**EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH**
Proposal to the ISOLDE and Neutron Time-of-Flight Committee

# Hyperfine interactions in hydrogenated $TiO_2$ thin films and powders for photocatalytic reactions

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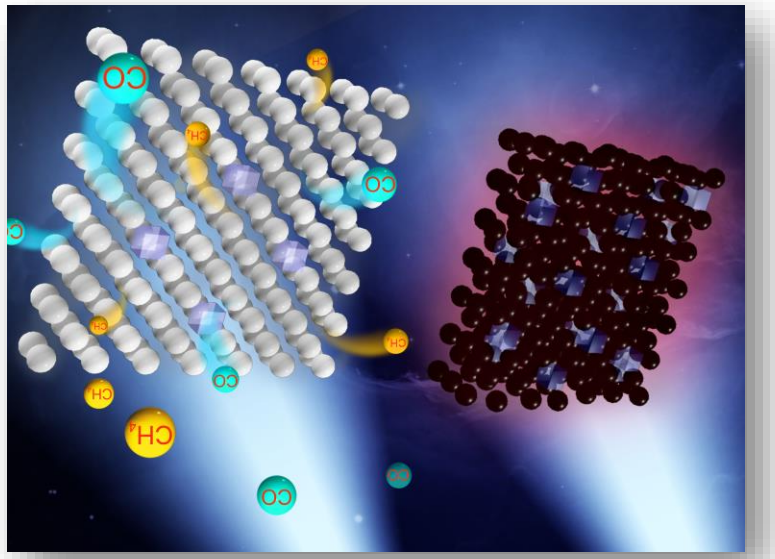
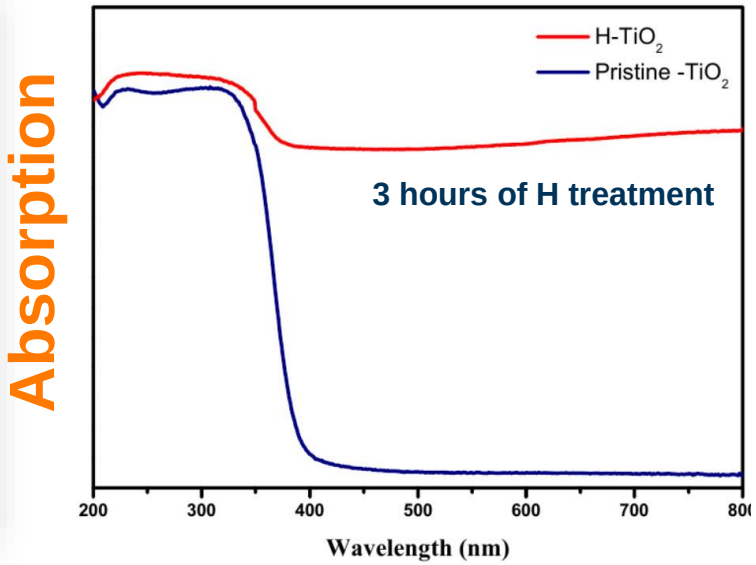
# Why study $TiO_2$:H?

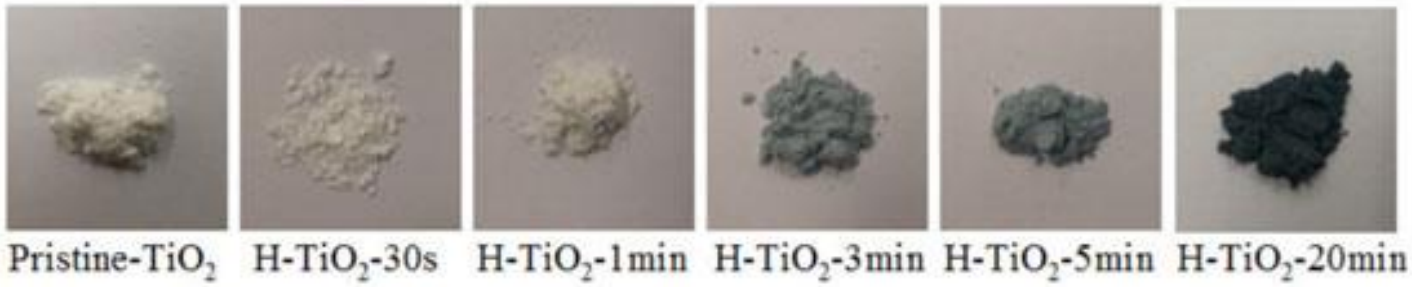
$TiO_2$+ $H_2$ Plasma → Black $TiO_2$

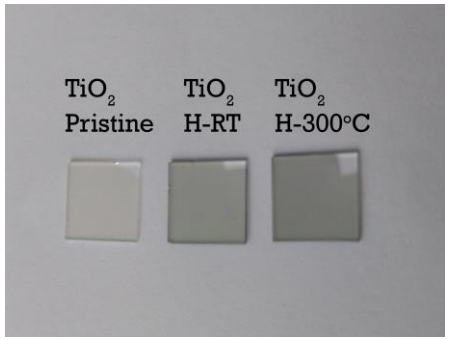





Lots of defects ($V_O$, $V_H$, Ti )

