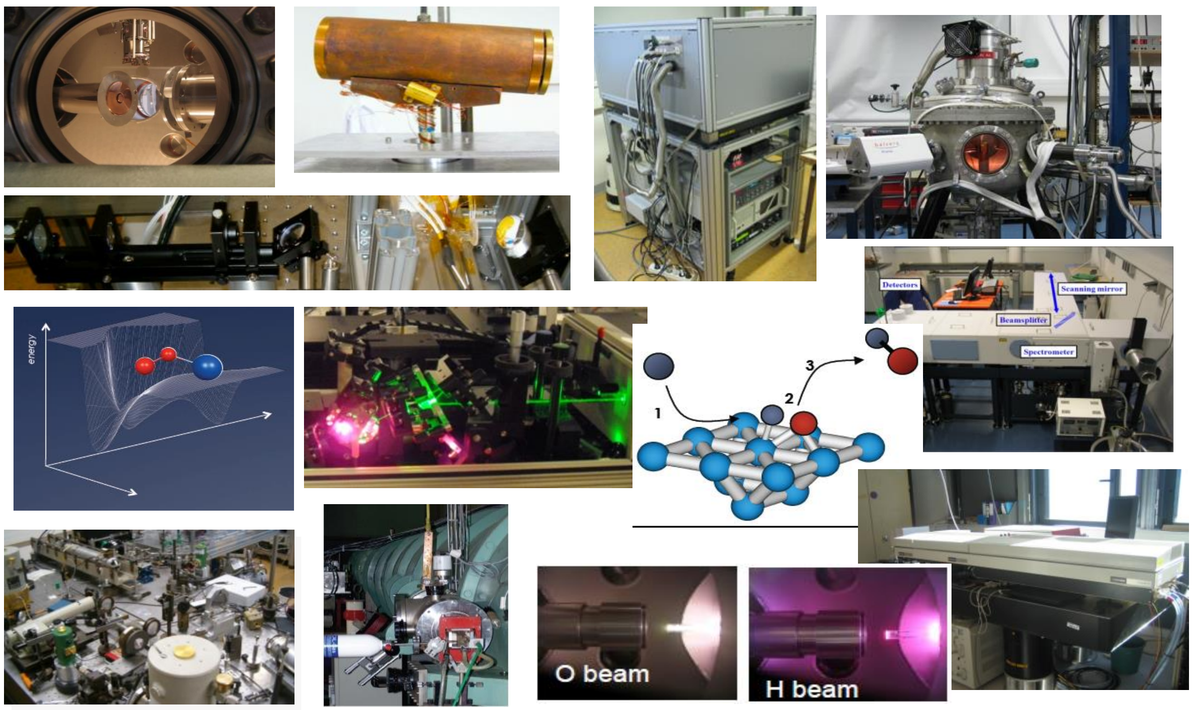
Molecules in the Universe

J.H. Fillion

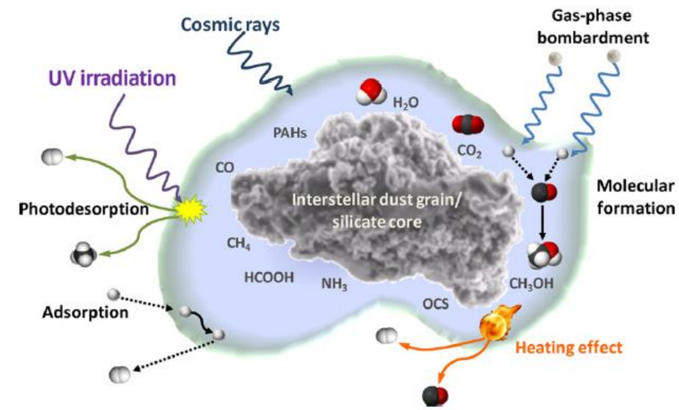
F Dulieu
C. Janssen



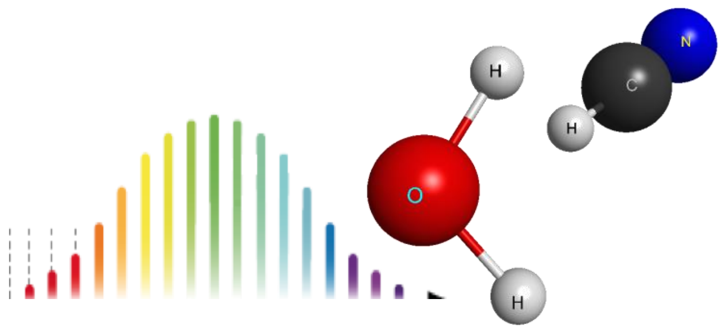
Various Laboratory Experiments and Theoretical devlopments dedicated to the study the molecular interactions in the gas/surfaces for astrophysical and atmospheric appplications

Research axes

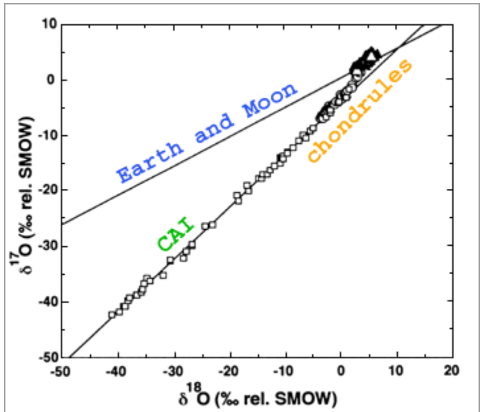
Reactivity and interaction at gas-solid interface and in the ice



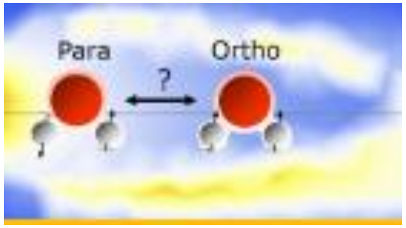
Molecular processes and parameters for atmospheres and ISM



Molecular anomalies



(From Clayton, R., 1993, Oxygen Isotopes in Meteorites, *Annu. Rev. Earth Planet. Sci.* v.21, p. 123.)



Molecules in the Universe

Jussieu Spin, photons and ices :	3.5 C/EC + 1 PHD	+ 2 IR + 1 IE + 1 tech
Jussieu SMILE (Molecular Spectroscopy and Laser Instrumentation for Environment)	5 EC+1Em + 2 PHD	
Cergy Reactivity on cold surfaces :	5 EC+1IR + 3 PHD	+ 1 IE+1 tech
Meudon van der Waals systems for Astrophysics and for Planetology	1.5 EC+ 1 IR 1 P.Doc	+ 2 IE
Collisional excitation, reacticity and high resolution VUV spectroscopy of interstellar molecules Meudon	2 EC + 2 Em	+ 1 IE+1 tech

Total 22 C/EC and 12 Ing. & Tech.
6 PHD students
1 post-doc

Scientific animation

Molecules in the Universe workshops

- Every two months: ~ 4 per year
- Location is cycling : Jussieu-Cergy-Jussieu- Meudon-Jussieu-Cergy-...
- 2 - 3 seminars

  + 1 « interpole » meeting per year

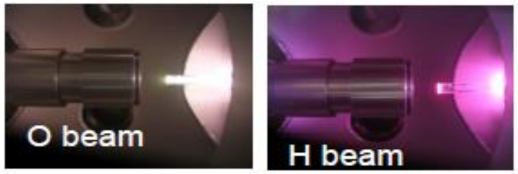
  ✦ Permanents of the pole
  ✦ PHD students
  ✦ Others poles LERMA
  ✦ External
  ✦ + news or short coms

