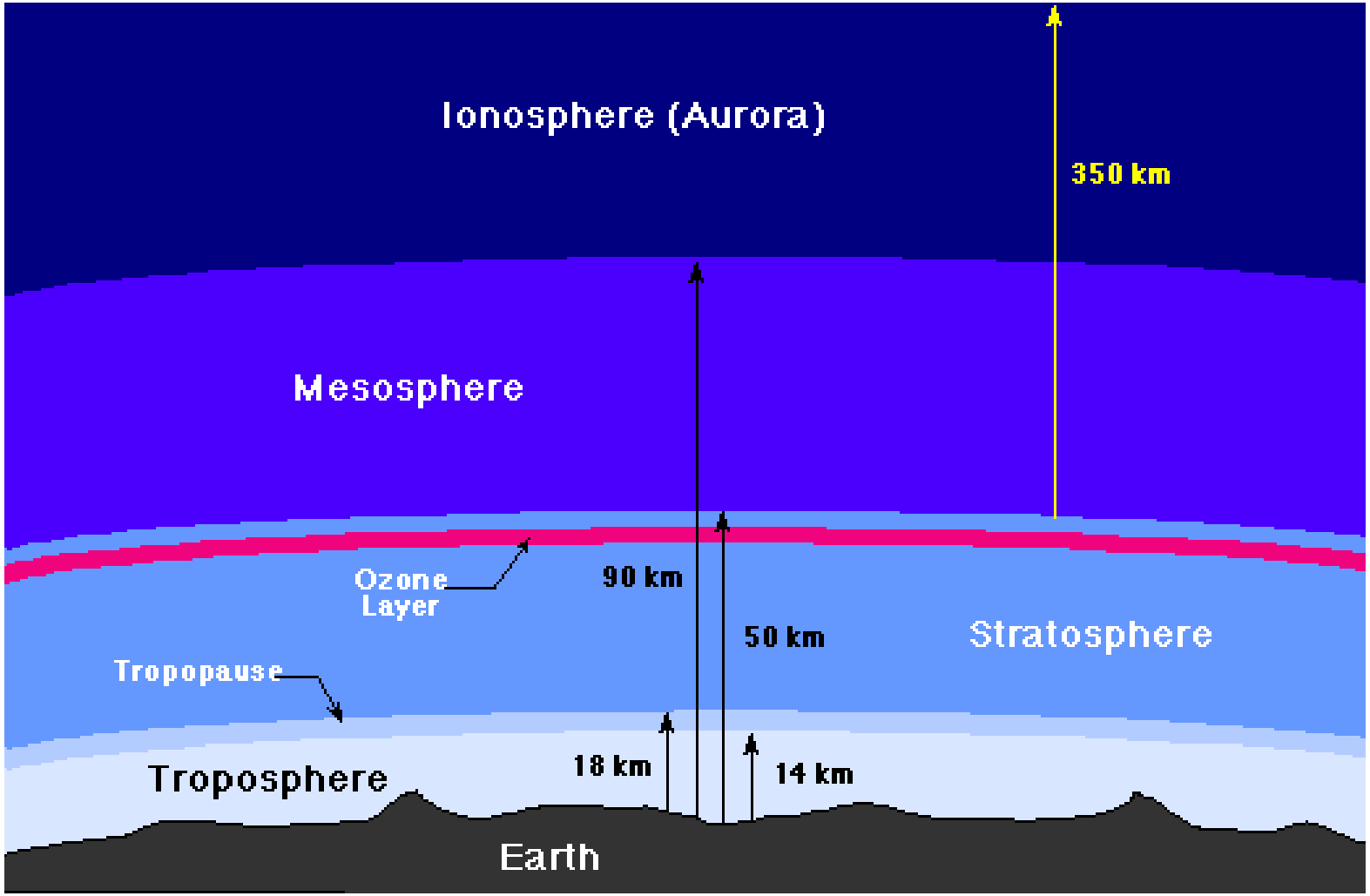
Line strength useful for simulating astrophysical spectra:

$$I = I_0 e^{-\sigma\cdot(Nl)} = I_0 e^{-S\cdot g(v-v_0)\cdot(Nl)}$$

- σ: cross section
- S': line strength or line intensity
- $g(\nu-\nu_0)$: line shape function
- *(Nl):* column density



the second Earth-Sun Lagrange point


Ionosphere (Aurora)
350 km
Mesosphere
Ozone Layer
90 km
50 km
Stratosphere
Tropopause
Troposphere
18 km
14 km
Earth

