

Formation of molecular hydrogen on silicates in conditions pertinent to the interstellar medium

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H₂ formation on surfaces

Basics (1)

- Inefficient formation in gas phase
- The gas-grain surface interaction is the main route for the molecule formation in the ISM

Gould and Salpeter (1963)

Interstellar grains acts as **catalysts**:

- Heterogeneous chemistry at the gas/surface interface
 - from the very simple H₂ formation
 - to the more complex chemistry

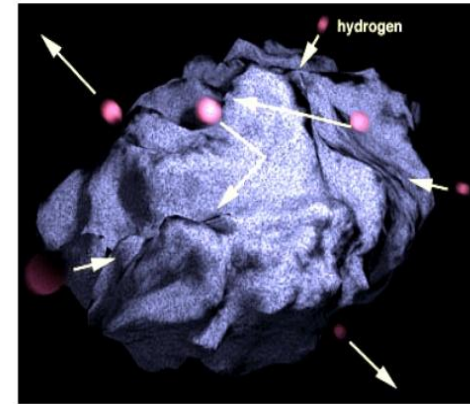


Figure 1.10- H atoms interacting with an interstellar dust grain. The surface of the grain is uneven, and the atoms travel on it, can recombine or be released into the gas phase.

The kinetics of the reaction under interstellar conditions is still not well understood

Experimental aspects

- what is a real interstellar grain ?
- what are the properties of atoms/molecules on it ?
- how to work in the laboratory under interstellar conditions ?

Low flux ($<10^{12}$ atoms/cm²/sec) **and E_k** (10-300 K) **of H atoms**

Low sample temperature (≥ 5 K), **Low background pressure** ($5 \cdot 10^{-11}$ mbar)

- Bare or ice covered material
- Morphology (amorphous ?, crystalline ?)
- Sizes
- Porosity
- Binding energy
- Mobility
- Sticking
-

H₂ formation on surfaces

Basics (2)

Theoretical aspects

- What are the physical and chemical mechanisms involved ?
- What formalism to use to give account of them ?

Observational evidences

Such evidence is (was) very rare

- * Probably mixed up with stronger excitations: PDRs or shocks

ρ Ophiuchi molecular cloud

- * H₂ formation on PAHs surfaces ?
- * ISO observations

Habart et al. (A&A, 2003)

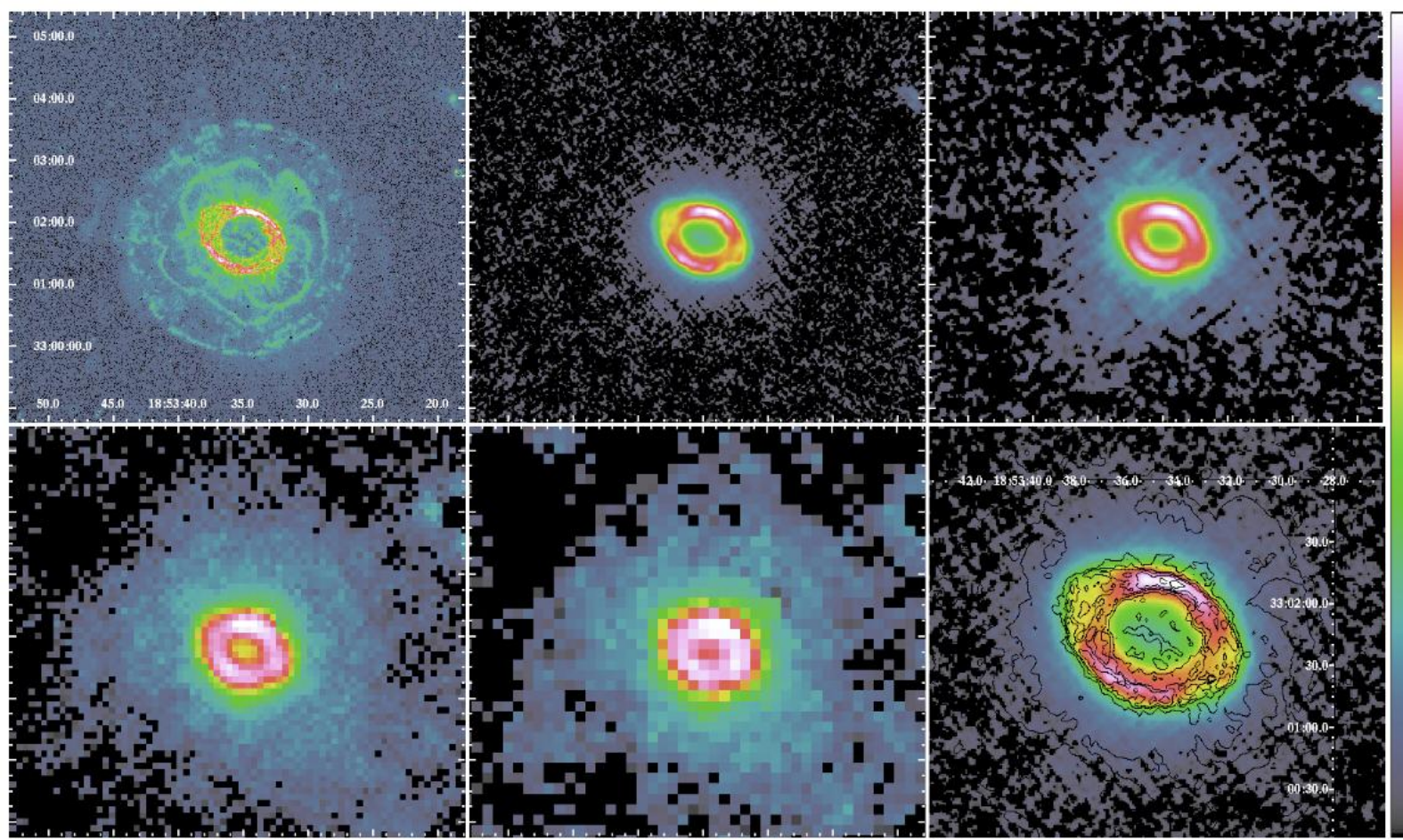
NGC 6720 (the Ring nebula)

- * H₂ emission very closely connected to dust emission
- * Evolved planetary nebula with a central star currently on the cooling track, due to which the outer parts of the nebula are recombining.
- * Presence of PAHs very unlikely
Most likely pristine material (Silicates ?, SiC ?)
- * Herschel observations

van Hoof et al (A&A, 2010)

Herschel: th

Herschel



P. A. M
M. A. T
H. L. G
E. T. Poleham

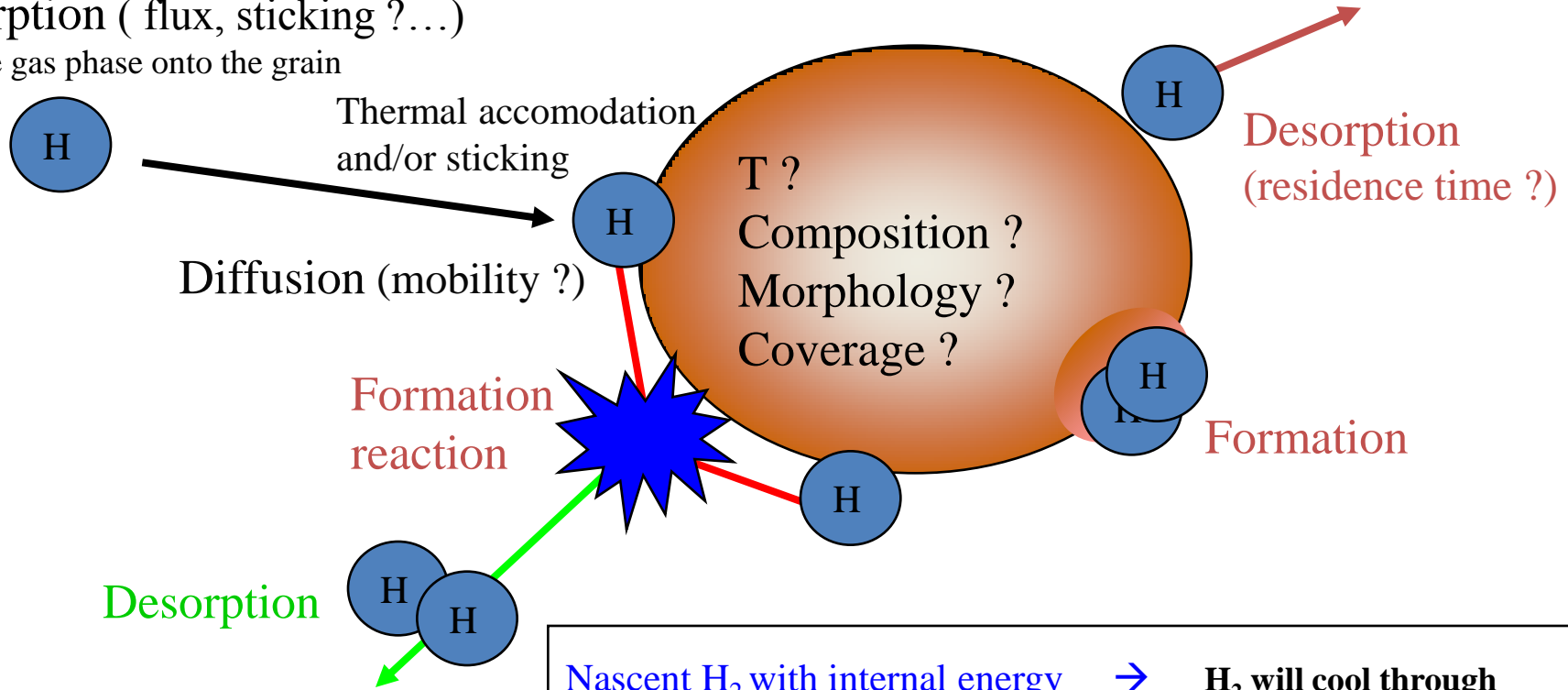
Fig. 1. NGC 6720 in five photometric bands. *Top row from left to right:* H₂ 2.12 μm, PACS 70 μm, PACS 160 μm. *Bottom row from left to right:* SPIRE 250 μm, SPIRE 350 μm, and an overlay of the Calar Alto H₂ contours on the PACS 70 μm image. The H₂ image is not flux calibrated. The maps have standard orientation (N to the top, E to the left).