T. Zanon, Meudon, 2015

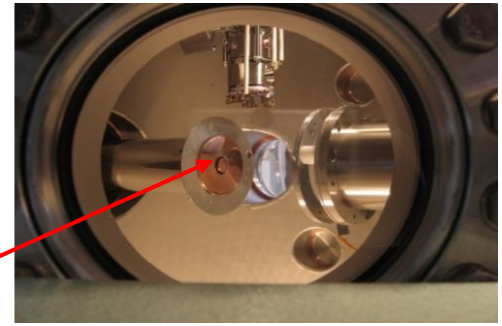

Discussion continues during our homemade buffet


June 14, Cergy: Bron & Minissale speakers

Gaz-surfaces interactions : reactivity



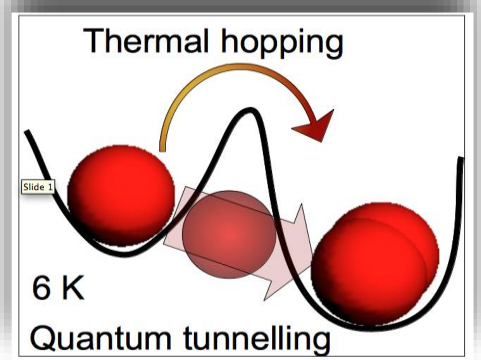
Plasmas Discharges
Atomic beams



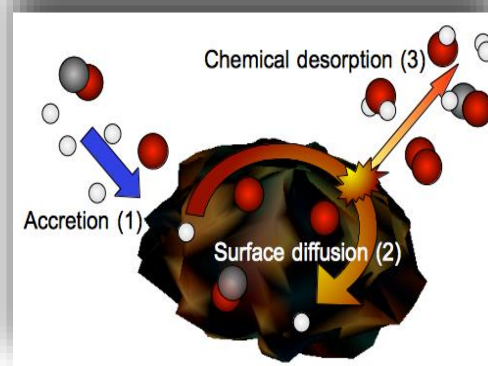
Analysis chamber
- IR Reflexion-Absorption
- Mass spectr.

Cold substrate (10 K)
(graphite, water ice, silicate)

O-atom diffusion at very low temperature

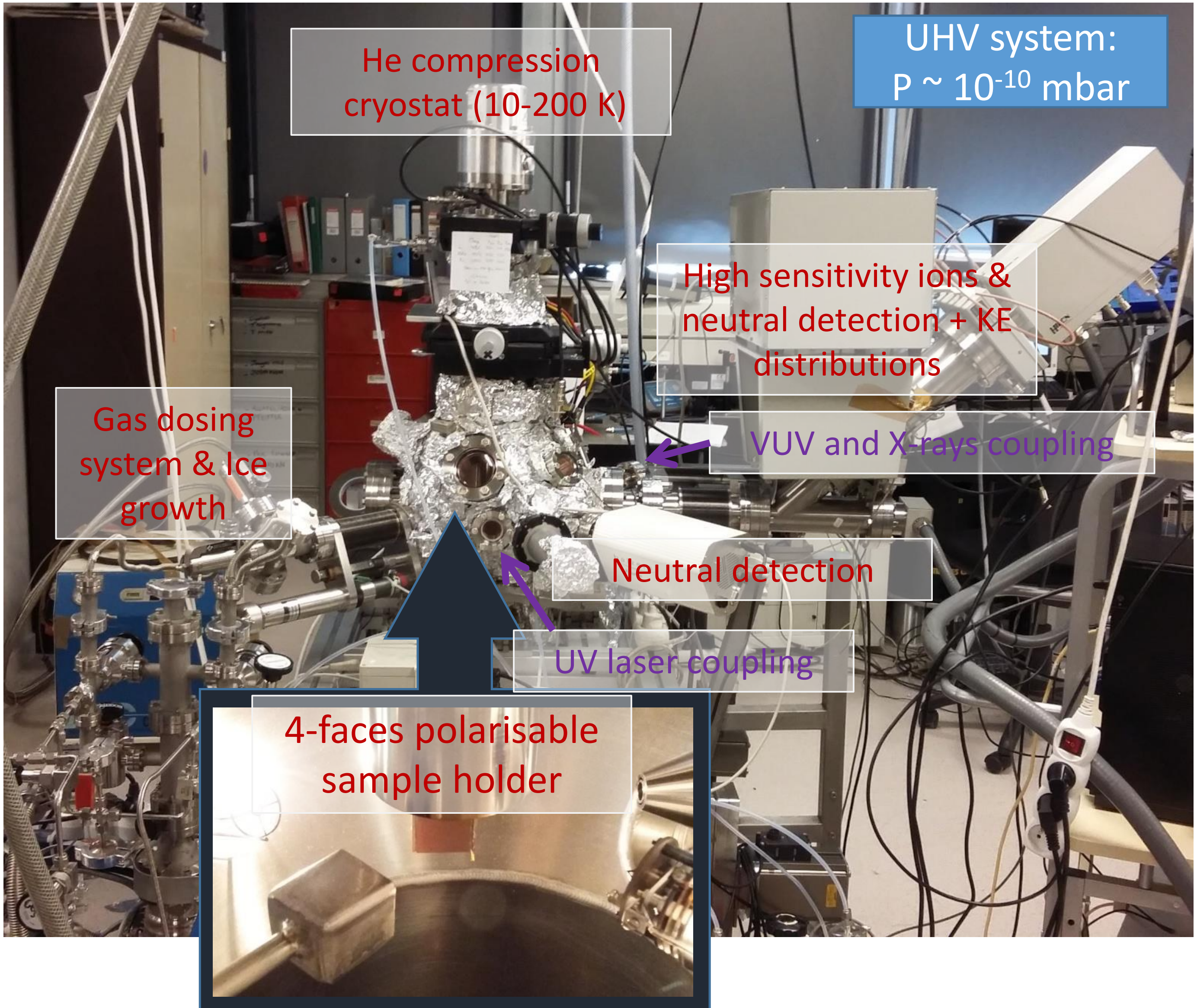


Towards Oxygenation reactions (not only hydogenation)



Desorption after reactions

« SPICES 2 » set-up : Surface Processes and ICES 2



Higher Sensitivity

- *Increase vacuum perfomance*
- *New analysis Chamber*
- *New mass spectrometer*

New achievements

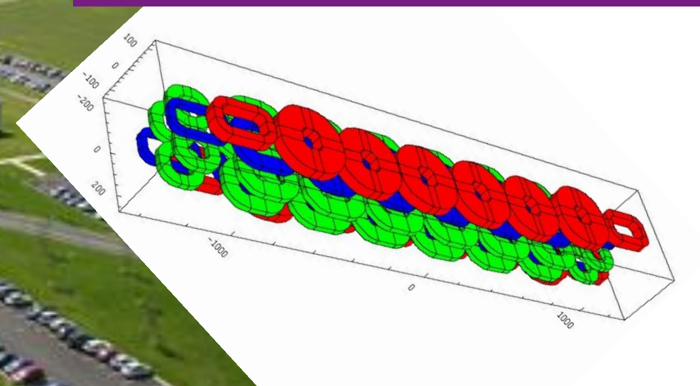
- Ion/neutral detection
- Kinetic energy measurement
- Compatible for : continuous (synchrotron) Or pulsed (laser) sources