Observed interstellar molecules

Number of Atoms							
2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
H_2	H_2O	NH_3	SiH_4	CH_3OH	CH_3CHO	$HCOOCH_3$	CH_3CH_2OH
OH	H_2S	**H_3O^+**	CH_4	NH_2CHO	CH_3NH_2	CH_2OHCHO	$(CH_3)_2O$
SO	SO_2	H_2CO	CHOOH	CH_3CN	CH_3CCH	CH_3C_2CN	CH_3CH_2CN
SO^+	**HN_2^+**	H_2CS	$HC{\equiv}CCN$	CH_3NC	CH_2CHCN	C_7H	$H(C{\equiv}C)_3CN$
SiO	HNO	HNCO	CH_2NH	CH_3SH	HC_4CN	H_2C_6	$CH_3(C{\equiv}C)_2H$
SiS	SiH_2	HNCS	NH_2CN	C_5H	C_6H	HC_6H	C_8H
NO	NH_2	CCCN	H_2CCO	HC_2CHO	C_6H^-	CH_3CO_2H	C_8H^-
NS	**H_3^+**	$CCCN^-$	C_4H	$CH_2{=}CH_2$	c-CH_2OCH_2	C_6H_2	$CH_3(C{\equiv}C)_2CN$
HCl	NNO	**HCO_2^+**	C_4H^-	H_2CCCC	CH_2CHOH		
NaCl	HCO	CCCH	c-C_3H_2	**HC_3NH^+**			**<u>10</u>**
AlCl	OCS	c-CCCH	CH_2CN	HC_4H			CH_3COCH_3
AlF	CCH	CCCS	SiC_4	C_5S			$CH_3(C{\equiv}C)_2CN$
PN	**HCS^+**	HCCH	H_2CCC	C_4H_2			$HOCH_2CH_2OH$
SiN	c-SiCC	**$HCNH^+$**	HCCNC	HC_4N			CH_3CH_2CHO
NH	CCO	HCCN	HNCCC	CH_2CNH			
SH	CCS	H_2CN	**H_3CO^+**				**<u>11</u>**
HF	C_3	c-SiC_3					$H(C{\equiv}C)_4CN$
CN	MgNC	CH_3					
CO	NaCN	**CH_2D^+**					**<u>12</u>**
CS	CH_2	AlNC					c-C_6H_6
C_2	MgCN						
SiC	**HOC^+**						**<u>13</u>**
CP	HCN						$H(C{\equiv}C)_5CN$
CO^+	HNC						
CH^+	CO_2						
CH	SiCN						
N_2	AlCN						
CF^+	SiNC						
	KCN						
	HCO^+						