From the PACS and SPIRE images we conclude that there is a striking resemblance between the dust distribution and the H₂ emission, which appears to be observational evidence that H₂ forms on grain surfaces.

we conclude
that H₂ forms
the physical
resides in
dynamical
ation in the
d may still

Formation of H₂ molecules on grains **Basics (3)**

Adsorption (flux, sticking ?...)
from the gas phase onto the grain



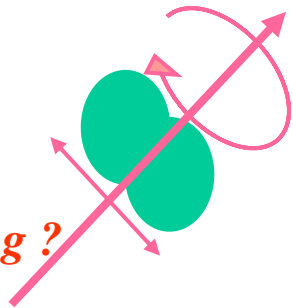
Formation energy partition

4.5 eV

$E_{v,J}$?

E_k ?

Grain heating ?



Nascent H₂ with internal energy → H₂ will cool through radiation of IR photons

The molecular cloud collapse more readily

Formation process → ISM dynamics
(results of the balance between internal pressure and gravitational forces)

Nascent H₂ with large translational and small internal energy and/or grain heating → Heating of the cloud

Slow collapse of the molecular cloud

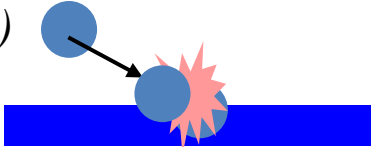
Surfaces, H₂ formation Theoretical aspects

Reaction mechanisms

- **Eley-Rideal** (*prompt mechanism*)

occur at high H atom coverage rate

→ creates "hot" H₂

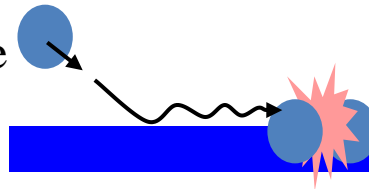


- **Harris-Kasemo** (*hot atom mechanism*)

several bounces before prompt reaction

occur at low and high H atom coverage rate

→ creates "hot" H₂



- **Langmuir-Hinshelwood**

(migration mechanism by *tunneling or thermal hopping*)

occur at low and high H atom coverage rate

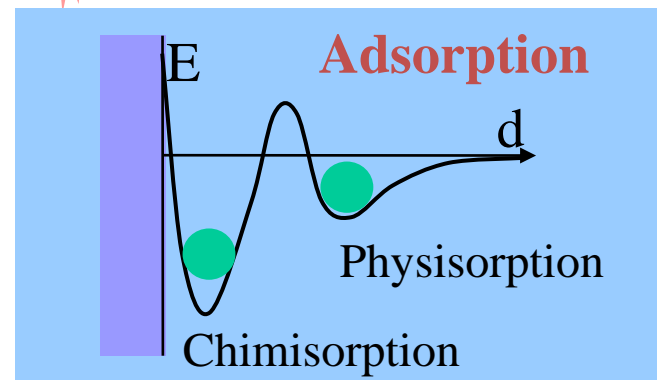
→ creates H₂ at surface temperature



Interaction of atoms and molecules with surfaces:

* physisorption (vdW interaction)

* chemisorption (covalent bond)



Experiments

Formation of molecular hydrogen
on a graphite surface at 15 K

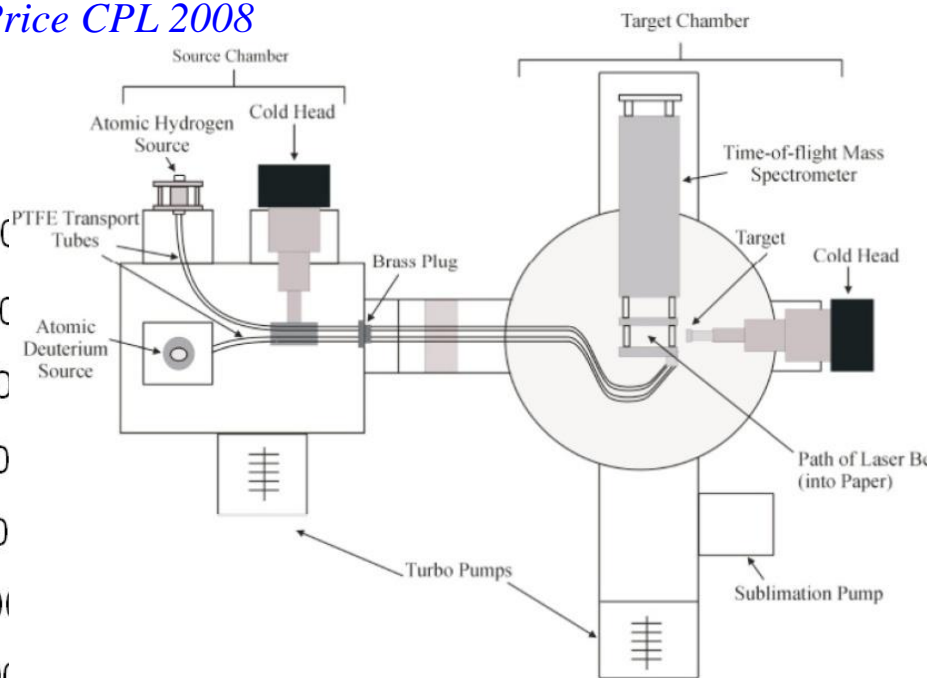
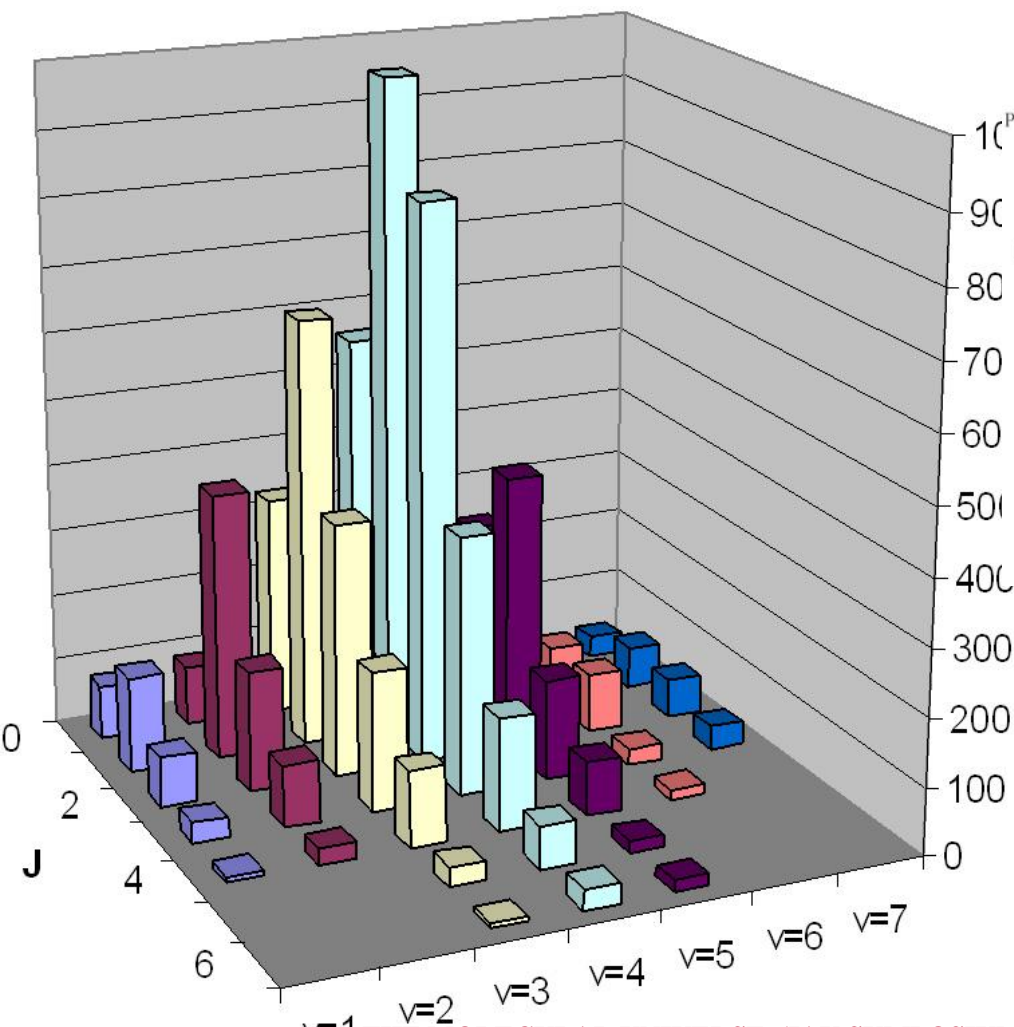
H + D → HD on graphite at 15 K