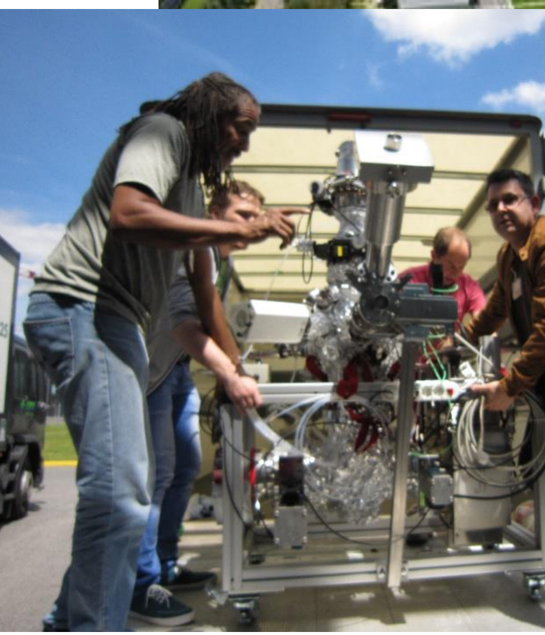
-> internal energy

DESIRS BEAMLINE

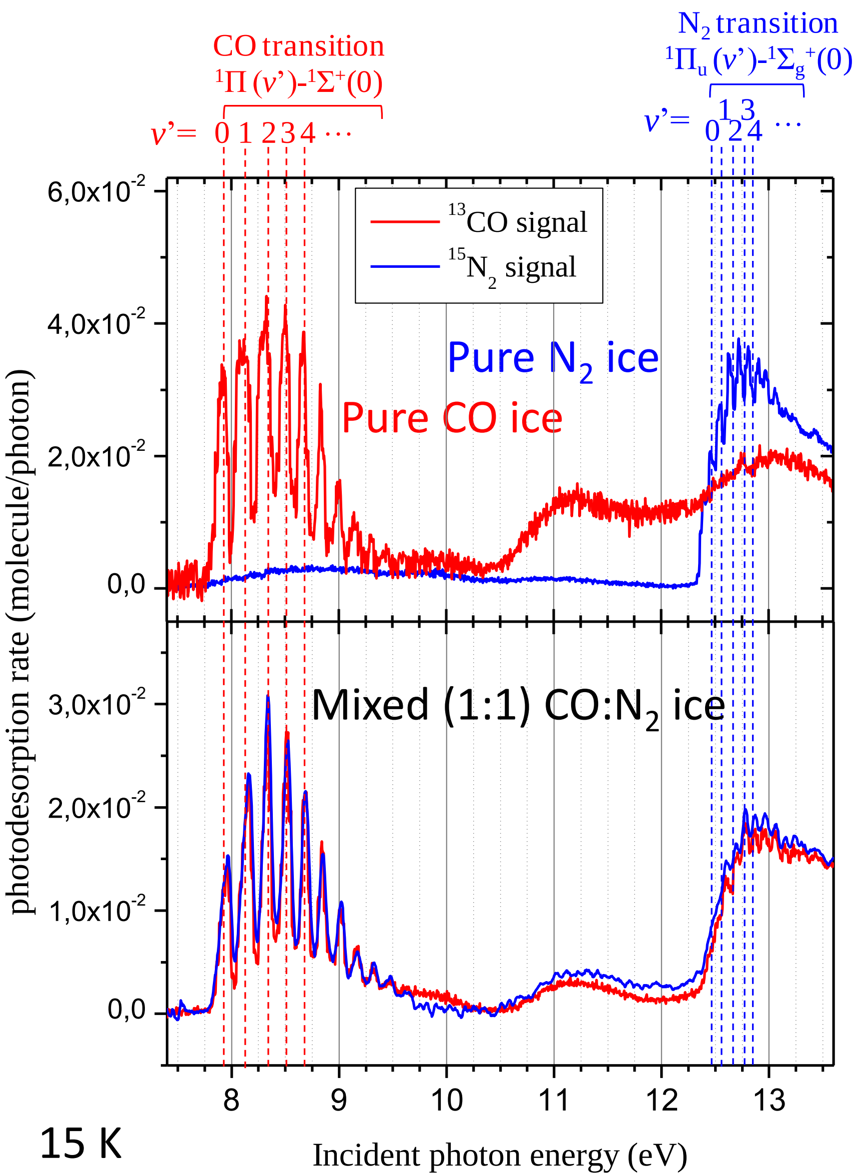
Fully tailored polarization

Undulator : 4.5 – 40 eV

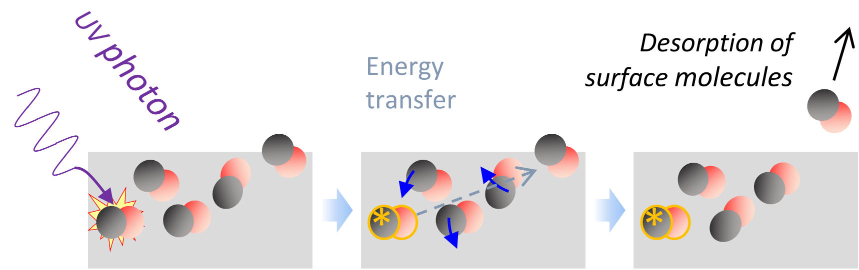




Gas-surfaces interactions : UV Photon Stimulated Desorption



15 K



Bertin et al., ApJ 2013

- Surface process : top few ML

$E_{des} < 100$ meV

@ 8.2 eV

- Yields ~ X 10^{-2} molecules/ photons
- Decrease with ice deposition Temp
- σ_{abs} ~ 1.5 10^{-17} cm^2

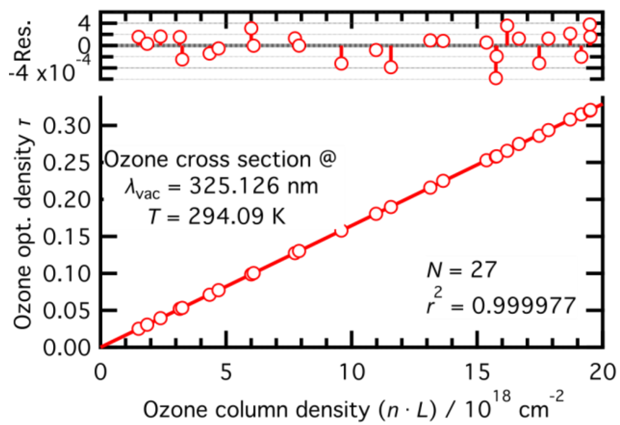
Quantum Yield

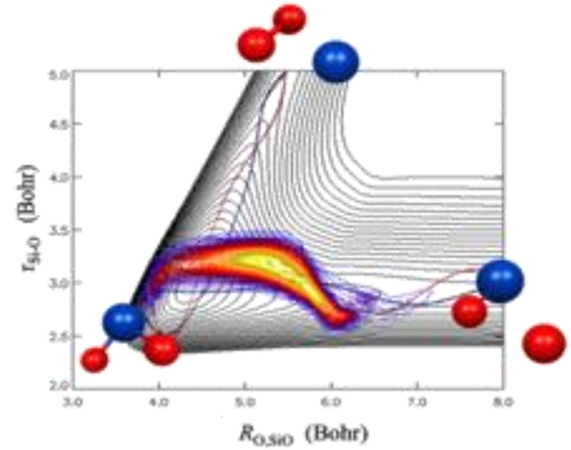
~ 1 molecule /absorbed photon

in top 3 ML (10-20 K)

Axis II – Molecular processes and parameters for atmospheres and ISM

- *Unique tools for providing traceable spectroscopic data: Molecular Metrology*
  - *High accuracy measurements*
    - *Theory and simulations*
      - *Reference data for physical and atmospheric research*





$\sigma = 16.470\ 10^{-20}\ cm^2\ (\pm\ 0.2\%)$

Janssen et al, AMT, 2017 under review

Driving force:

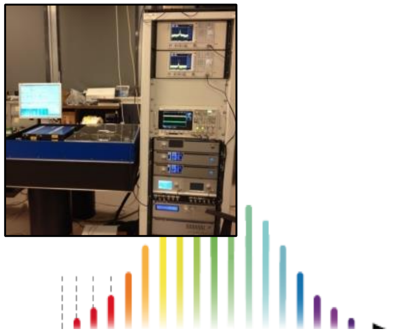
- *Provide fundamental molecular data for*
  - *understanding and studying climate and atmospheric composition change*
  - *modelling cometary and stellar atmospheres as well as the interstellar medium*
  - *fundamental physics*
- *Study terrestrial & planetary atmospheres*
  - *understanding and studying climate and atmospheric composition change*
  - *develop new analytical tools and techniques of observation (axis III)*

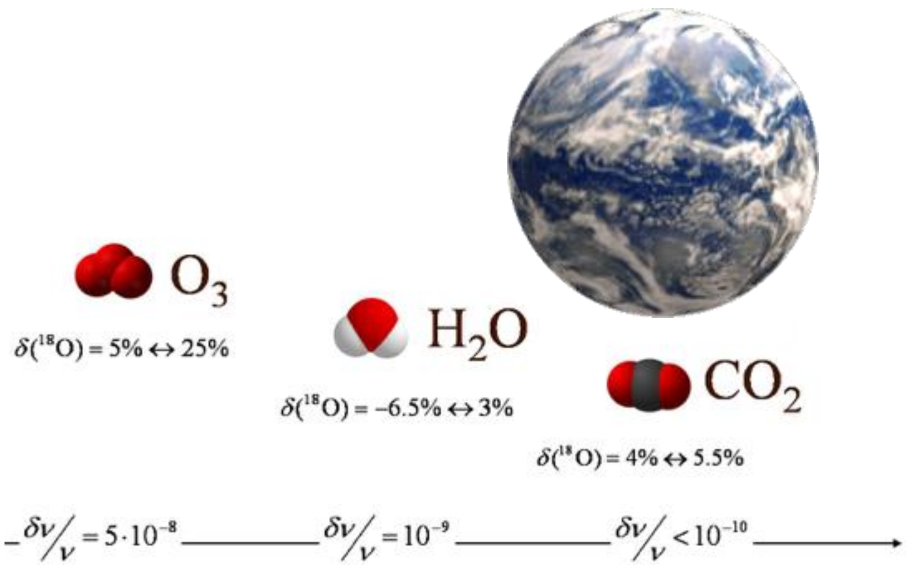
Axis II – Molecular processes and parameters for atmospheres and ISM

Towards traceable IR spectroscopic data for planetary research (PRESPASS)

- Setup of frequency-comb stabilised laser spectrometer @ 10 µm under way (FCS-DL)
- Suitability of laser unit for line shift measurements (Minissale et al *JMS* 2017, accepted).
- Michelson interferometer stabilised diode laser spectrometer (MIS-DL)
- Coupling to UV and VIS laser : most precise absolute cross section of ozone so far (more than 10 x better than actual reference, Janssen et al. AMT, 2017 under review)

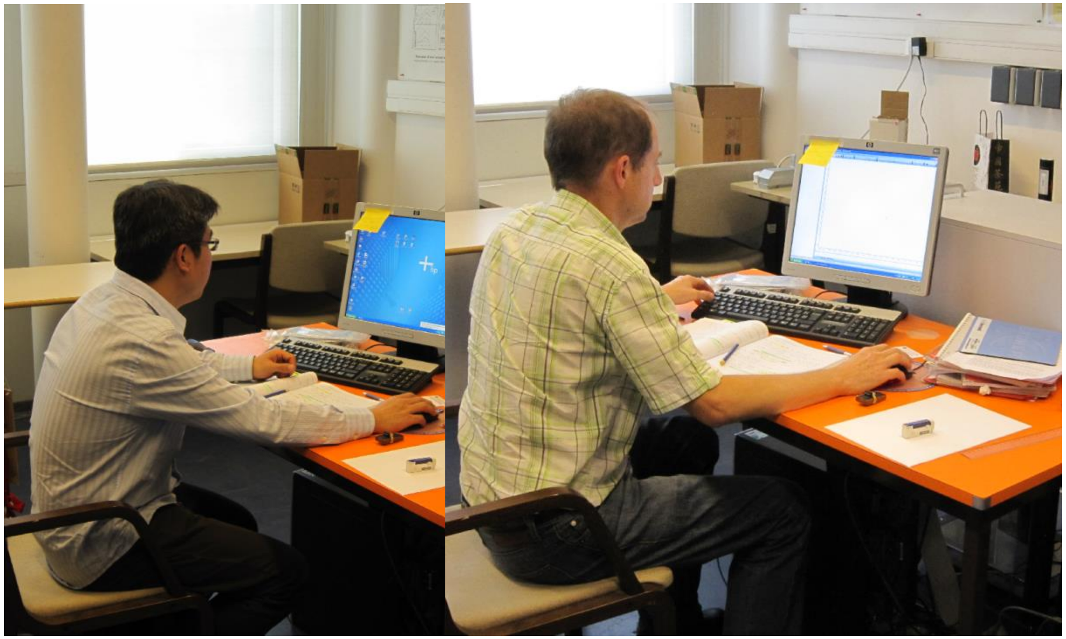
Frequency comb Jussieu





Projects

- Long term-goal: provide very high resolution data for remote sensing of isotopes
- Finalize stabilization scheme
- Link to frequency reference (REFIMEVE+/FIRST-TF) from SYRTE
- Retrieve line parameters and line profile information on oxygen bearing key compounds: O_3, H_2O and CO_2
- Link to isotope anomalies in atmosphere & solar system.

