Topics in Evanescent Wave Cavity Ring-down Spectroscopy (EW-CRDS)

Andrew C. R. Pipino
Applied Physics Department
Equilibrium and Transport in Plasmas (ETP) Group
Eindhoven University of Technology (TU/e)
5600 MB Eindhoven
The Netherlands

Topics in Evanescent Wave Cavity Ring-down Spectroscopy (EW-CRDS)

Outline

1. EW-CRDS preliminaries
2. Monolithic Optical Resonators for EW-CRDS

   a. Total-internal-reflection (TIR)-ring resonator

   b. Monolithic folded resonator
3. Recent results on H-atom interactions in a-Si

Relevant to a-Si solar cells (Staebler-Wronski effect)

Motivation

To extend CRDS to thin films, interfaces, nano-materials

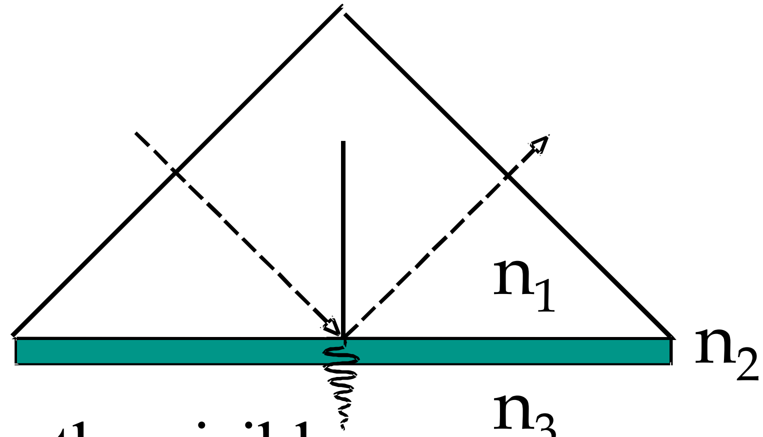
> Use evanescent waves – ideally suited probe

> Maintain sensitivity compared to gas-phase CRDS

> Permit polarization-dependent measurements

To enable unique measurements - otherwise unachievable.

Evanescent waves: Properties & Advantages



R=1 in principle for TIR for $\Theta_i > \Theta_c$

In practice, limited by surface scattering.

R~0.999999 for RMS roughness ~0.05 nm in the visible.

Broad bandwidth (n_1 changes slowly with wavelength).

Surface selective:

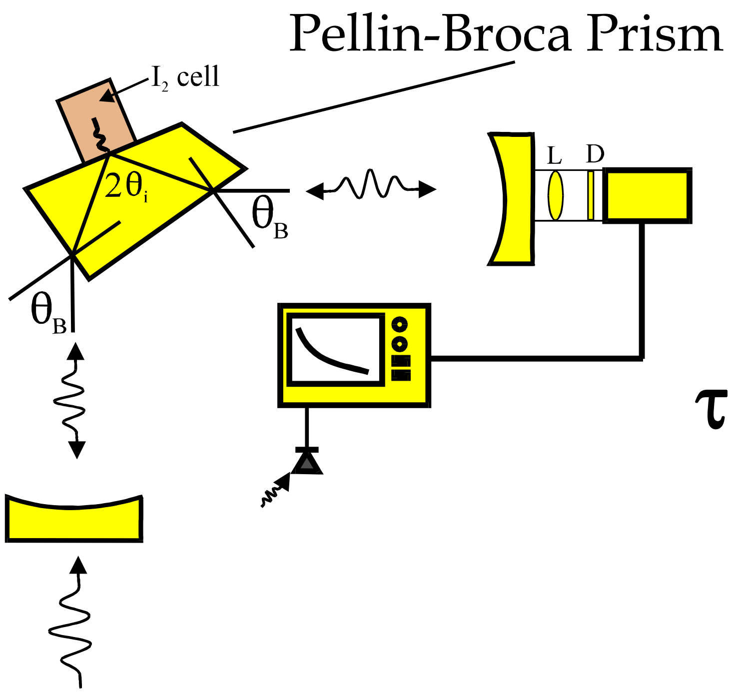
Locally enhanced surface E-field

Surface E-field direction easily controlled

E-field components in all directions: (x, y, z)