S. Price team at UCL

Creighan et al JCP 2006

Islam et JCP 2007

Latimer, Islam & Price CPL 2008



**Formation of HD in $v=1-7$
from recombination
on a cold HOPG surface**

Experiments

Formation of molecular hydrogen
on a silicate surface
at different temperatures

Formation of H₂ molecules on a silicate surface

Bare grains of silicates are (together with carbonaceous material) the main original constituent of interstellar matter in diffuse clouds

Polycrystalline silicates (telluric olivine) *Pirronello, Vidali et al. 1997*

Amorphous silicates

(Fe_x, Mg_{1-x})₂SiO₄,

x=0.5 *Vidali et al. 2007*

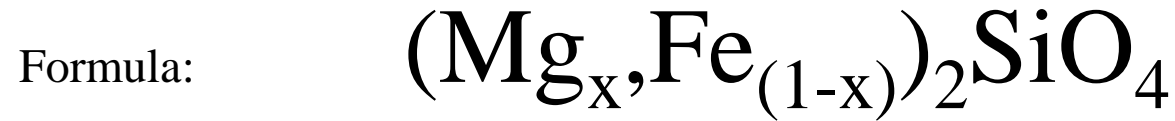
0<x<1 *Vidali et al. 2009, 2010*

TPD (Thermally Programmed Desorption) experiments (HD Formation)

Combined TPD & REMPI (Resonantly Enhanced Multi Photon Ionization) experiments

→ New results on the detection of ro-vibrational states of the just-formed D₂ as it leaves a silicate surface suggesting new and unexpected answers to the formation question
Lemaire, Vidali et al, 2010, ApJ Letters

Mineral **olivine**: **magnesium iron silicate**



One of the most common minerals on Earth

also identified in meteorites, the Moon, Mars, in the dust of comet Wild 2, and within the core of comet Tempel.

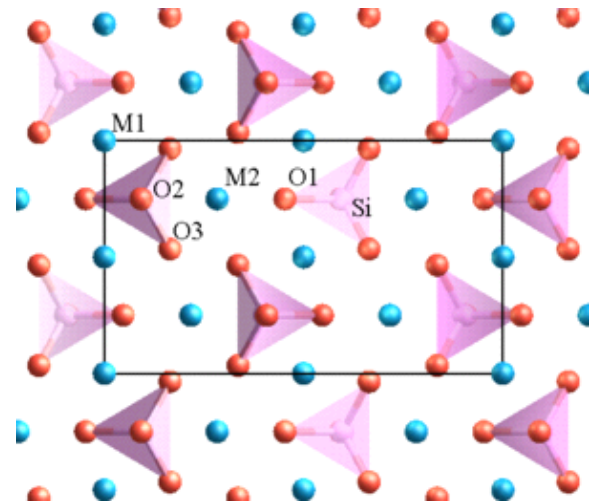
The ratio of magnesium and iron varies between the two endmembers of the solid solution series: **Forsterite** (**Mg**-endmember, $x=1$) and **Fayalite** (**Fe**-endmember, $x=0$).

Forsterite has an unusually high melting temperature at atmospheric pressure, almost 1900°C , but the melting temperature of **Fayalite** is much lower (about 1200°C). The melting temperature varies smoothly between the two endmembers, as do other properties.

Olivine incorporates only minor amounts of elements other than oxygen, silicon, magnesium, and iron: Manganese and nickel are the most present additional elements.

Crystal system: orthorhombic

The atomic scale structure of olivine looking along the a axis. Oxygen is shown in red, silicon in pink, and magnesium/iron in blue. A projection of the unit cell is shown by the black rectangle



Laboratory synthesis of interstellar dust analogs

Several techniques (extensive review in *Colangeli et al. 2003*)

- laser pyrolysis (*Herlin et al. 1998*)
- laser ablation (*Brucato et al. 1999*)
- sol-gel synthesis (*Jäger et al. 2003*)
- reactive thermal evaporation (*Rietmeijer et al. 1999*)
- ion sputtering (*Hanley & Sinnott 2002*)

Sample prepared here by electron-beam evaporation in a high vacuum chamber (10^{-7} mbar)

Djouadi, d'Hendecourt, Leroux, Jones, Borg, Deboffle, Chauvin, A&A (2005)

- **San Carlos olivine** ($\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$) as solid precursor.
- Locally transformed into liquid in a crucible.
- Vapor kinetically deposited onto the substrate ($p < 10^{-6}$ mbar, mean free path ~ 30 cm).
- Vapor deposition rate (~ 0.2 to 0.5 \AA/s) both on our sample holder and on a KBr window
- Deposition rate and final film thickness controlled with a quartz micro balance.
 - thin amorphous films (**~ 100 nm at most**)
with a high surface-to volume ratio analogous to interstellar dust grains.
- Amorphous character verified by IR spectroscopy
- Exact chemical composition not well determined from only IR spectroscopy
(broad bands and uncertainties in the band position)

-Silicates comprise the majority of the earth's crust, as well as most planets and moons.

-Silicate compounds, including the minerals, consist of silicate anions whose charge is balanced by various cations.

- Then **silicates** have specific mineralogical spectroscopic signatures which can be observed in space and recreated in the laboratory.

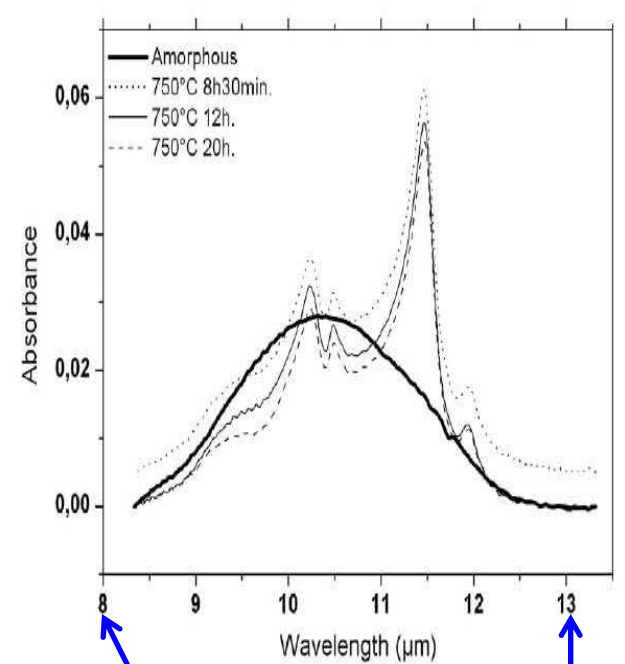


Fig. 5. The evolution of the 10 μm silicate band in going from initial amorphous state (thick solid line) to a final crystalline state:

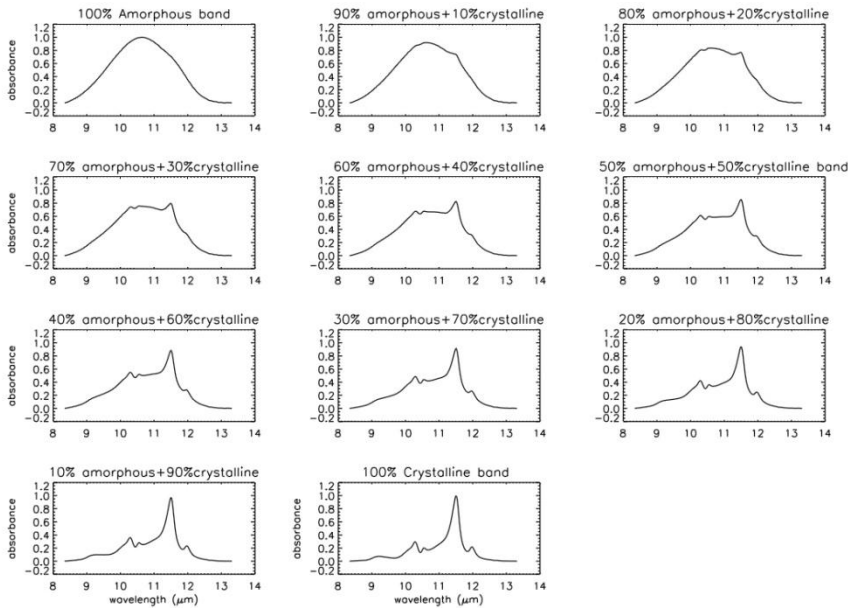
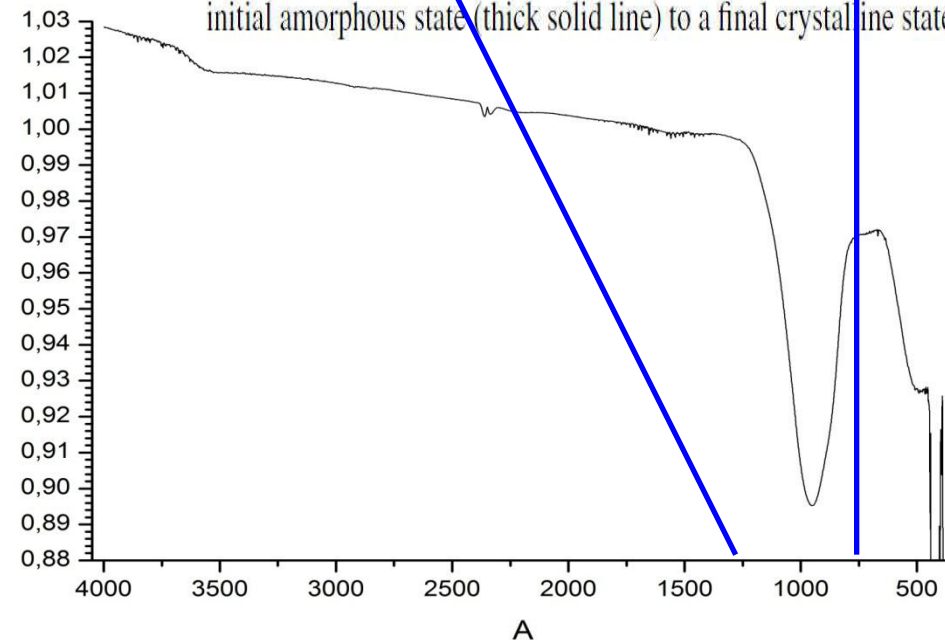
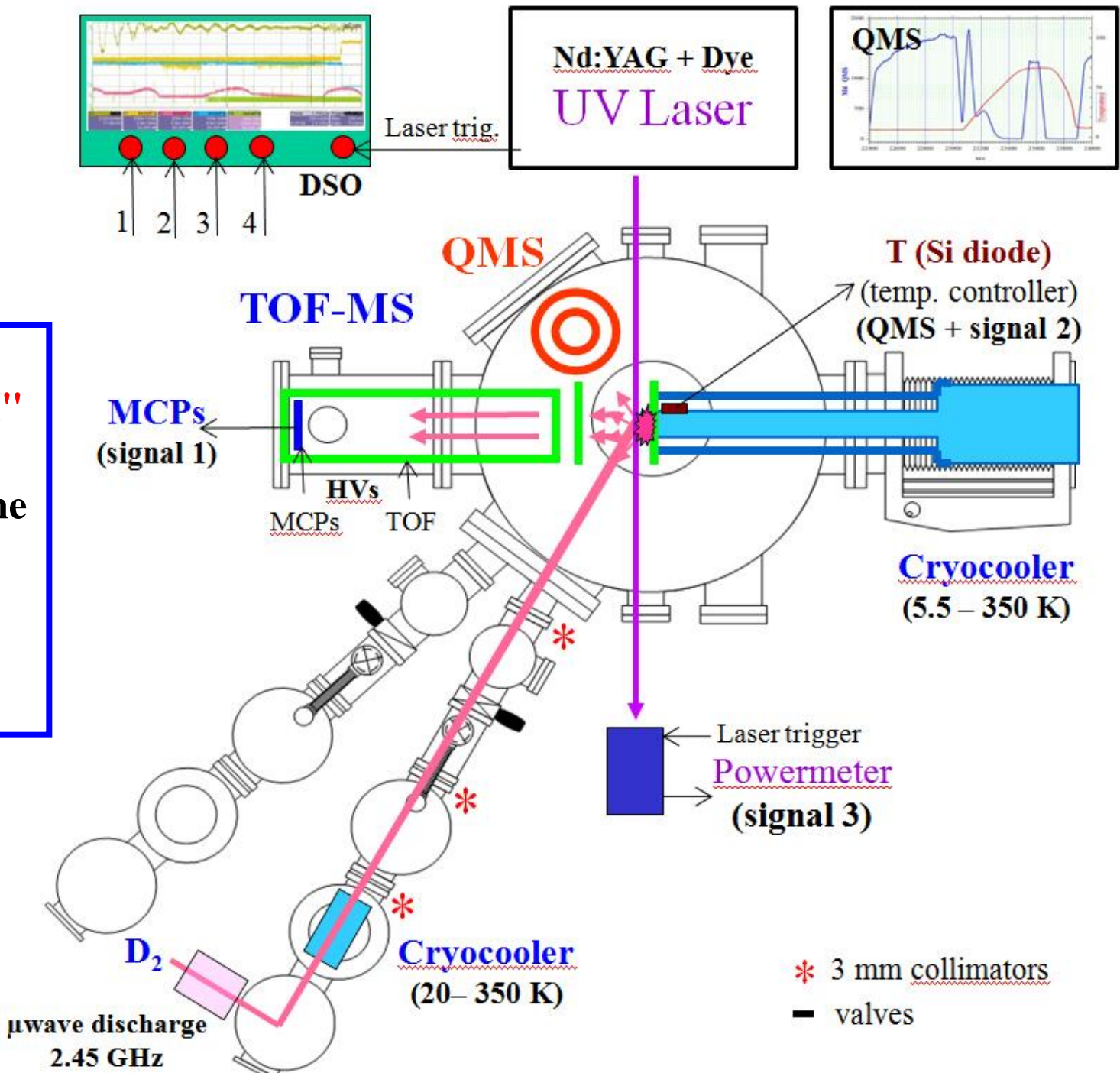


Fig. 6. The 10 μm band evolution as a function of the amorphous/crystalline fraction. These profiles were obtained by using a

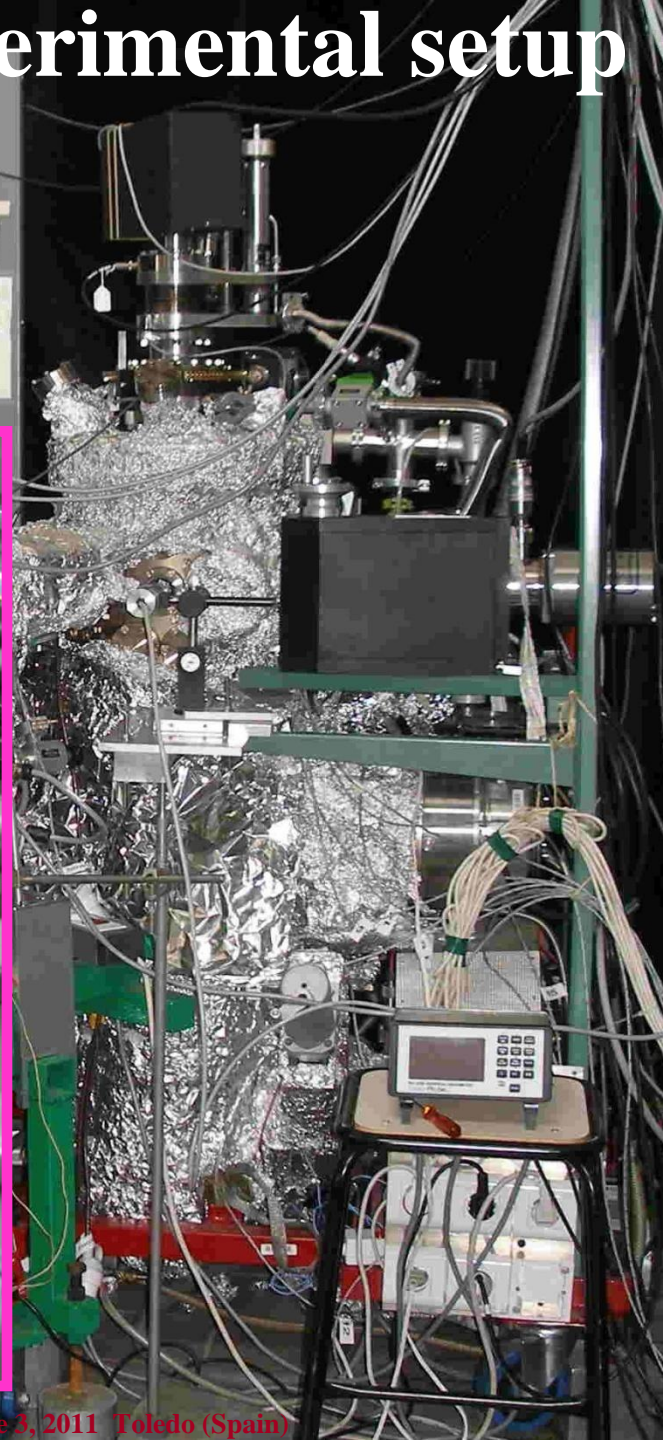
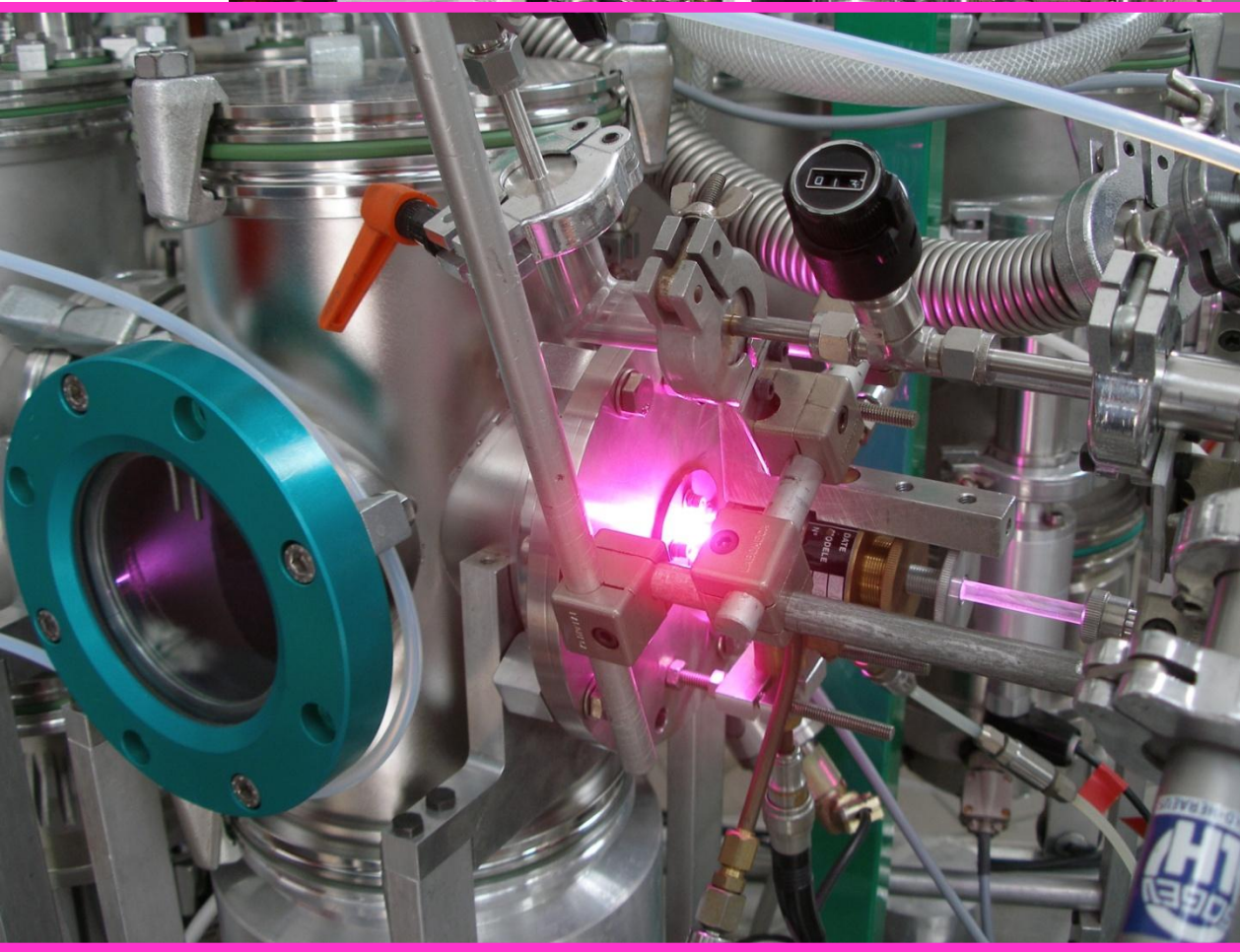