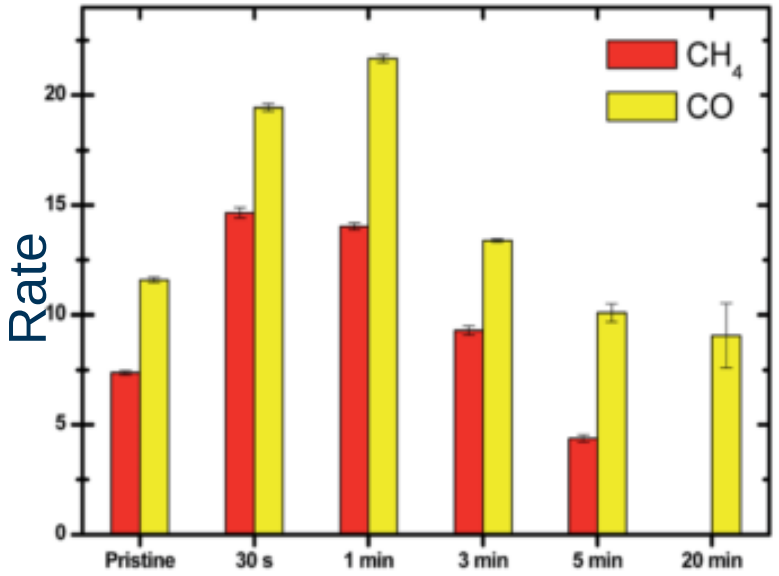
- Absorption improved
- More electron-hole pairs
- Better performance?



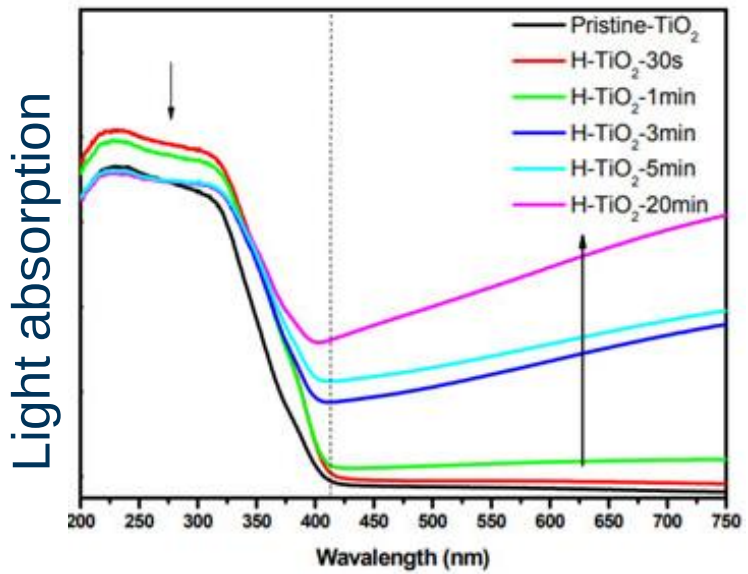
# Why study $TiO_2$:H?

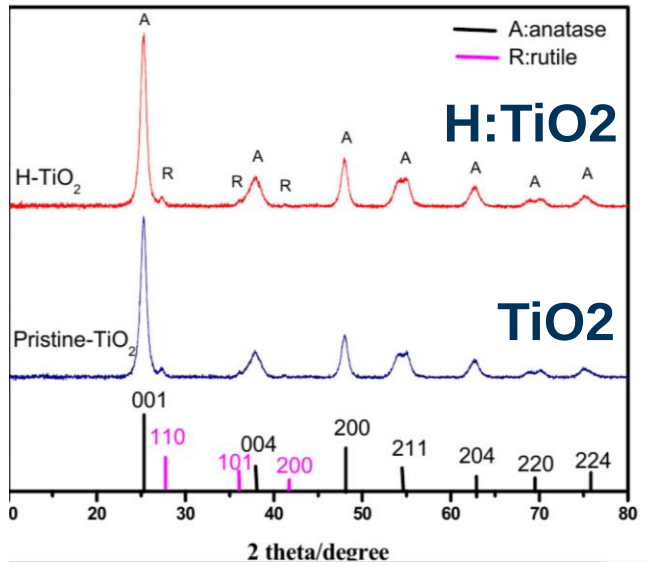
**Generation rates for methane and CO in the photocatalytic reduction of $CO_2$ with $H_2O$ through H-$TiO_2$: $H_2$**




## MILD PLASMA

- doesn't alter structure
- photocatalytic performance rates better
- defects (Ti2+,Ti3+ $V_O$, $V_H$)




$TiO_2$ → $H_2$ 30 sec → $H_2$ 1 min

# OBJECTIVES

Investigation of

- local defects induced with plasma in the nanostructured $TiO_2$ materials by PAC and eMS having a significant impact on the electron-hole recombination;
- dopants and $H_2$ interactions i.e. possibly leading to a “new” black $TiO_2$ ;
- charge transfer?
- defects evolution under various atmospheres and conditions.