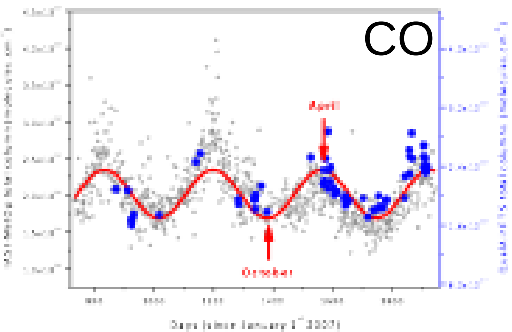


Sondage de l’atmosphère Terrestre

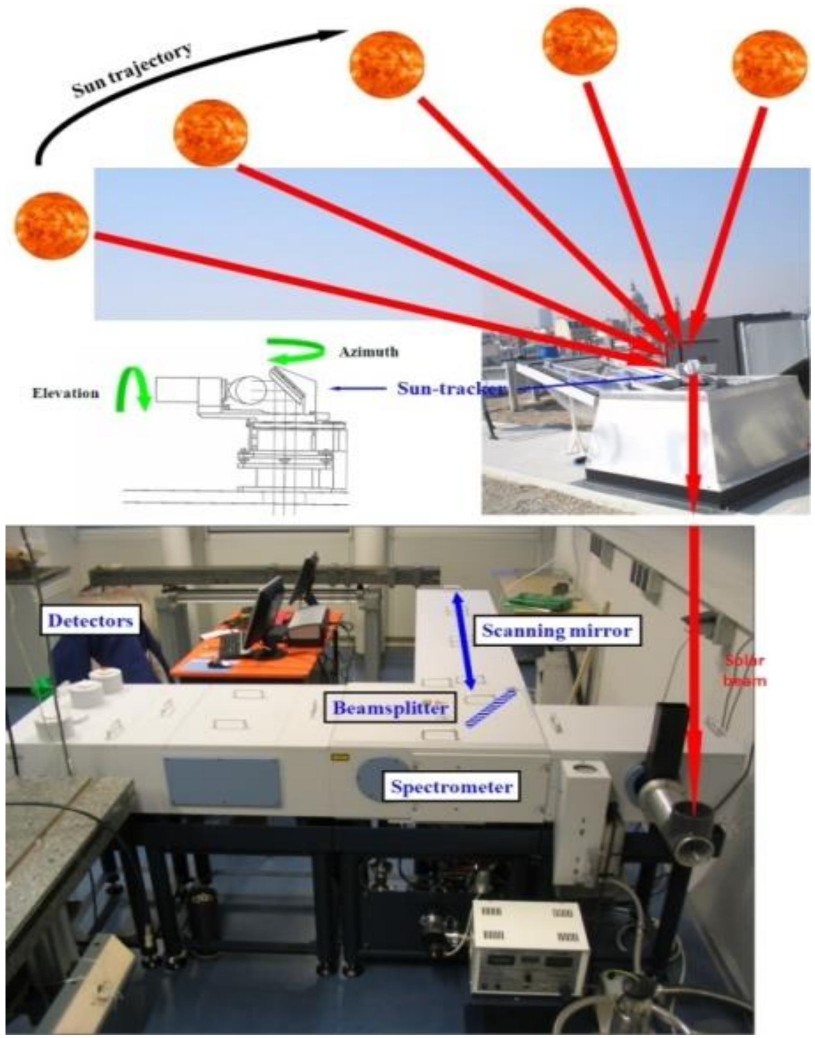
- Télédétection FTIR de la **composition atmosphérique**
- **Physico-chimie atmosphérique**
- **Spectroscopie haute résolution**
- TCCON-Paris et Absorption long parcours entre les tours de Jussieu

Ground Based GAS STATION

High-resolution Fourier transform spectrometer FTS-PARIS



Té et al. (2012)



- - high-resolution FTS ($2.4 \cdot 10^{-3}$ cm^{-1}) + sun tracker
- measurement of 10+ species:
- O_3, CO, CO_2, CH_4, H_2O, HD
- - satellite validation

-air quality and pollution studies (megacity
- impact) GHG trend
- + variability (TCCON/NDACC in 2014)
- - vertically resolved information

Axis II – Molecular processes and parameters for atmospheres and ISM

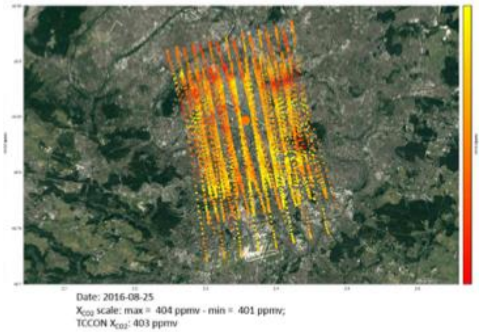
Study of atmospheric pollutants and greenhouse gases above Paris

- High resolution FTS-Paris is in operation since 2007
- Part of international TCCON network (since 2015)
- Part of OCAPI (IPSL observation network) & QualAir (UPMC)
- Provides unique data: only one other mega-city station worldwide
- Validation target for on-going and future satellite missions
- Strong society impact

Sun tracker FTS-Paris

Té et al, JAOT 2012

OCO-2 Paris overflight



Wunch et al, AMT 2017

Projects

- GHG satellite validation projects (OCO-2, GOSAT-2, CNES: MicroCarb, Merlin, …)
- Development of WMO calibration for TCCON-Paris (CNES)
- Systematic study of site-specific effects (a-priori, …)
- Participation in regional air quality campaigns (DIM QI^2, …)
- Extension of spectral coverage and development of NDACC-IRWG capabilities (validation IASI-NG …)

Axis II – Molecular processes and parameters for atmospheres and ISM

VUV spectra of molecules and multiply charged heavy element ions

- High resolution (R = 150000) VUV normal incidence spectrograph Meudon
- Image plates with 5 decades of linear intensity response
- Penning discharge or HV vacuum sparks
- Wavelength range 200-3000 Å

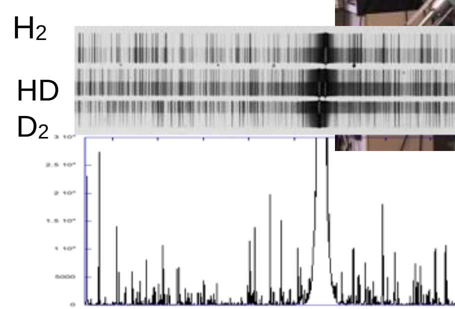
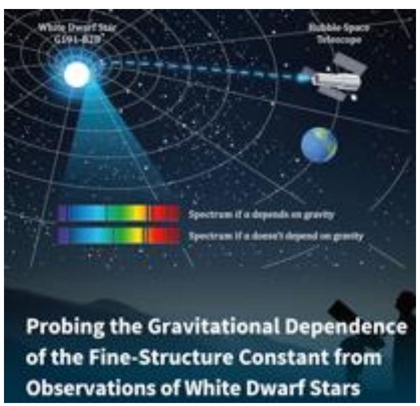


Image plate of HD emission spectra



Bainbridge et al, Universe 2017

Projects

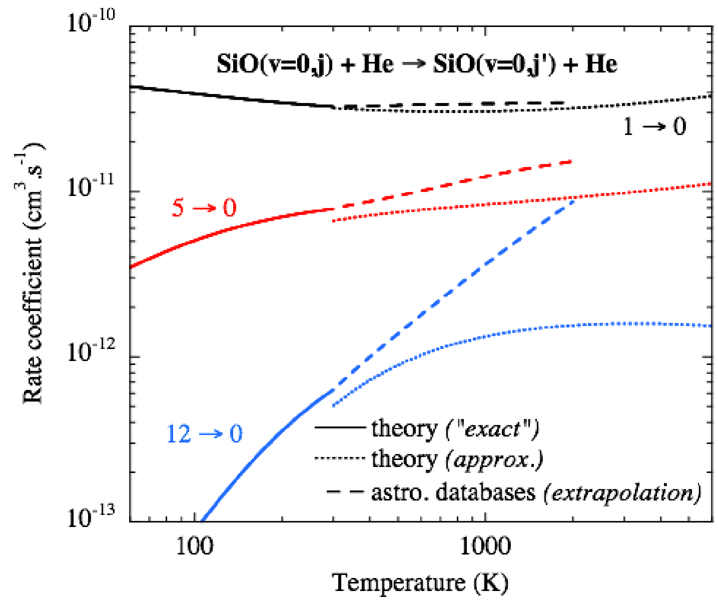
- Emission spectra of the hydrogen isotopologue HD (theory & experiment)
- Emission spectra of iron group multiply charged ions (Fe-V, Ni-V) as laboratory references for possible change of the fine structure constant α in white dwarfs observed by HST
- Study of transition energies and probabilities of heavy element (Eu, Er, Tm) ions for abundance studies and radiative transfer simulations of Neutron Star Merger Ejecta

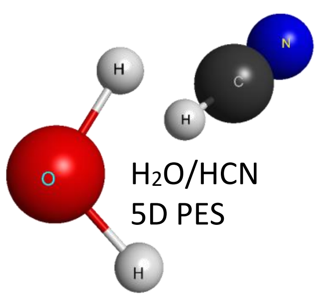
Axe II – Molecular processes and parameters for atmospheres and ISM