15 positive ions

4 negative ions

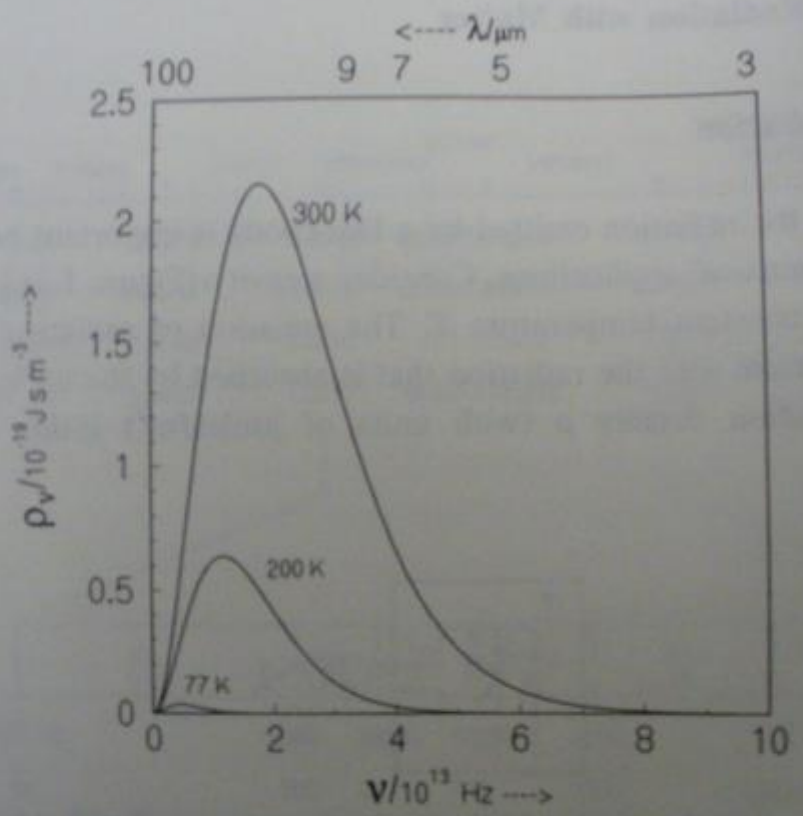
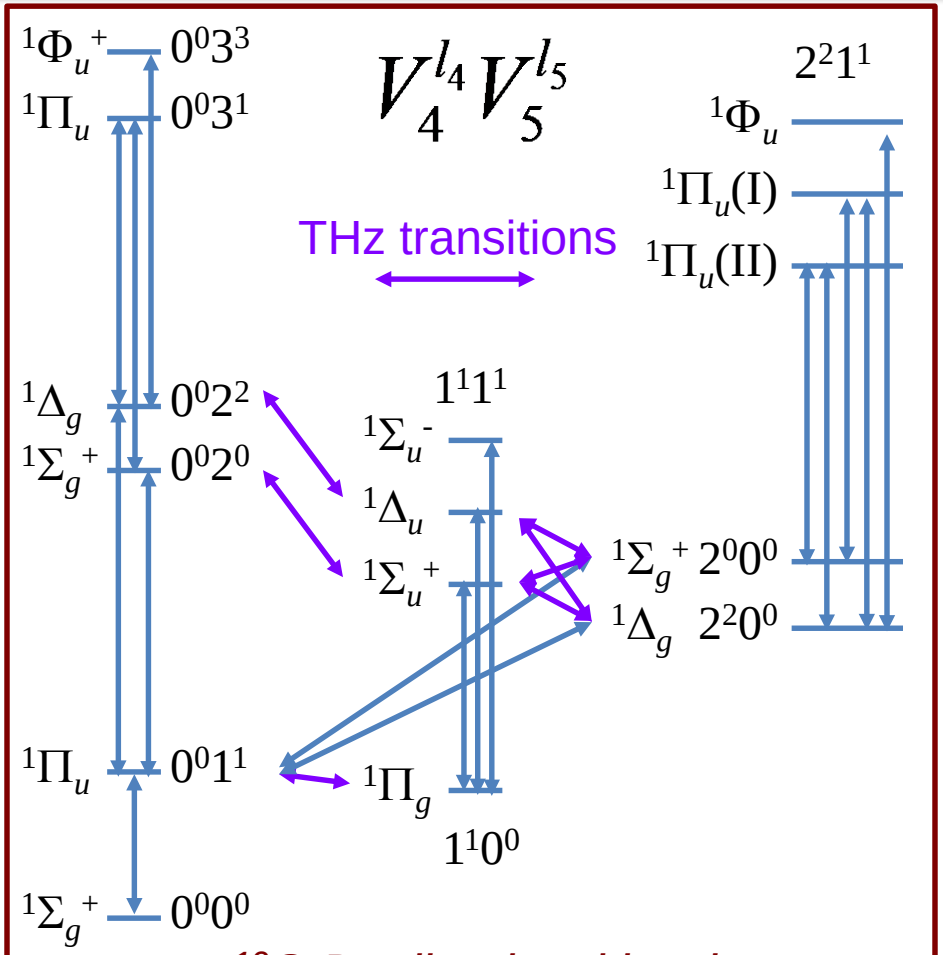


Figure 1.4. The Planck function at 77 K, 200 K, and 300 K.