# PAC SPECTROSCOPY at ISOLDE

- $^{111m}Cd$ is used in doping of $TiO_2$ and only at ISOLDE
- Experience and sufficient amount of setups
- Interactions of Cd with $V_H$, $V_O$ and Ti defects

**How?**

- + no after-effect

As a function of

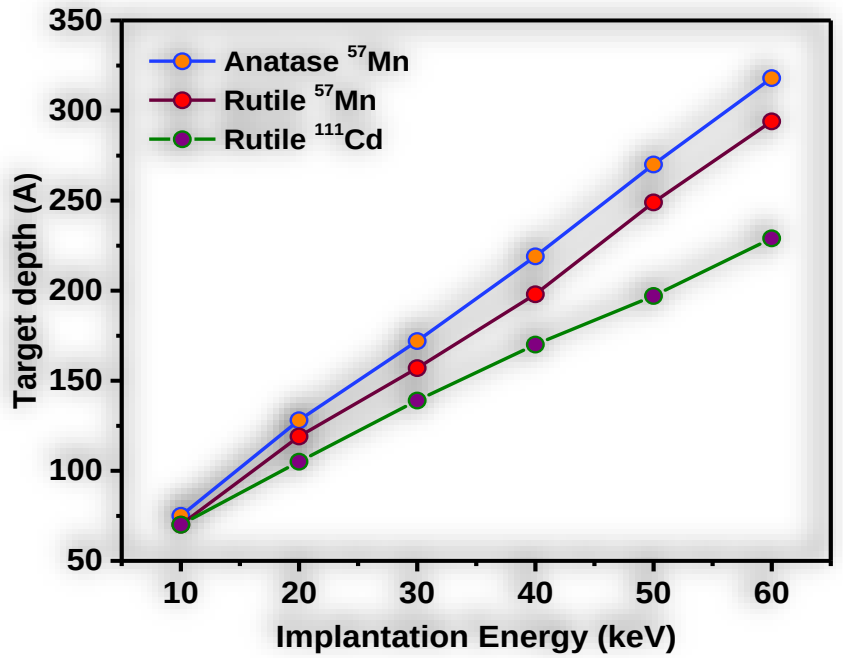
- sample **stoichiometry** with different amount of defects $H_2$ annealing and measuring **temperature** from **450-700 K**

Implantation depth at 30 keV is ~ **10-12 nm ($^{111m}Cd$ in $TiO_2$)**

# *Emission* MÖSSBAUER SPECTROSCOPY at ISOLDE

## Complement of the PAC study:

- Probe-host or probe-defect interaction
- Valence(/spin) state of probe atom ($X^{n+}$)
- In earlier work (2014)* Ti and Vo defects were probed




## HOW?

As a function of

- Sample **stoichiometry**
- Annealing and measuring **temperature**

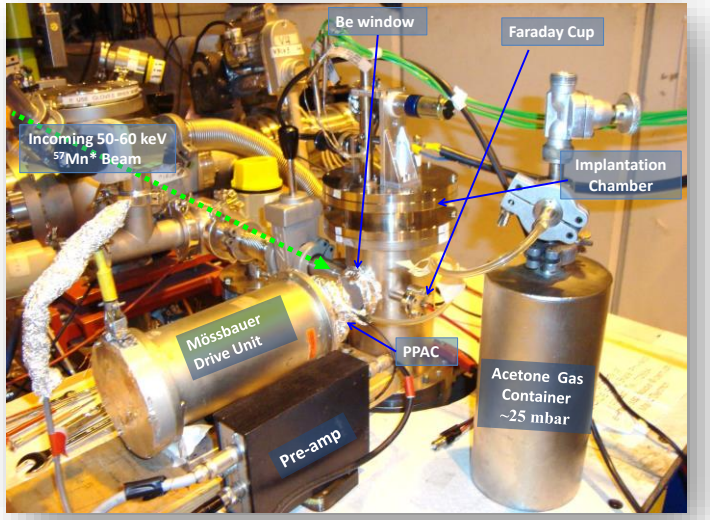
Implantation depth at 30 keV is ~ **11-16 nm ($^{57}$Mn in $TiO_2$)**