The "FORMOLISM" (FORMATION of MOLECULES in the Inter Stellar Medium) setup



"FORMOLISM" experimental setup

Atomic hydrogen source

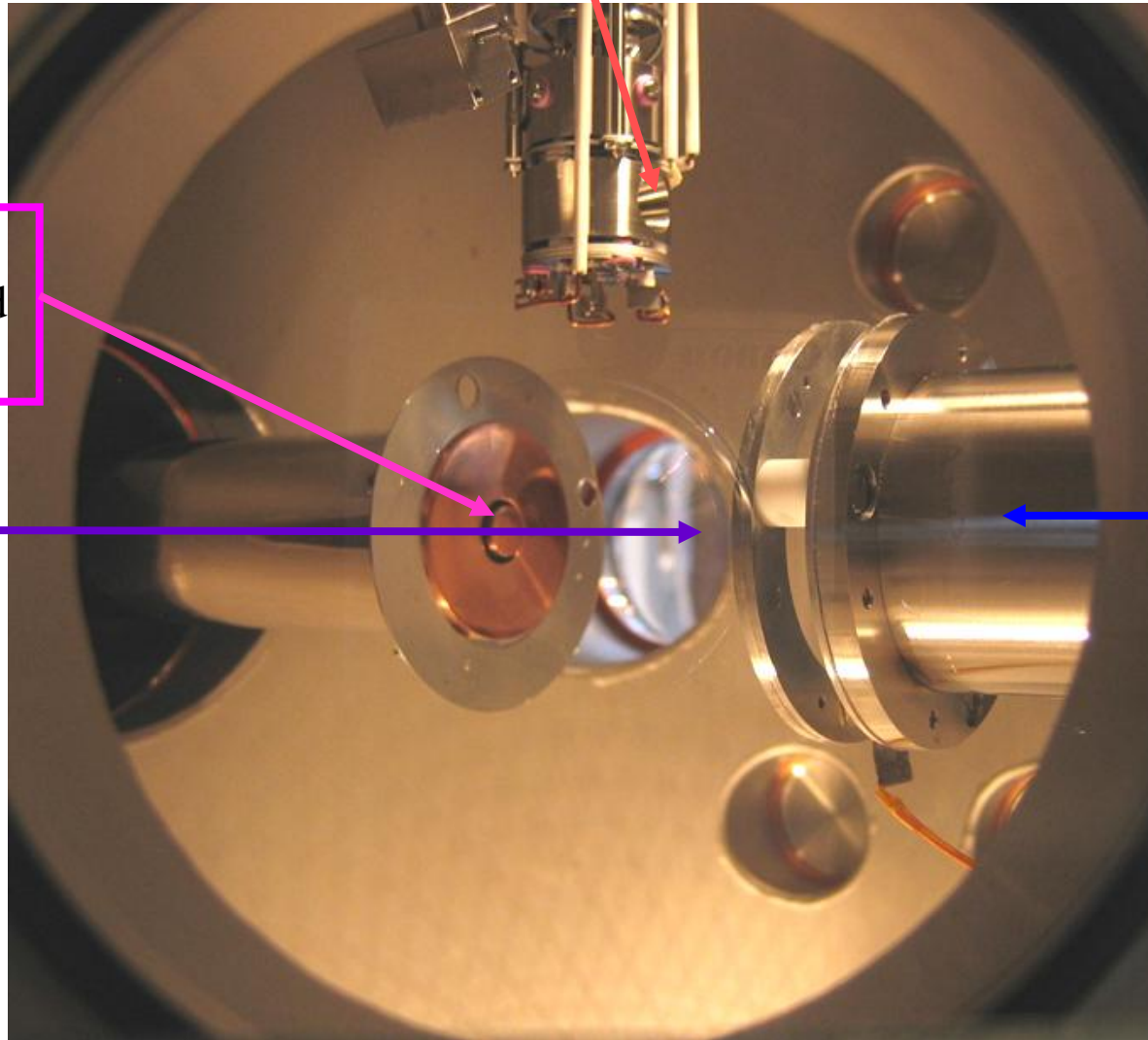


Quadrupole Mass Spectrometer
(+ translation + rotation)

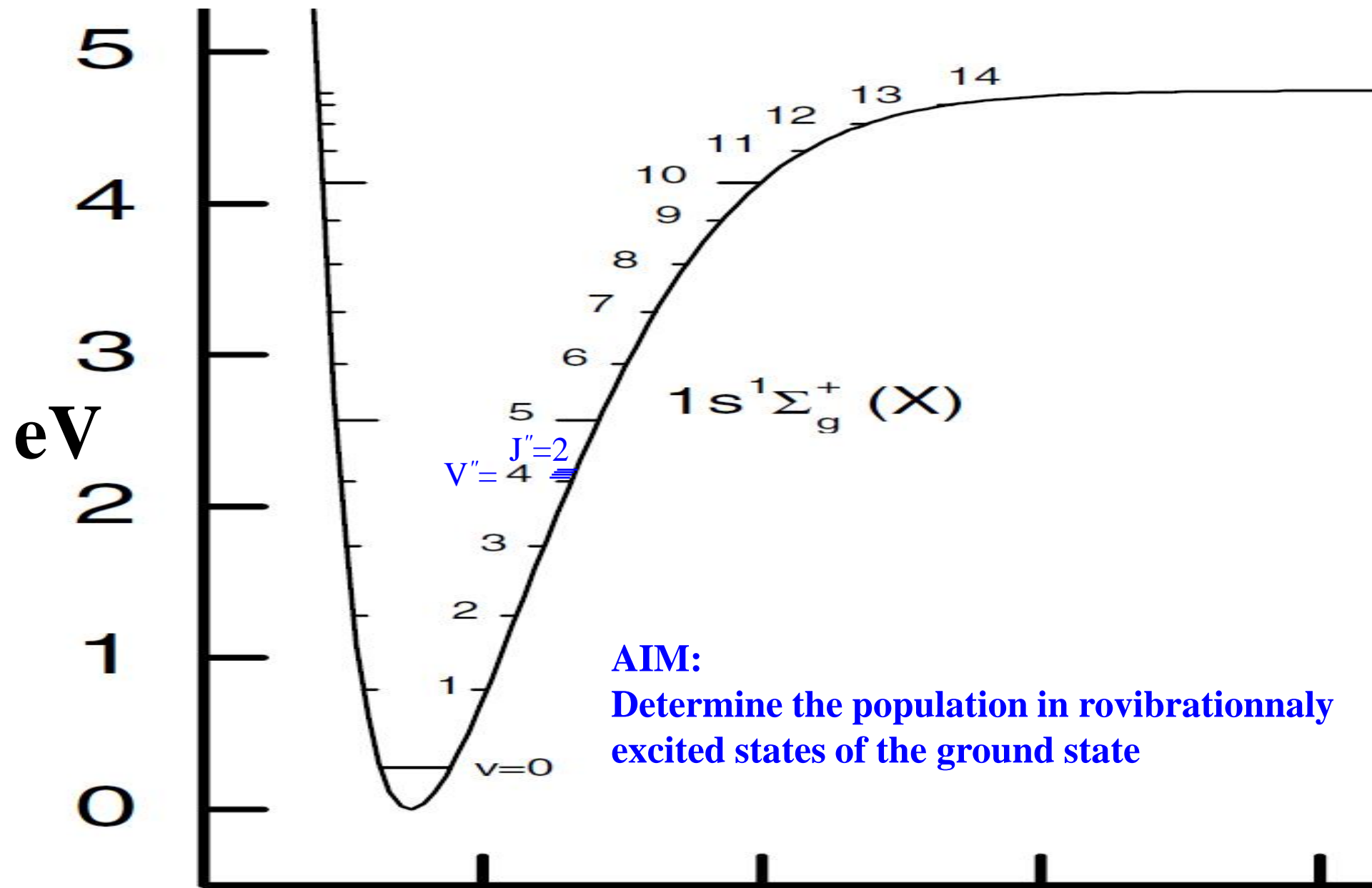
Cold head
+ thermal shield
(+translation)