THz spectroscopy of $^{12}C_2D_2$ $\nu_5 - \nu_4$ difference bands



$^{12}C_2D_2$ vibrational levels in SPFIT (2090 lines total; 251 THz transitions from this work)

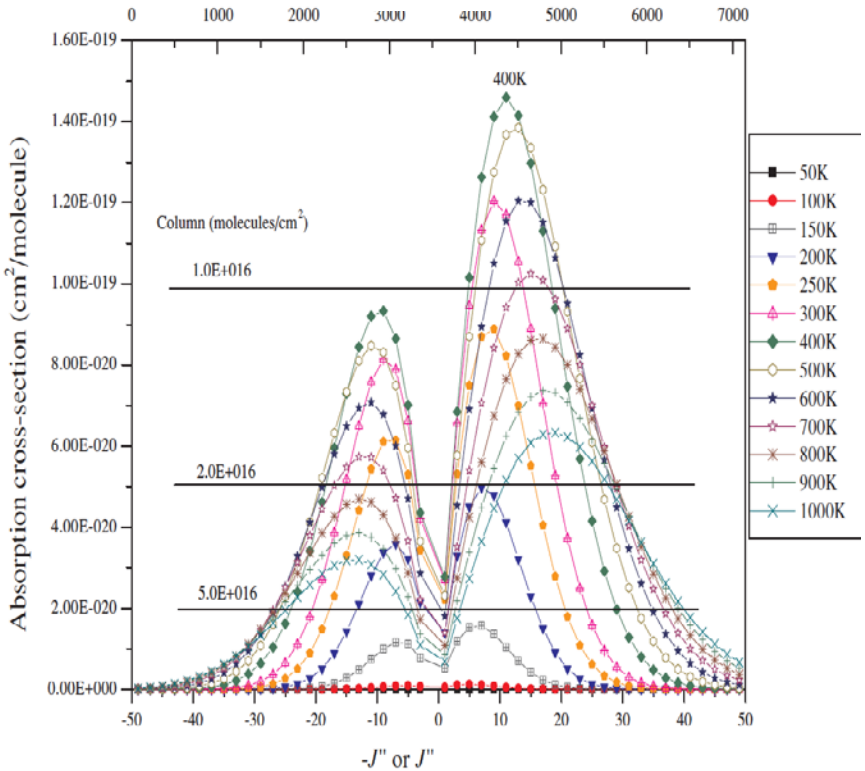
Motivation: ★ Interpolated frequencies from analysis of 10 MW lines and IR data on the order of 100 MHz ★ lab rest frequencies with uncertainty less than 1 MHz required.

Finding: ★ 202 new transitions were detected in the 0.2 – 1.6 THz region with accuracy of 50 – 100 kHz and fitted to experimental accuracy together with literature data.

Significance: ★ Results will enable proper analysis of astrophysical observations from high-resolution spectroscopy telescopes.

Yu et al, *Terahertz spectroscopy of the bending vibrations of $^{12}C_2D_2$*, APJ 698, 2114 (2009).

THz spectroscopy of $^{12}C_2H_2$ $\nu_5 - \nu_4$ difference bands



Absorption cross-sections of $^{12}C_2H_2$ $\nu_5 - \nu_4$ difference band to guide its astrophysical search

Motivation: ★ No MW data were available ★ Interpolated frequencies from analysis of IR data are on the order of 100 MHz, which are not accurate enough for proper analysis of velocity resolved astrophysical observations.