***Gunnlaugsson et al J. Phys. D: Appl.Phys.47 (2014)**

# The eMS setups

## The old setup:

- Limitations (such as temperatures, additional vibrations, long-sample-changing option)
- Complexity of extension for chemical experiments



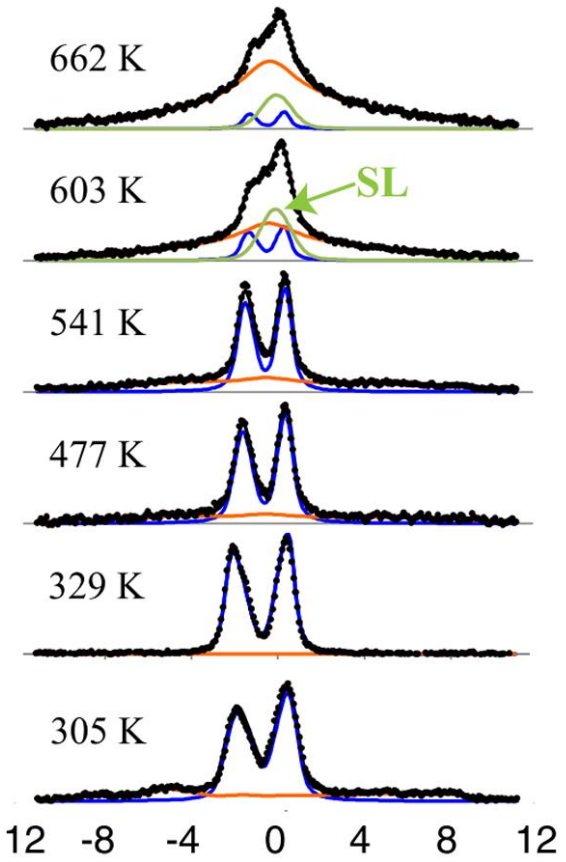

## The new setup:

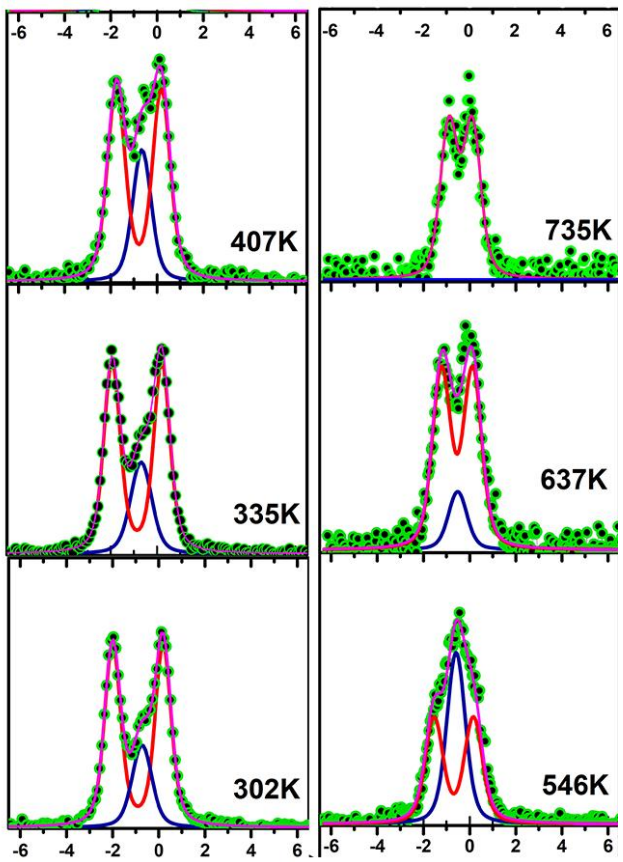
- UV irradiation (laser 365 nm, 3B class)
- Better vibration isolation
- Less pumping time
- Compact & easy to assemble for a run
- Precise T-control
- Compatible with old cryo, magnetic lids

# FEASIBILITY OF CURRENT PROPOSAL

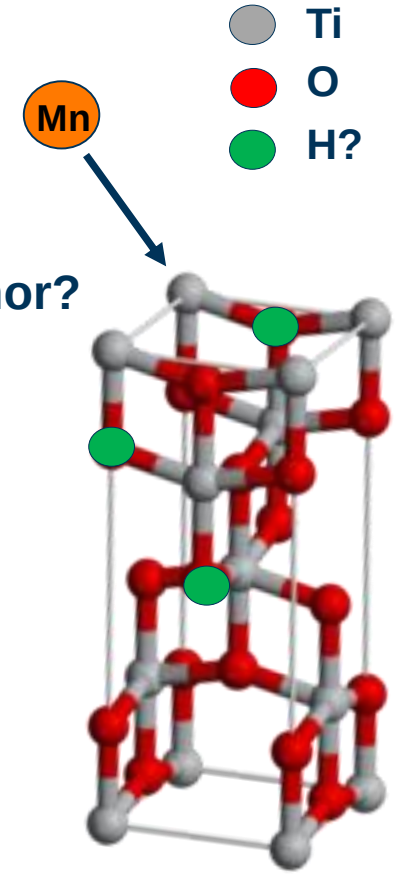
**Gunnlaugsson et al J. Phys. D: Appl.Phys.47 (2014)**