UV
Laser beam

Time of Flight
Mass
Spectrometer

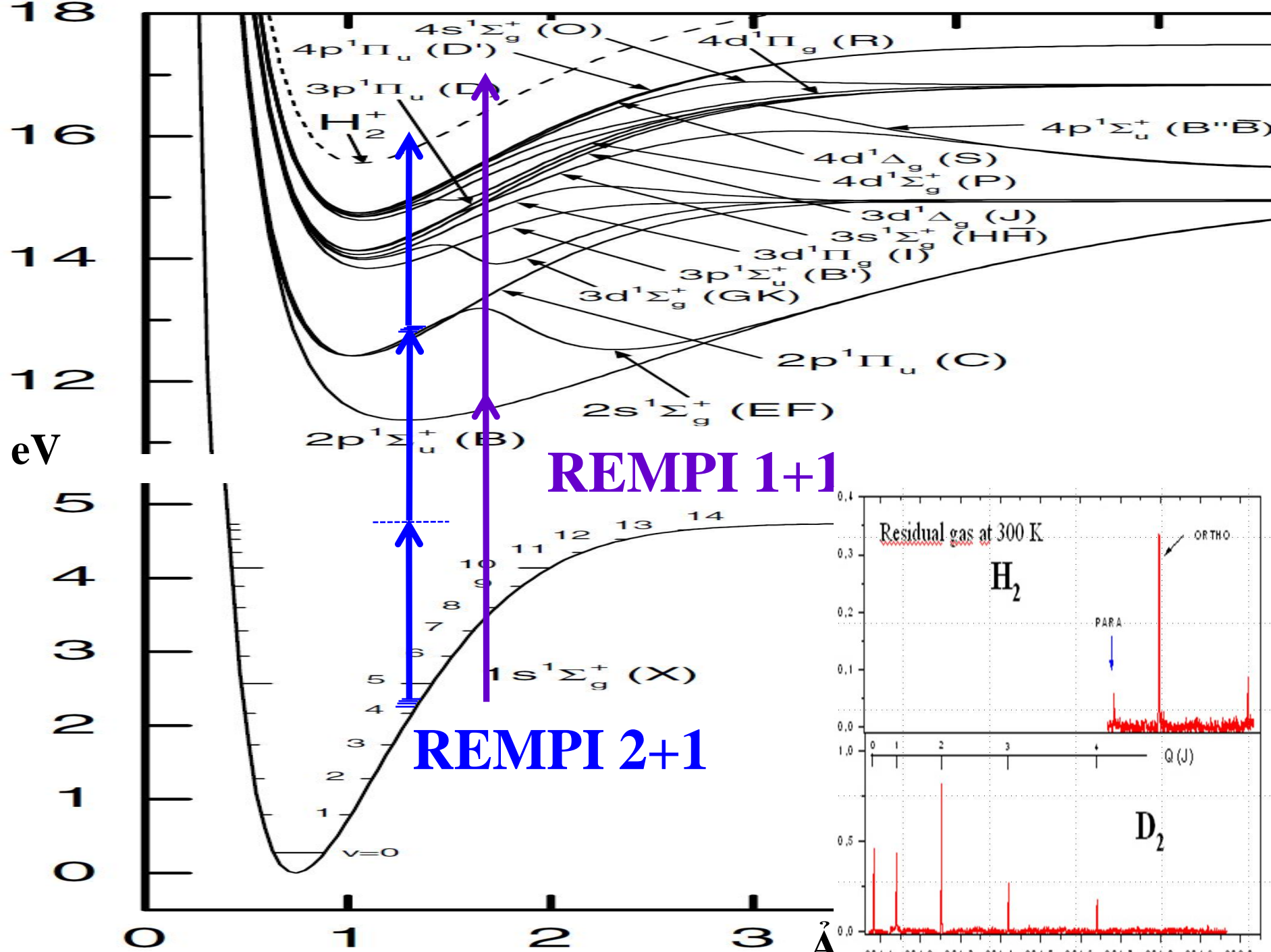


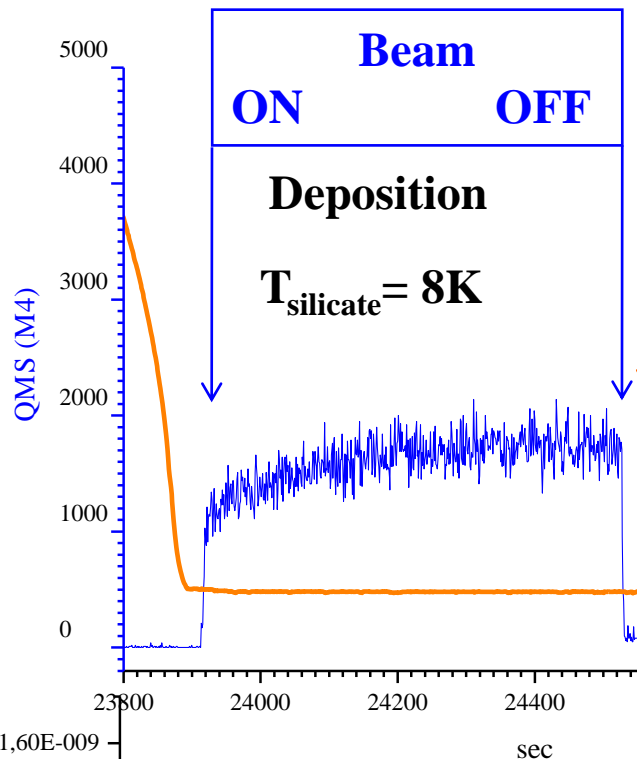
Inside the UHV chamber (seen from the **molecular or atomic gas beams** entrance port)



AIM:
 Determine the population in rovibrationally excited states of the ground state