Collisional parameters for the modelling of non-LTE media

- Simulations based on quantum chemistry and quantum dynamics
- Rotational excitation of molecules (ISM)
- Electronic excitation of atoms (stellar atmospheres)
- Variety of systems and temperature conditions
- Development of the BASECOL database (since 2004)
- Creation of the worldwide VAMDC e-infrastructure

Balança et al., 2017





H_2O/HCN
5D PES

Quintas-Sanchez et al., 2017

Projects

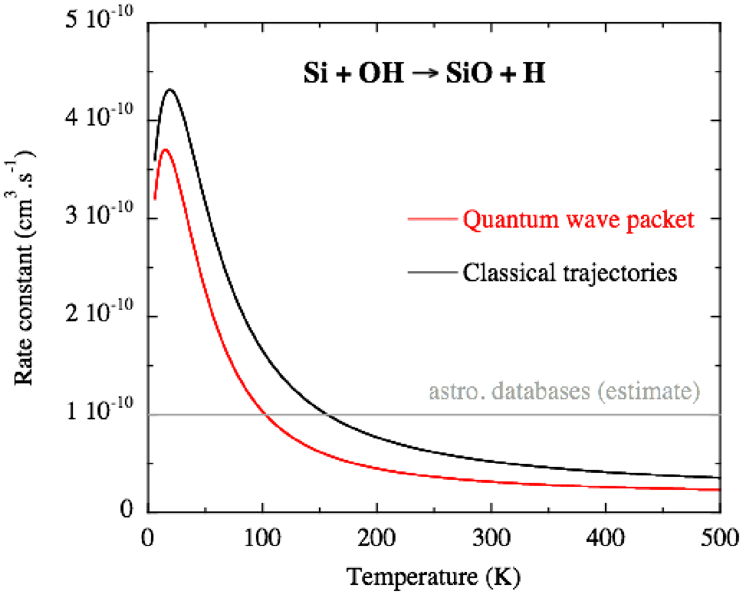
- Support of ALMA, Herschel, NOEMA, GAIA, Rosetta, … exploitation
- Systems with more degrees of freedom (larger species, vibration,…)
- Improved description of processes for high-temperature media
- Collisions of molecules with water (cometary atmospheres)
- Update of BASECOL database and development of VAMDC platform

Axe II – Molecular processes and parameters for atmospheres and ISM

Reaction rates for the chemical modelling of astrophysical media

- Simulations based on quantum chemistry and quantum dynamics
- Use variety of complementary approaches
- Low-temperature reactions between unstable radicals
- Deep insight into reaction mechanisms
- State-to-state reaction rates

Merged-beams apparatus (Columbia Univ.)



Rivero-Santamaria et al., 2017

Projects

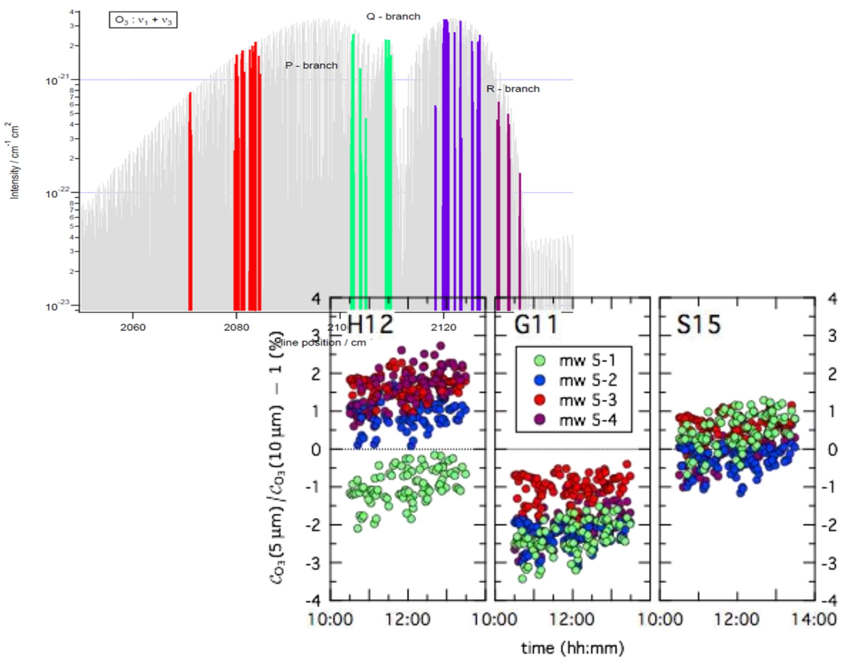
- Study of low-temperature isotopic effects ($C+H_2^+/HD^+/D_2^+$ reactions)
- Joint experimental/theoretical study (D.W. Savin group, Columbia Univ.)
- Study of state-resolved photodissociation processes (diffuse ISM)

Axis II – Molecular processes and parameters for atmospheres and ISM

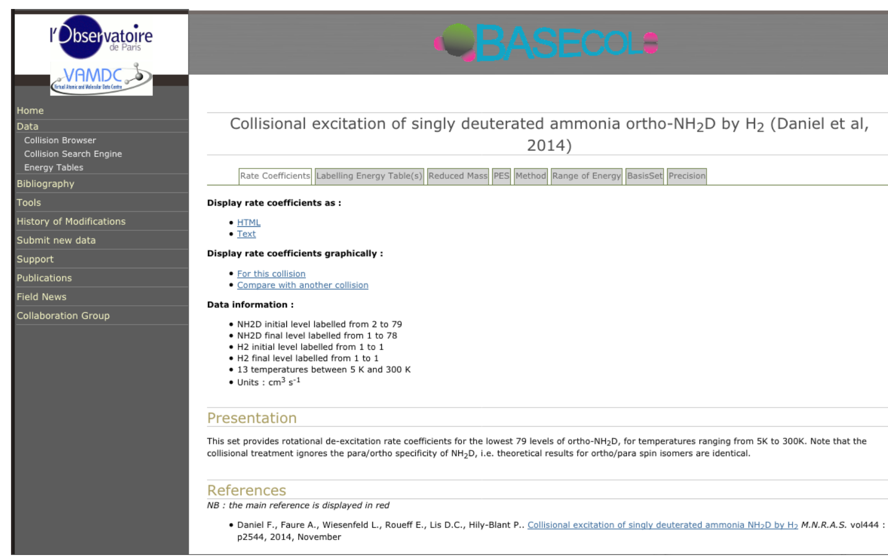
Close links between observation, simulation, laboratory studies and databases

- Molecular VUV data (H_2, CO) are fed into MOLAT database
- Calculated collision rates are directly integrated into BASECOL
- Consistency of spectroscopic data bases (HITRAN, GEISA, S&MPO) is verified through remote sensing

  ➞ triggers new laboratory studies



Janssen et al, JMS 2016

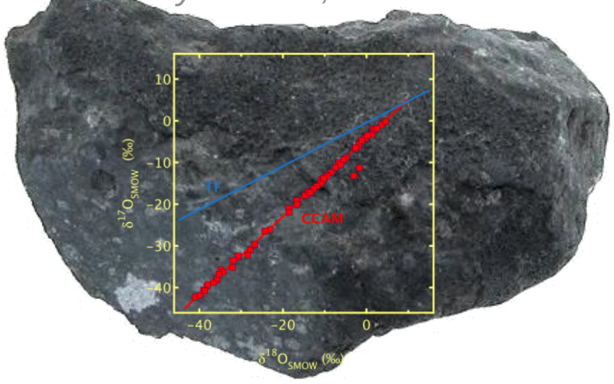


ortho-NH_2D + H_2 *(Daniel et al MNRAS 2014)* added to BASECOL database *(Dubernet et al, A&A, 2013)* in 2016