**eMS spectra of $TiO_2$ :H-RT TU Ilmenau/ISOLDE 2017**



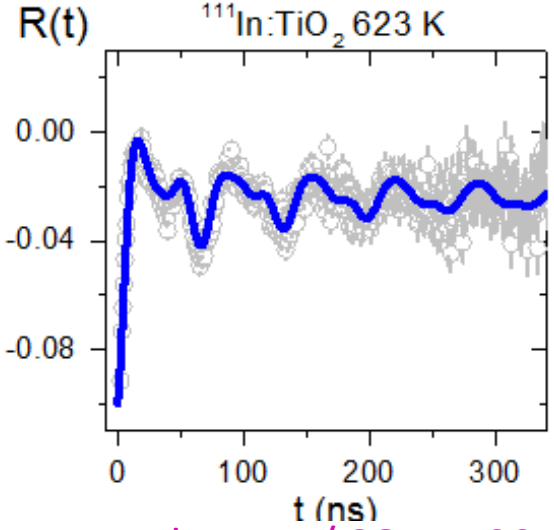




- **Fe $^{2+}$ S=0 or S=2 ?**
- **Fe $^{3+}$ ?**
- **Does H act as an electronic donor?**
- **Leading to a charge transfer?**
- **$Fe^{3+} + Ti^{3+} <-> Fe^{2+} + Ti^{4+?}$**



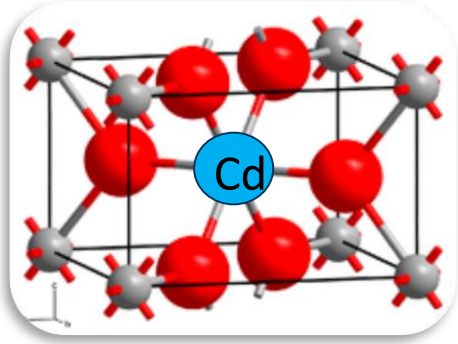
# $TiO_2$ pristine films (TDPAC)

Schell et al, JAP 121, 145302 (2017)