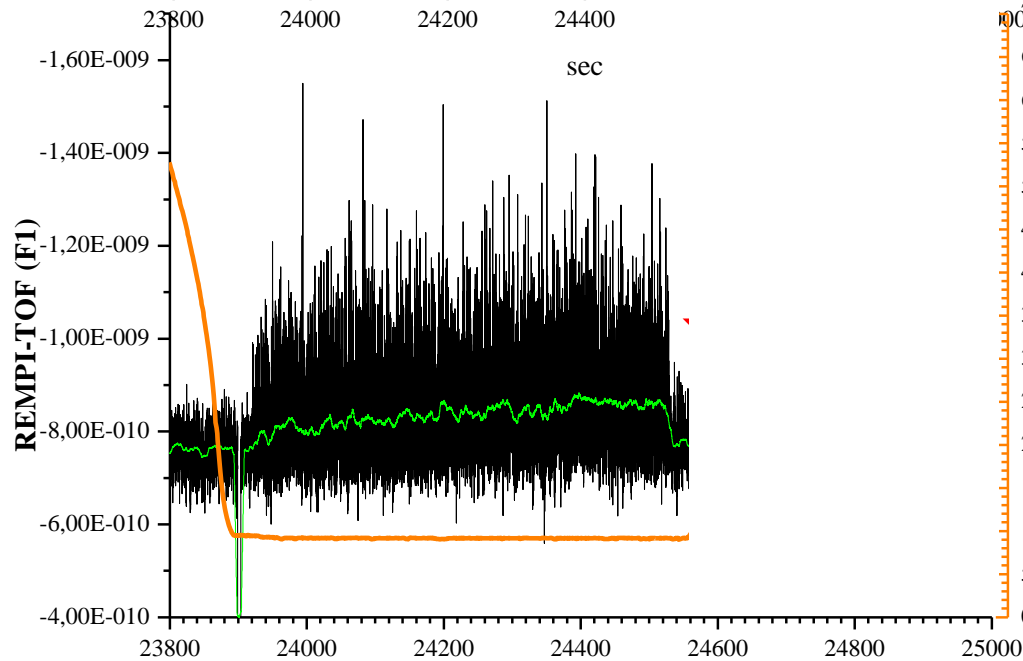




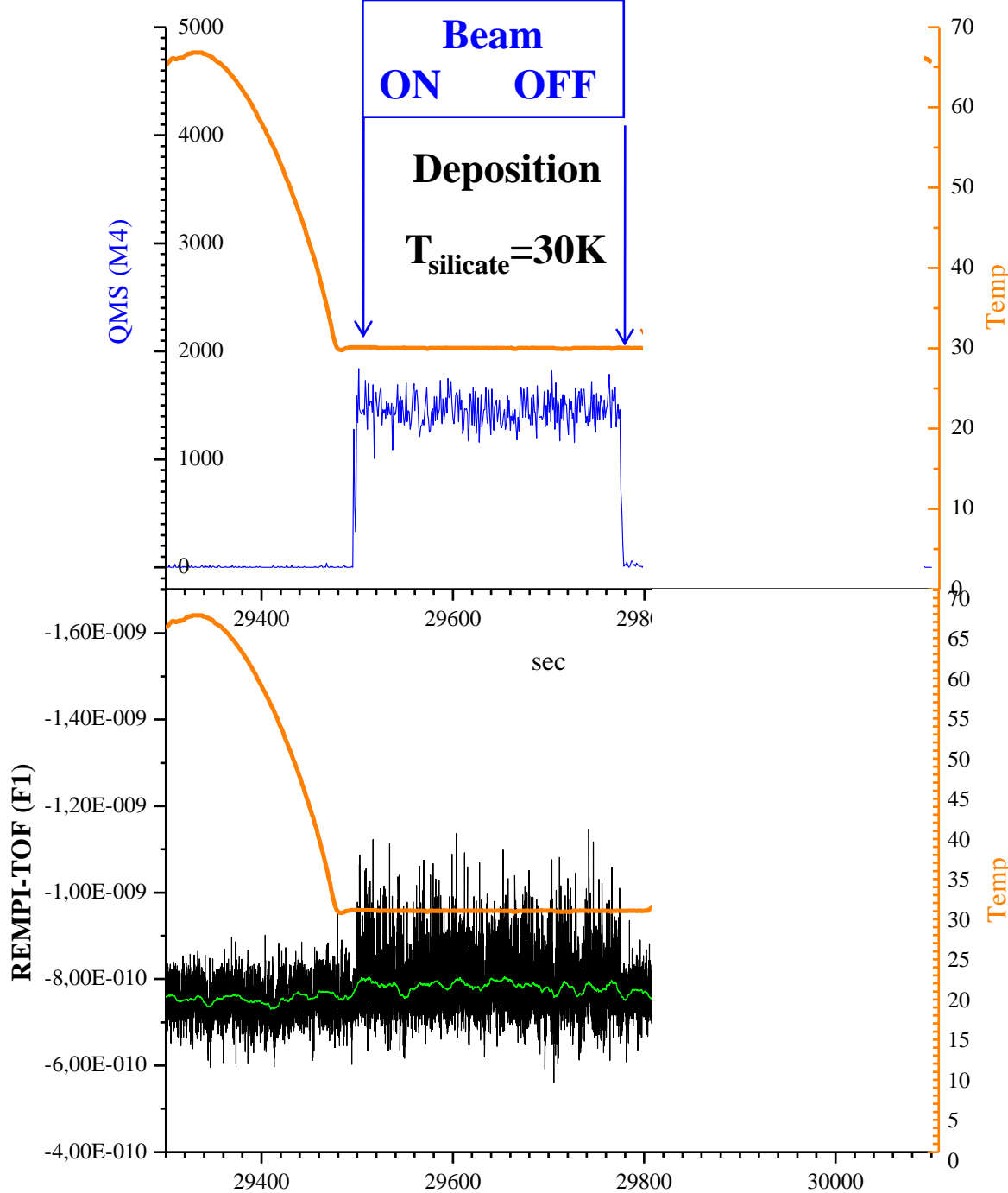


D+D₂ deposition (75% dissociation in the μ wave discharge)

D₂ stuck on the surface after formation is released during TPD in the $v''=0$ state
 → its formation energy transferred into the substrate



REMPI records the population of D₂ in its ground state in the $v''=4, J''=2$ rovibrationally excited quantum state

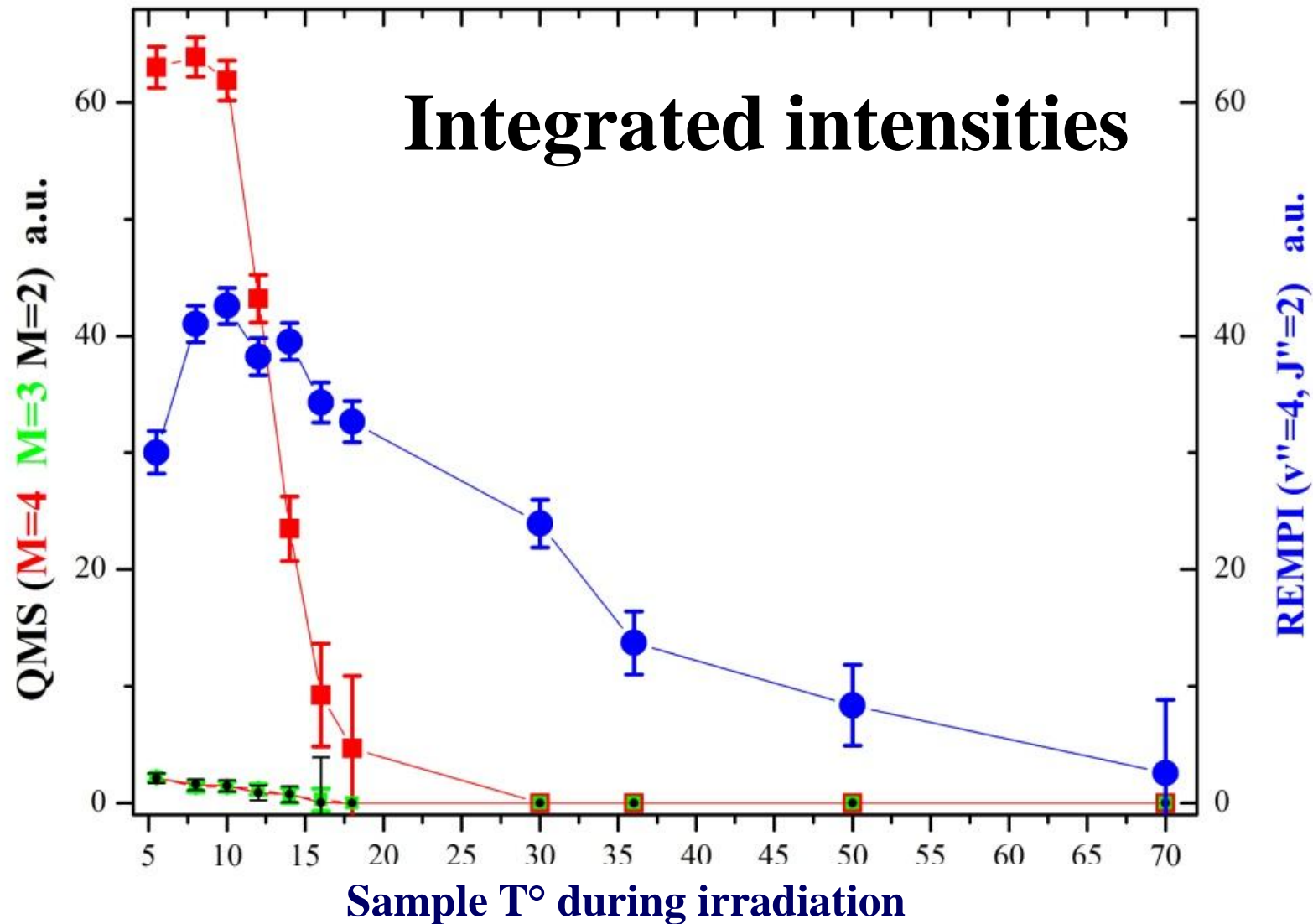


Same experiment
with $T_{\text{silicate}}=30\text{K}$

D_2 not stuck on the
surface after formation

still some formation
in the $v''=4, J''=2$
**rovibrationally excited
quantum state of D_2**

... and lastly
the same experiment
with $T_{\text{silicate}}=70\text{K}$
→ almost no signal



- REMPI (D_2) signal (during irradiation)

- QMS (D_2) TPD signal (after irradiation)

- The HD signal is due to exchange reactions on the sample and/or walls of the apparatus.

First conclusions

- Rovibrationally excited molecules are ejected into the gas phase immediately after formation over a **much wider range of grain temperature** than anticipated.
- Presence of **two mechanisms** of molecule formation that operate in partially overlapping ranges of grain temperature:
L-H restricted at low temperature while **H-K** spans a larger temperature range.
- At high temperature H-K more efficient than L-H: due to the rms distance an atom can travel compared to the distance between atoms on the surface
- Larger range of adsorption energies on an amorphous surface
- If microcrystalline: defects, steps ...
- About 30% of the molecules are formed in an excited state, 13.5% in $v''=4$ and 3.5% in $v''=4, J''=2$ (extrapolation based on the graphite study)

Prospects

These experiment and results open a vast field of research on bare silicates

- Our work has to be completed by a full range of v'' , J'' measurements
- Differences between crystalline and amorphous silicates
- Different silicate Mg,Fe composition

($\text{Mg}_x\text{Fe}_{(1-x)}\text{SiO}_3$, SiO_2 , SiC, Graphene, Silicene)

- H_2 formation on silicates

This work should also triggers a renewed interest to theoreticians:

- **Modelers of the dynamics** of infall of an interstellar cloud as well as to those working on **models of the chemical evolution** of a cloud, where the inclusion of **gas-surface processes** is recognized to be important.
- Modelers of the **atom/molecule interaction with silicate surfaces**

This work should also orientates astronomical observations:

Towards specific locations in the ISM or star forming region to look for pure H_2 formation emission lines in the J or H bands

Formation of molecular hydrogen on silicates in conditions pertinent to the interstellar medium