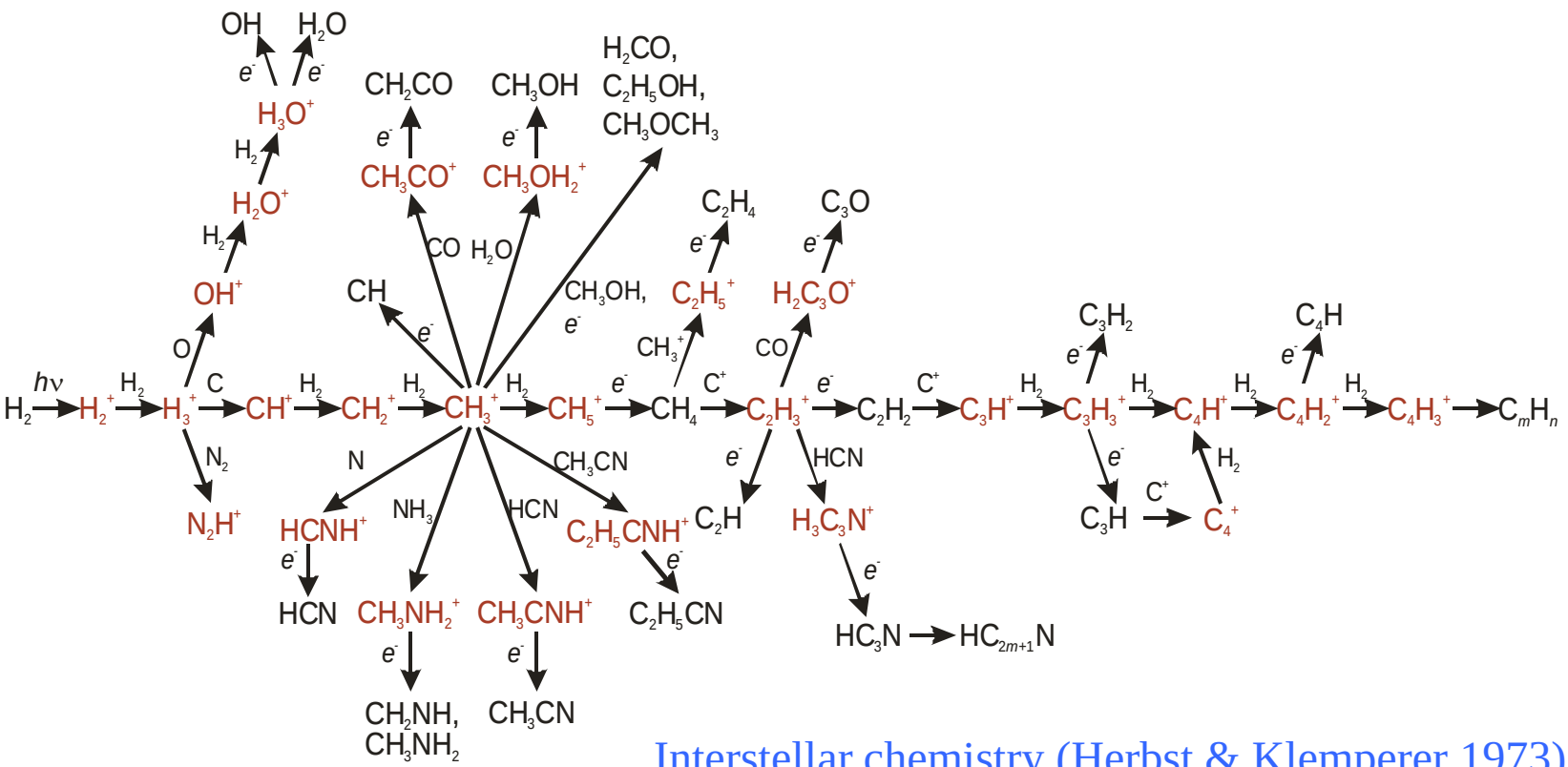
Finding: ★ 20 new transitions were detected in the 0.8 – 1.6 THz region with accuracy of 100 kHz and fitted them together with 1386 literature data to experimental accuracy.

Significance: ★ Results will guide astrophysical search of $^{12}C_2H_2$.

Yu et al, *Terahertz spectroscopy of the bending vibrations of $^{12}C_2H_2$*, APJ 705, 786 (2009).

Laboratory Terahertz spectroscopy of ions

- Observed molecular ions in space (as of 11/2012, observed in or after 2010 in blue)
  - Twenty two positive ions: CH^+, CO^+, SO^+, CF^+, OH^+, SH^+, HCl^+, HCO^+, HCS^+, HOC^+, N_2H^+, H_3^+, H_2D^+, HD_2^+, H_2O^+, H_2Cl^+, $HCNH^+$, HCO_2^+, H_3O^+, C_3H^+, H_2COH^+, HC_3NH^+
  - Six negative ions: CN^-, C_3N^-, C_4H^-, C_5N^-, C_6H^-, C_8H^-,



Interstellar chemistry (Herbst & Klemperer 1973)