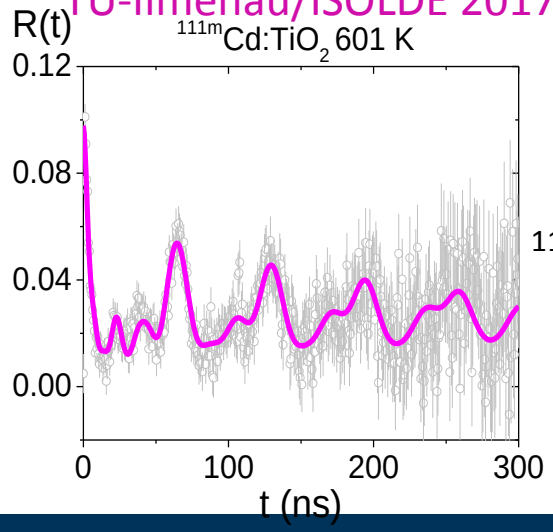



$^{111}$In($^{111}$Cd) in $TiO_2$

Rutile structure
$\omega_0$ ~**100 Mrad/s**
and $\eta$ ~**0.1**




TU-Ilmenau/ISOLDE 2017

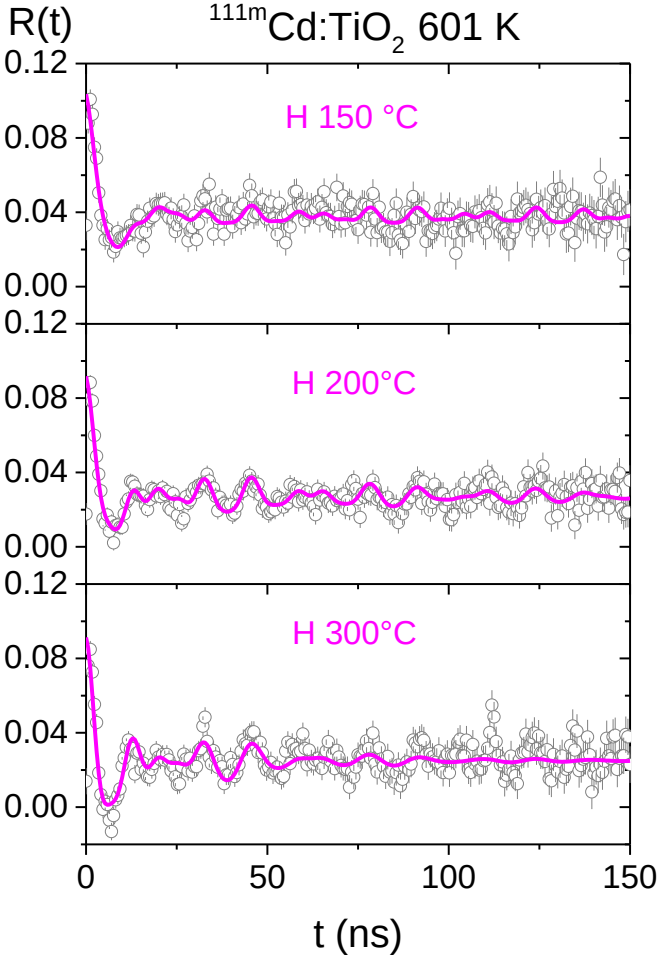


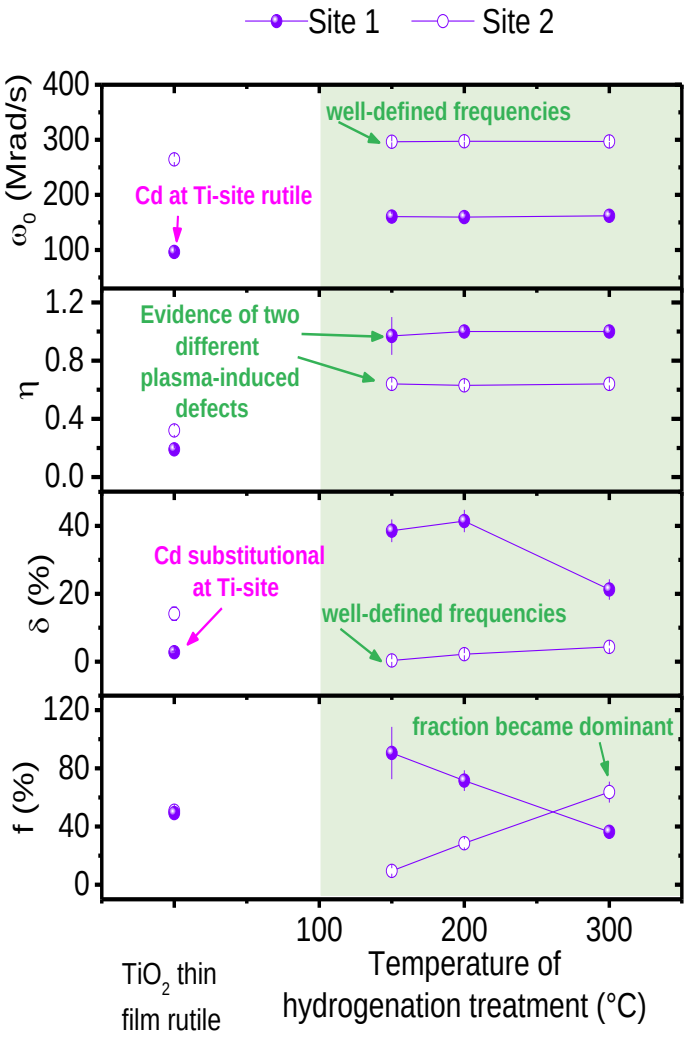

$^{111m}$Cd($^{111}$Cd) in $TiO:H_2$

Rutile structure
$\omega_0$ ~**100 Mrad/s**
and $\eta$ ~**0.2**

# $TiO_2$ hydrogenated films (TDPAC)

TU-Ilmenau/ISOLDE 2017



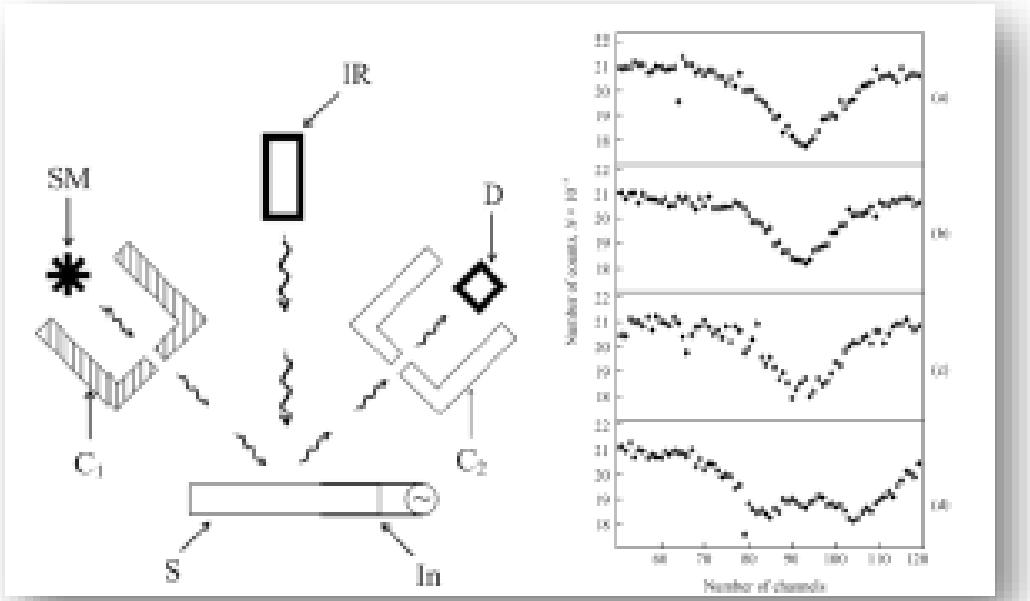

**Two local enviroments with static nuclear quadrupole interactions:**

**Site 1**: well-defined frequency for Cd at the Ti-site with distortion caused by the presence of H atoms (η ~**0.5**).

**Site 2:** major fraction at 150ºC and 200ºC

Hydrogenation treatment with high frequency distribution. Higher EFG asymmetry in respect to site 1 (η ~**1**).

# Mössbauer spectroscopy under light irradiation




**Sample:**
**CdS:57Fe(0.2%)**

A. H. Mkrtchyan, R. P. Vardapetyan, E. M. Harutyunyan, A. V Khachatryan, V. V Nalbandyan, and H. R. Muradyan, “Modification of Mössbauer Reflection Spectra of Group AIIBVI Single Crystals with Fe 57 Nuclei under Influence of Infrared Radiation,” J. Contemp. Phys., vol. 44, no. 4, pp. 194–196, 2009.

# BEAM TIME REQUEST

| Perturbed Angular Correlations Studies | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Required isotope** | **Implanted beam** | **Probe element** | **Type of experiment** | **Intensity [at/μC]** | **Target / Ion source** | **Atoms per sample** | **№ of shifts** |