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G. Vidali**, J.L. Lemaire

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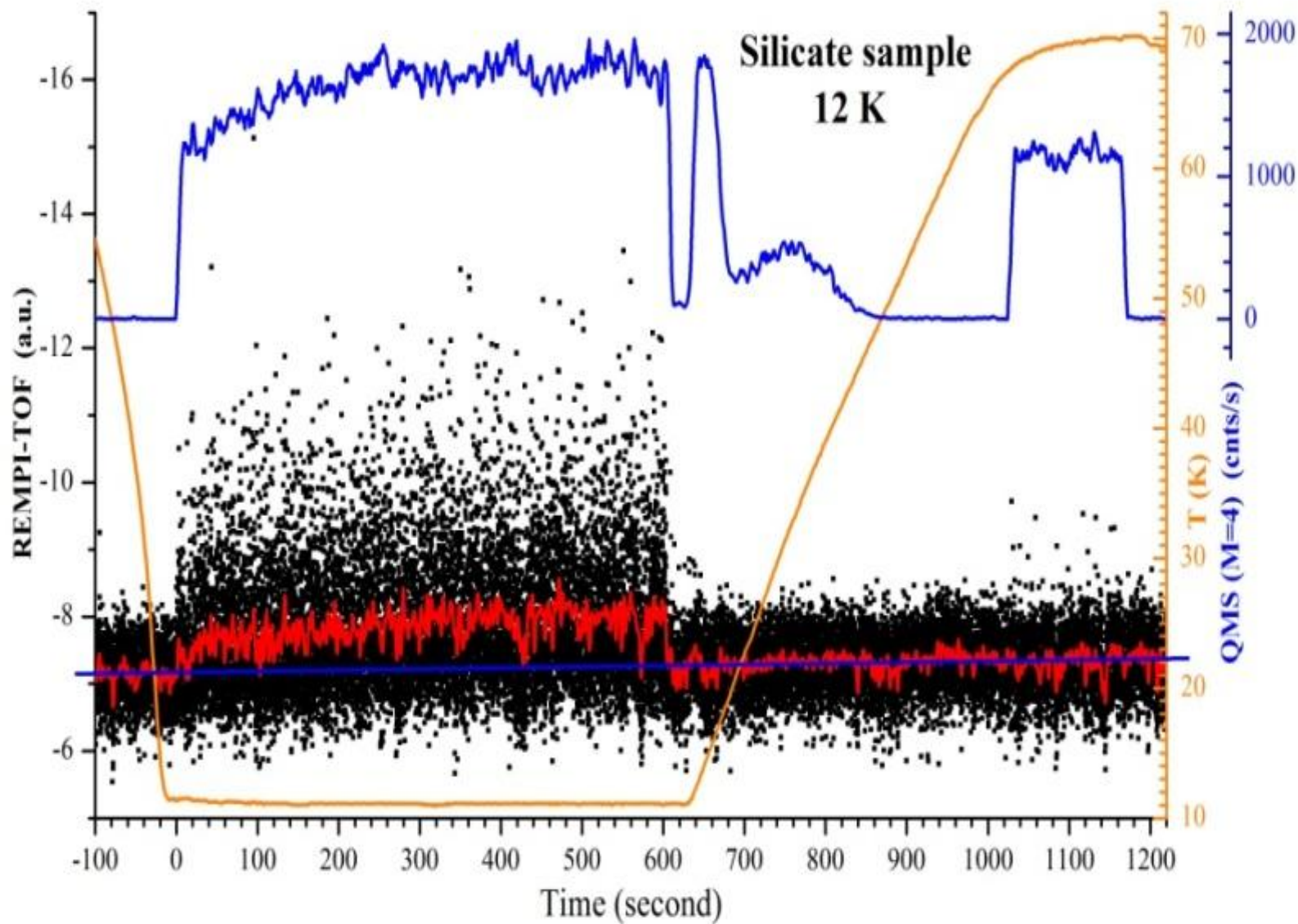
** Visiting Professor (Syracus University, NY)

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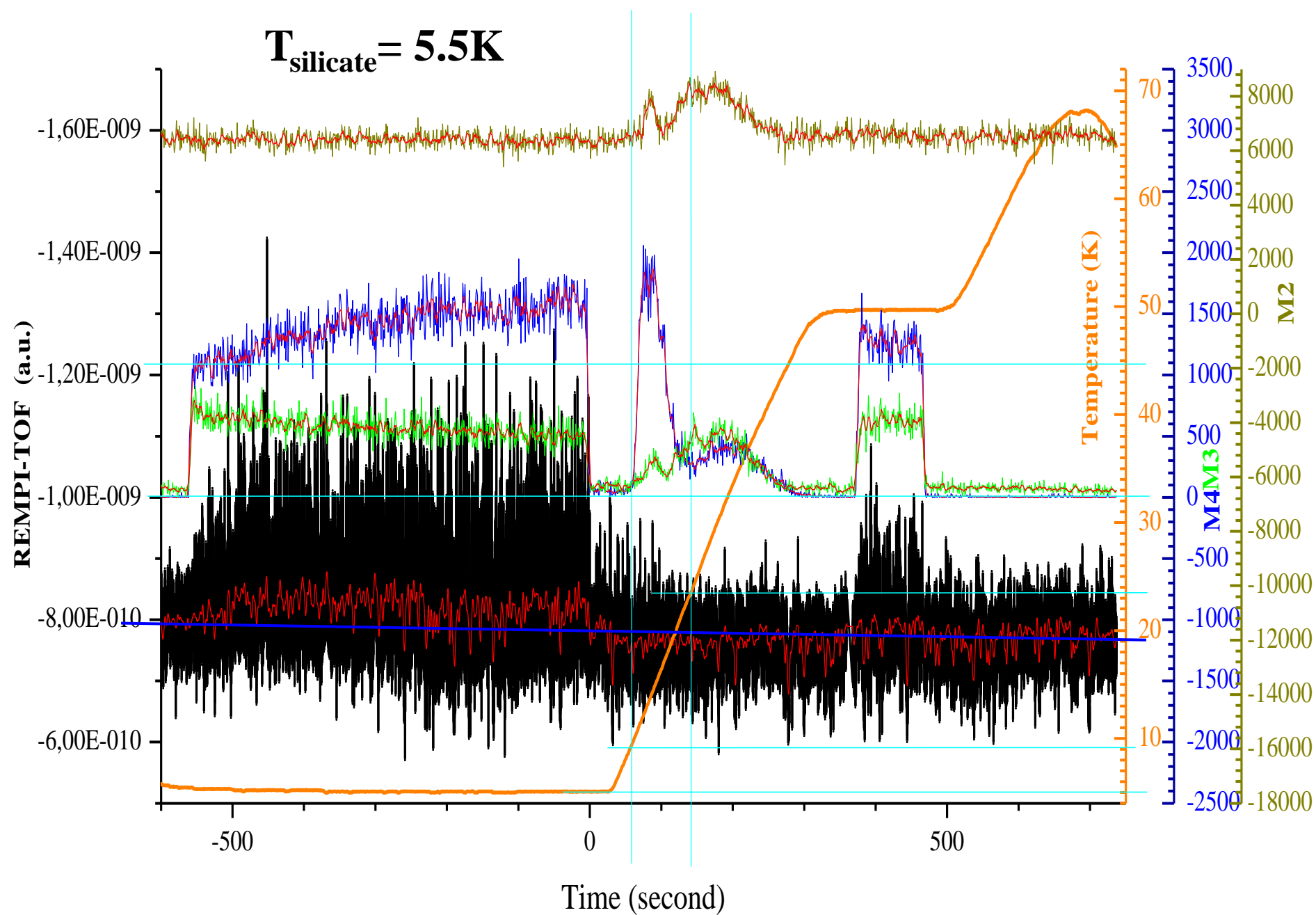
L. Gavilan (LASSIE ESR)



and thank you for your attention



$T_{\text{silicate}} = 5.5\text{K}$



COMPETING MECHANISMS OF MOLECULAR HYDROGEN FORMATION IN CONDITIONS
RELEVANT TO THE INTERSTELLAR MEDIUM

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ABSTRACT

The most efficient mechanism of the formation of molecular hydrogen in the current universe is by association of hydrogen atoms on the surface of interstellar dust grains. The details of the processes of its formation and release from the grain are of great importance in the physical and chemical evolution of the space environments where it takes place. The main puzzle is still the fate of the 4.5 eV released in H₂ formation and whether it goes into internal energy (rovibrational excitation), translational kinetic energy, or heating of the grain. The modality of the release of this energy affects the dynamics of the ISM and its evolution toward star formation. We present results of the detection of the rovibrational states of the just-formed H₂ as it leaves the surface of a silicate. We find that rovibrationally excited molecules are ejected into the gas phase immediately after formation over a much wider range of grain temperature than anticipated. Our results can be explained by the presence of two mechanisms of molecule formation that operate in partially overlapping ranges of grain temperature. A preliminary analysis of the relative importance of these two mechanisms is given. These unexpected findings, which will be complemented with experiments on the influence of factors such as silicate morphology, should be of great interest to the astrophysics and astrochemistry communities.

Key words: astrochemistry – ISM: H₂ formation – ISM: molecules – molecular processes

Reaction mechanisms

- **E-R** (*prompt mechanism*) → "hot" H_2

- **H-K** (*hot atom mechanism*) → "hot" H_2

- **L-H** → H_2 at surface temperature