Axis III – Molecular anomalies

- *Unusual and unexplained molecular signatures, such as ortho-para ratios and anomalous isotope ratios, provide new and exciting probes for their environment*
  - *New and highly sensitive tools for laboratory studies are developed*

Clayton et al, Science 1973



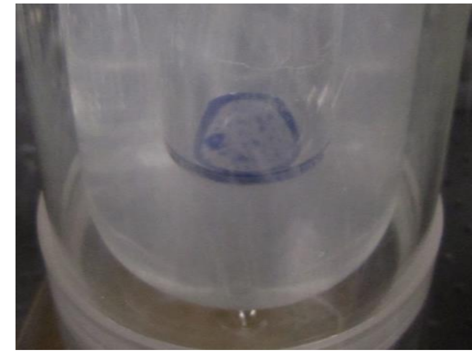
Key questions:

- *Understand physico-chemical origin of unusual isotope and ortho-para ratios (OPRs)*
- *Why do observed OPRs in cometary atmospheres, protoplanetary disks, PDRs and diffuse clouds often differ from what is expected from these environments ?*
- *Can we understand low T isotope fractionation on icy films : tunnelling and large isotope effects ?*
- *Where does heterogeneity of oxygen isotopic composition of the solar system come from ?*
- *What can we learn from isotope signatures of multiply substituted isotopologues ?*

Axis III – Molecular anomalies

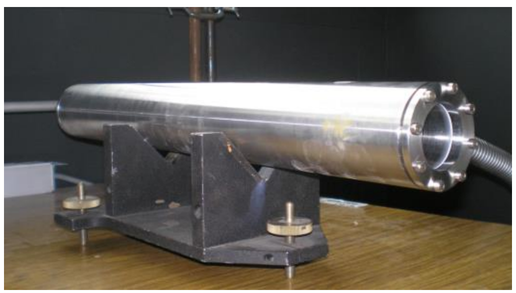
Isotope anomalies in O + XO reactions

- Ozone formation ($O + O_2 \rightarrow O_3$) is the prime example for chemically induced mass independent (MIF) isotope anomalies
- Current laboratory evidence is ambiguous and in contradiction to models

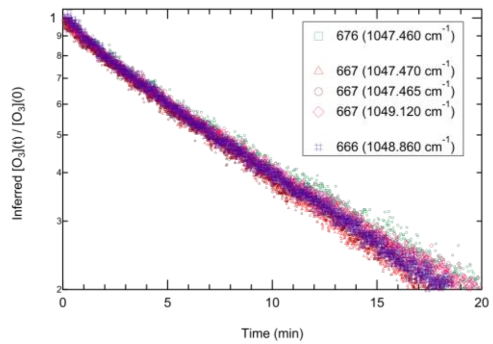


Liquid ozone

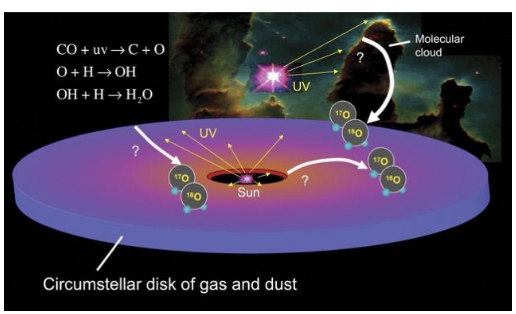
Reactor



Isotope selective decomposition rates



Self shielding in the solar system



from *Rumble et al. GSE 2013*

Projects & goals

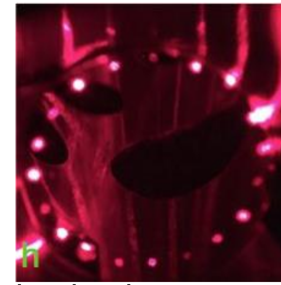
- Investigate ozone decomposition $O_3 \rightarrow O + O_2$ as inverse kinetic problem (gas & surface)
- Resolve contradiction between models & experiments
- Confirm or reject hypothesis of MIF in surface reactions:

Test chemical models of solar system isotope heterogeneity

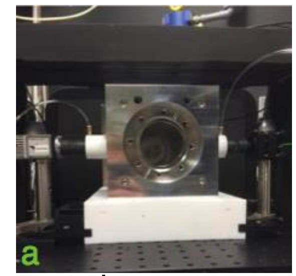
- Study $O + CO \rightarrow CO_2$ using newly developed instrument

Axis III – Molecular anomalies

multi-pass absorption cell



back mirror

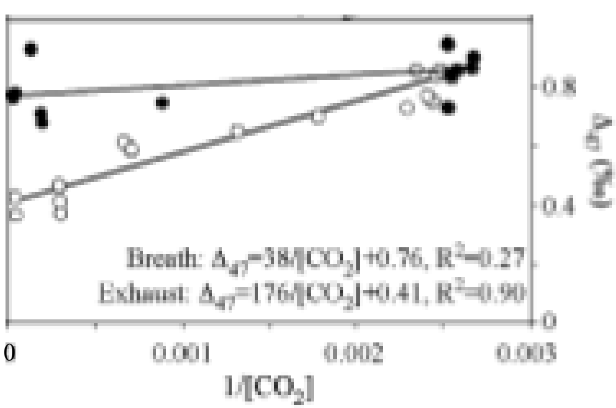


container

New tools for new isotope research

- *Doubly substituted isotopologues are currently studied by mass spectrometric techniques that require extremely long analysis time (~ several h /sample) and suffer from interferences*
- *Optical methods have the potential to avoid these drawbacks*
- *New multi-isotopologue analyzer is being developed at LERMA*

$^{16}O^{13}C^{18}O$ (Δ_{47}) signatures of two different sources



Affek et al, GCA 2006

Projects & goals

- Develop new tools for isotope research: optical multi-isotope analyser

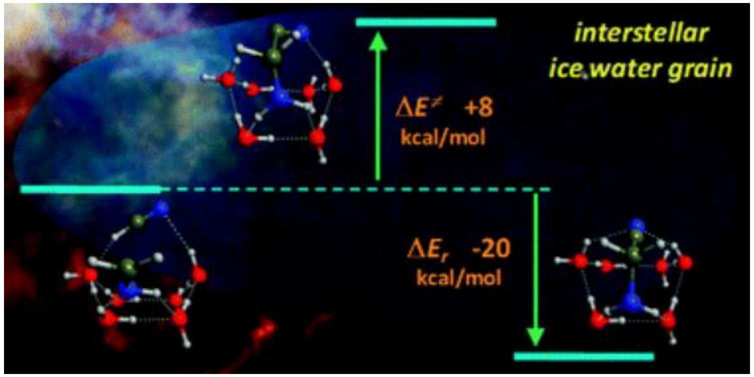
(Collaboration U Heidelberg (D) / thesis co-direction)

- Study large set & extremely rare isotopologues of CO_2 ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{16}O^{13}C^{18}O$, $^{16}O^{13}C^{17}O$)
- Investigate & understand sources and processes of atmospheric CO_2
- Investigate link to ozone chemistry and O+CO reaction (previous slide)

Axe III – Molecular anomalies

How efficient is the H/D isotope exchange in ice desorption ?