| **$^{111m}$Cd (48 min)** | $^{111m}$Cd | $^{111}$Cd | γ-γ PAC | $10^8$ | Molten Sn; plasma | $2x10^{10}$ | 3 |
| **Mössbauer studies** | | | | | | | |
| **$^{57}$Mn (1.5 min) + TESTING of eMS** | $^{57}$Mn | $^{57}$Fe | eMS | $2 \times 10^8$ | UCx, RILIS (Mn) | $1x10^{12}$ | 2 + 2 |

# FUNDING INVOLVED

**BMBF**
Bundesministerium für Bildung und Forschung

Erforschung kondensierter Materie mit Großgeräten
Ausbau und Unterhalt der Einrichtungen an ISOLDE/CERN
Germany, contract: 5K16SI1

# Thank you for your attention!

# Additional information TDPAC

**Similar frequency value (257 Mrad/s) in respect to the well-defined frequencies obtained with H:$TiO_2$ (300 Mrad/s),** but since it had no H and the sample was a single crystal, it presents lower EFG asymmetry:

$^{111m}$Cd:$TiO_2$ Syngle Crystal

$\omega_0$ ~**257 Mrad/s**

and η ~**0**

**Schell et al, Hyp. Int. (2017) 238:2.**

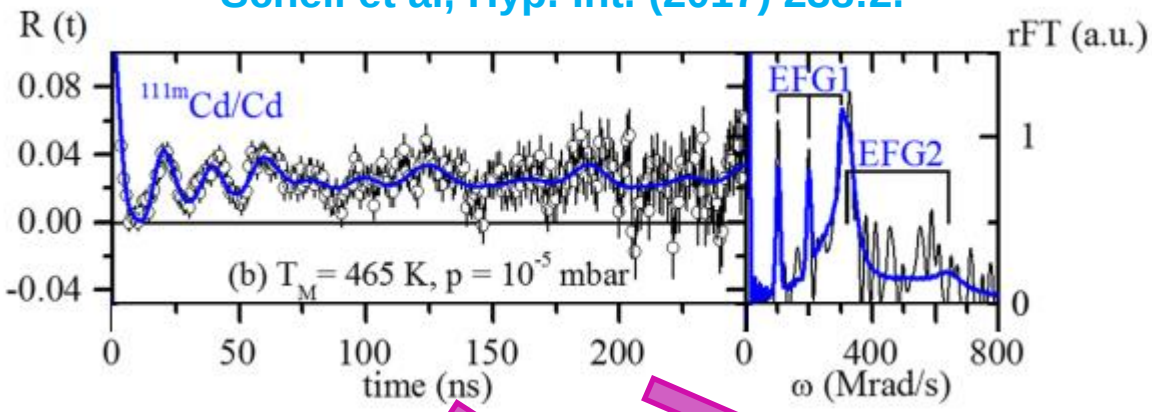



**Fig. 1** Experimental $\gamma - \gamma$ R(t) perturbation functions obtained for $^{111m}$Cd/Cd at 295 K (**a**) and at 465 K (b) and $^{111}$In/Cd (c) PAC probes on $TiO_2$. Additionally, their real part of the R(t) Fourier transform. Measurement temperature and pressure are quoted on each spectrum. Spectra (b) and (c) belong to the sample that were implanted with $^{111m}$Cd and $^{111}$In simultaneously