- *Small differences in binding energies might have huge impact on isotopic desorption rates in the sub-monolayer regime (Amiaud et al 2015)*
- *Expect large H and D isotope effects due to quantum tunnelling*



Rimola et al, PCCP 2010

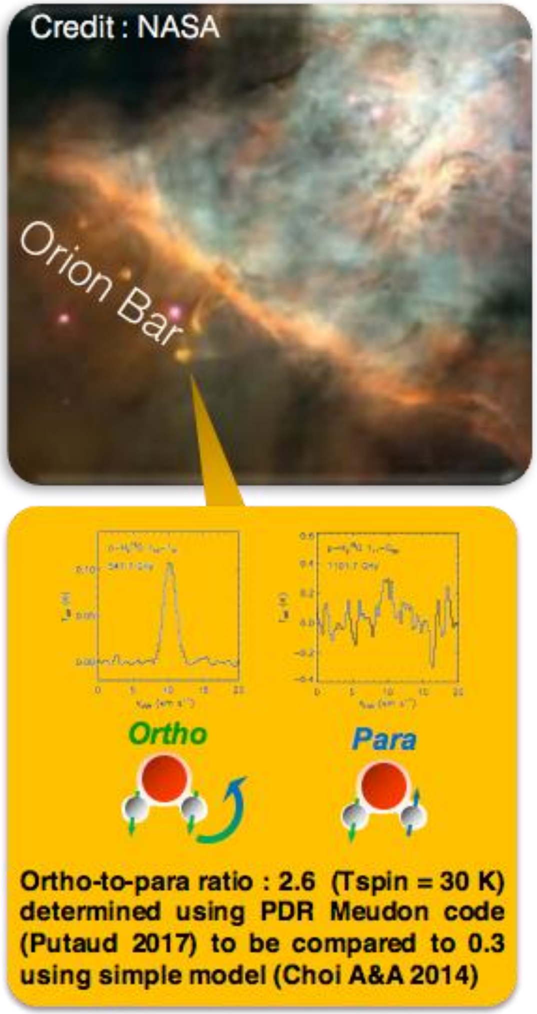
Project:

- *Determine the H/D exchange of water and ammonia in presence of reactive traces (e.g. H_2CO).*
- *Study the isotope effect in the reactivity of H and D in the building of the ice*

Impact: Possible transformation of ices in the solar system during sublimation.
Collaboration: Cazaux, Delft (NL), Rimola, Barcelona (S).

Axis III – Molecular anomalies

What is the link between the thermal history of ices and spin temperatures measured in space ?



New experiments to

- *study small hydrogenated molecules (H_2O, H_2CO…) in link with observations*
- *better understand the role of nuclear spin states of H_2, water and other hydrogenated molecules on the global chemistry*
- *determine the influence of adsorption & desorption from grains on the abundance of ortho and para species in the medium*
- *prepare "pure" spin state populations, which will provide unambiguous and precise spin conversion rates*

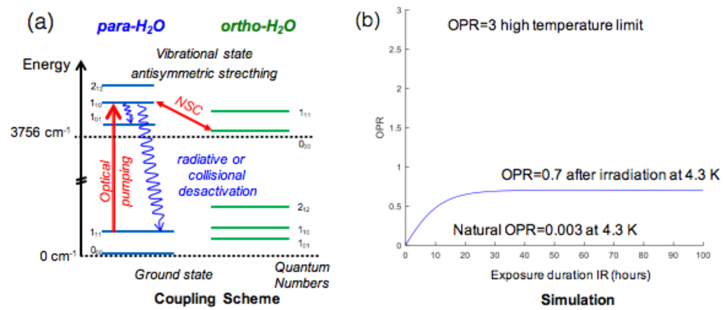
Collaboration with pole ISM

International collaboration (U Sherbrooke, CA)

Axis III – Molecular anomalies

What is the link between the thermal history of ices and spin temperatures measured in space ?

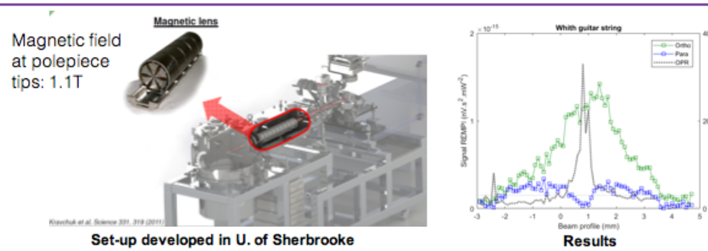
OPTICAL PUMPING



Potential enrichment OPR x 233

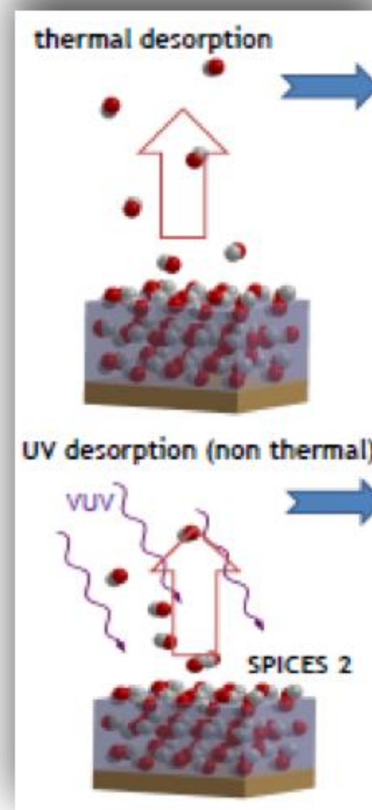
Putaud 2017

MAGNETIC LENS



Potential enrichment OPR x 30

Vermette, Brault, & Putaud 2017



Ortho

Para

Ratios

Project & goals

- Develop new experimental tools
- Measure characteristic times for nuclear spin conversion on icy mantle
- Establish link between OPR on ice and OPR in gas phase
- Understand the influence of the desorption (thermal or non-thermal) on the OPR in the gas phase

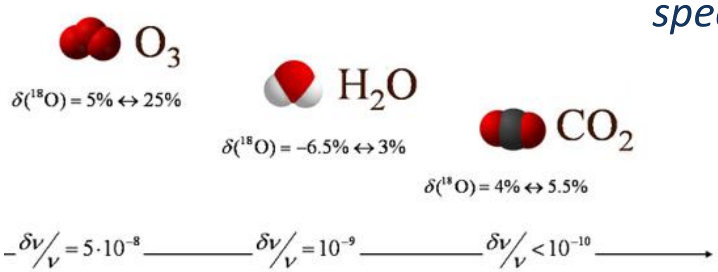
Summary and highlights

- *Fundamental physics approach for understanding mechanisms at the molecular level that can solve astrophysical and atmospheric research problems*
- *Strong & unique laboratory astrophysics activity*
- *Atmospheric observation and lab spectroscopy have strong social relevance and close link to gas metrology activities is established via participation in international WG*
- *Activities span whole range from laboratory measurements/simulation to observation and results are distributed to the international community via databases*
- *Development of new and unique technologies for using & studying molecular anomalies as probes:*
  - *Rare (doubly substituted) isotope analyser for CO_2*
  - *Nuclear spin state enrichment*

Why do we need high resolution spectroscopy ?

Instrument Resolution *R*	3 10^{-6}	2.5 10^{-4}	5 10^{-5}	1.5 10^{-7}	**10^{-8}**
Spectroscopic Requirement ($\Delta\nu/\nu$)		10^{-7}	3 10^{-8}	3 10^{-9}	**~ 10^{-10}**
		-	0.3	.1	**< 0.1**

* *for calibration*



- *Isotope abundance of HDO measured by MIPAS satellite limited by spectroscopy (Frankenberg et al, Science 2009) ?*
- *Ground based remote sensing of H_2O isotopologues (D, ^{18}O) limited by spectroscopy (Rokotyan et al, AMT 2014)*
- *Accuracy of molecular parameters limits correction of telluric spectra in ESO instruments (Smette et al, A&A 2015)*