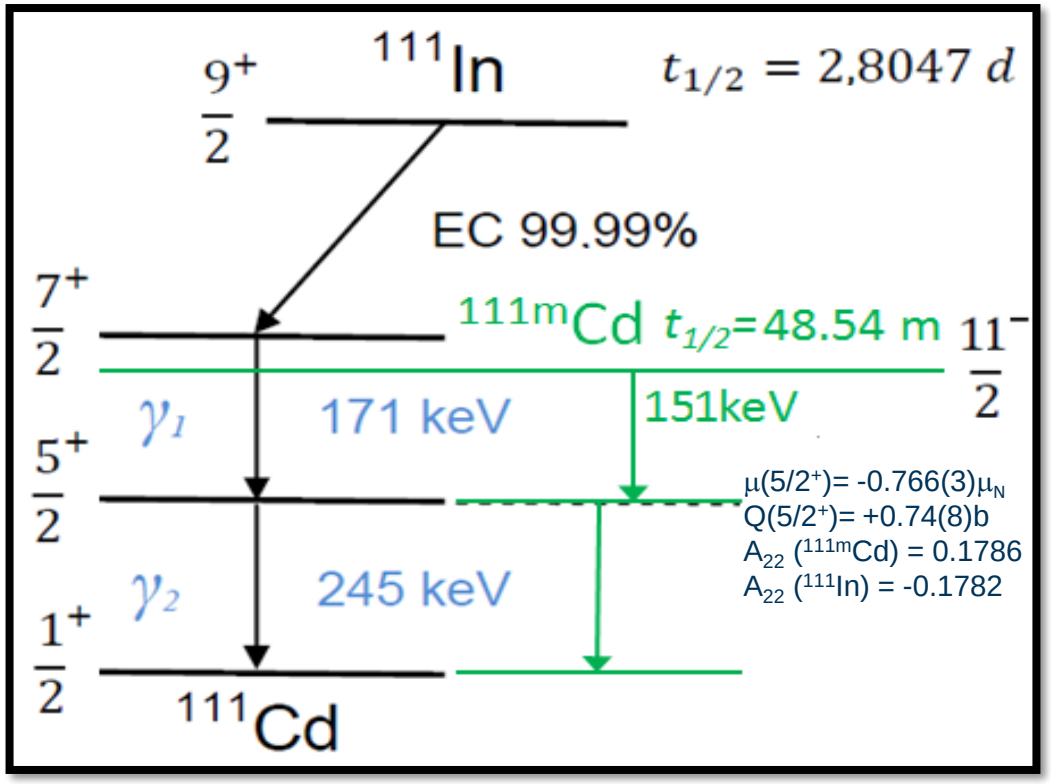
**Table 1** Hyperfine fitting parameters of PAC experiments performed in $TiO_2$ single crystals

| Spectrum | | $T_M(K)$ | EFG | $w_0$(Mrad/s) | η | σ (Mrad/s) | Fraction (%) |
|---|---|---|---|---|---|---|---|
| implanted $^{111m}$Cd/Cd | The *missing / attenuated* fractions $f_d$ could still be interpreted as due to the remains of unrecovered distributions of defects, which do not establish well defined configurations with the Cd probing atoms. | | | | | | |
| | | | *a* | *253(8)* | *0* | *117(10)* | *78(6)* |
| implanted $^{111m}$Cd/Cd + $^{111}$In/Cd | b | 465 | 1 | 100.0(7) | 0.15(2) | 0.0(1) | 12(2) |
| | | | 2 | 182(2) | 0.99(3) | 15(2) | 42(3) |
| | | | *d* | *257(14)* | *0* | *68(16)* | *48(5)* |
| | c | 295 | 1 | 99.01(16) | 0.175(12) | 0(1) | 70 |
| | | | *d* | – | – | – | *30* |

Cd can attract the vacancies according to partial pressure. The *missing / attenuated* fractions are likely due to multiple attracted vacancies (or charging / discharging vacancies) that alter the environment.

# Additional information TDPAC

## $^{111m}Cd(^{111}Cd)$



# Additional information eMS

## $^{57}Mn/^{57}Fe$