Nano-length scale ($d_p \sim \lambda$); Reduces bulk signal

Early EW-CRDS Prototype



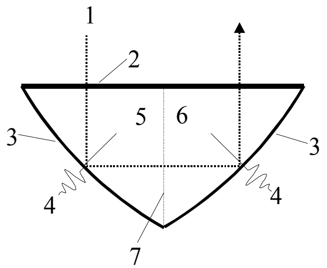
$$\tau = \frac{t_r}{L_{mirrors} + L_{bulk} + L_{surf} + L_{pol} + L_{ads}}$$

Adsorbed I_2 detection limit ~4% of a monolayer estimated

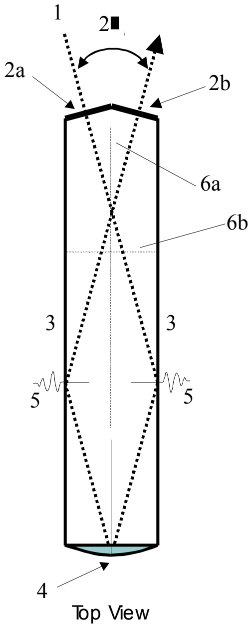
Only P-polarization is resonant; S-information is lost

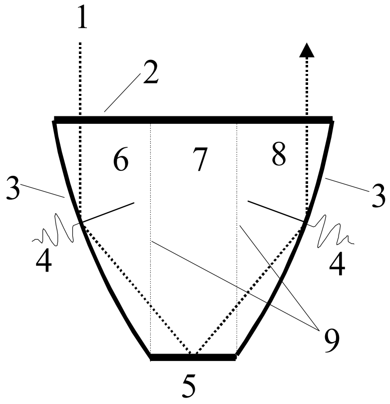
Large losses for P-polarization: Total loss >5000 ppm!

Monolithic Resonators



1. Eliminate intra-cavity interfaces.
2. Small size ~ 1-3 cm^3 for small bulk loss.
3. Relatively easy to use *in-situ*.



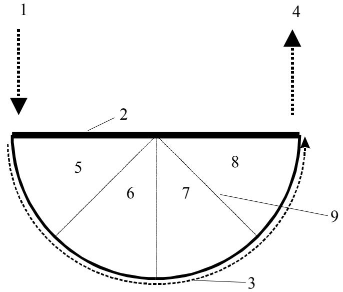


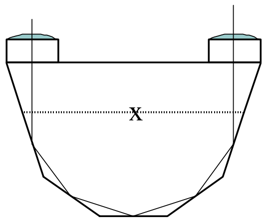
Choose optimal design:

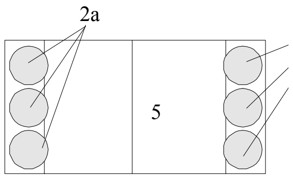
Broadband, narrowband, or multi-region

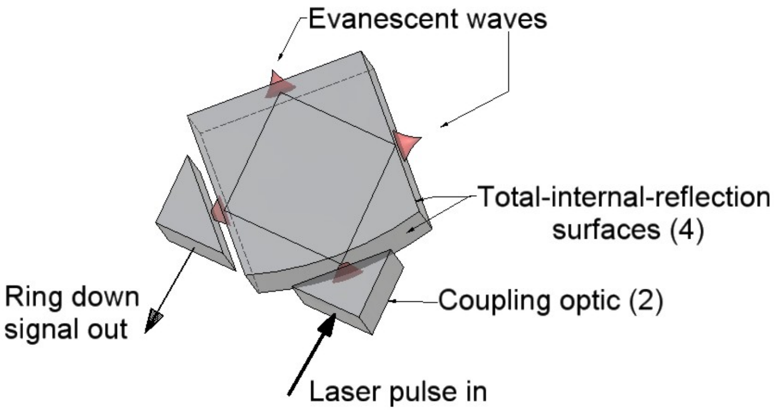
Choose Θ_i : Thin films or Liquids

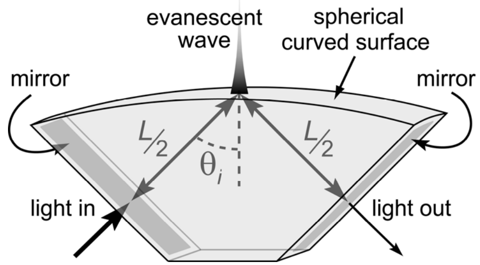
Minimize Loss - Maximize Sensitivity

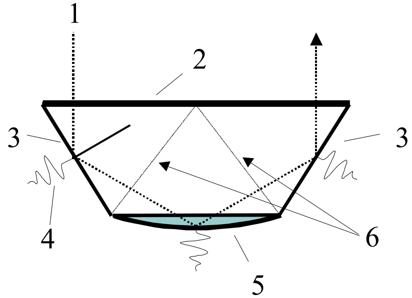






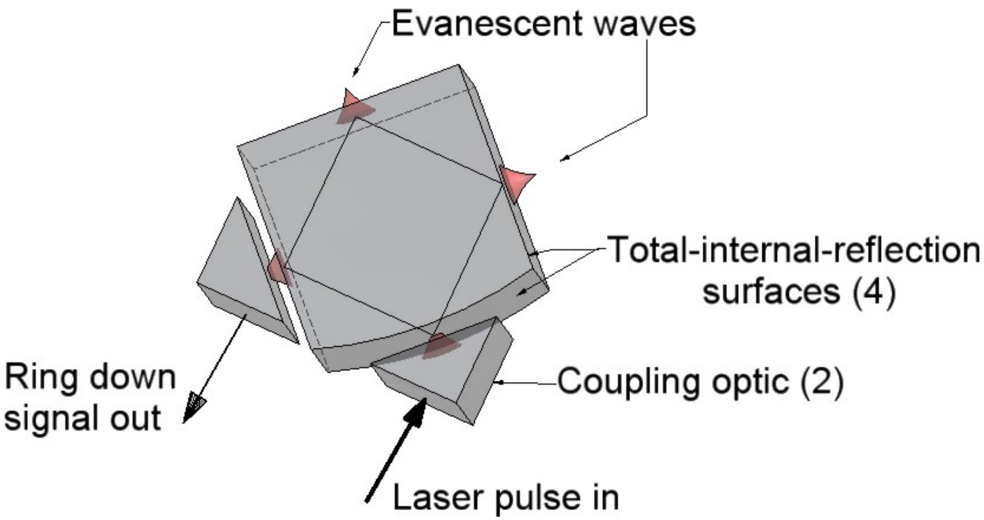


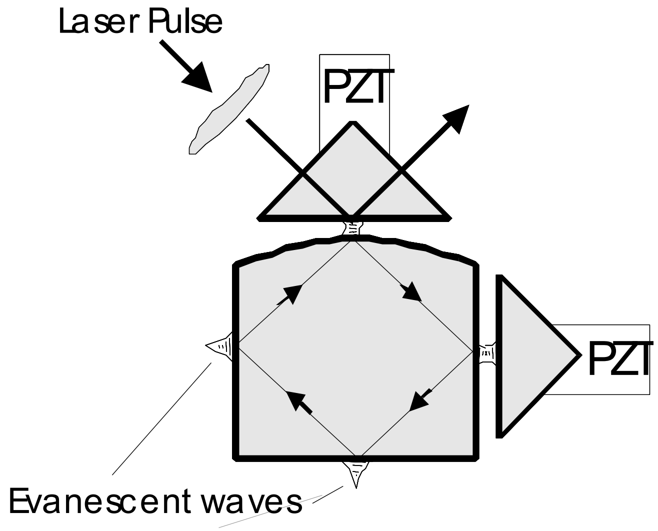




Cost ~ A few flashlamp replacements (~2K Euros/optic)

Monolithic TIR-ring Resonator





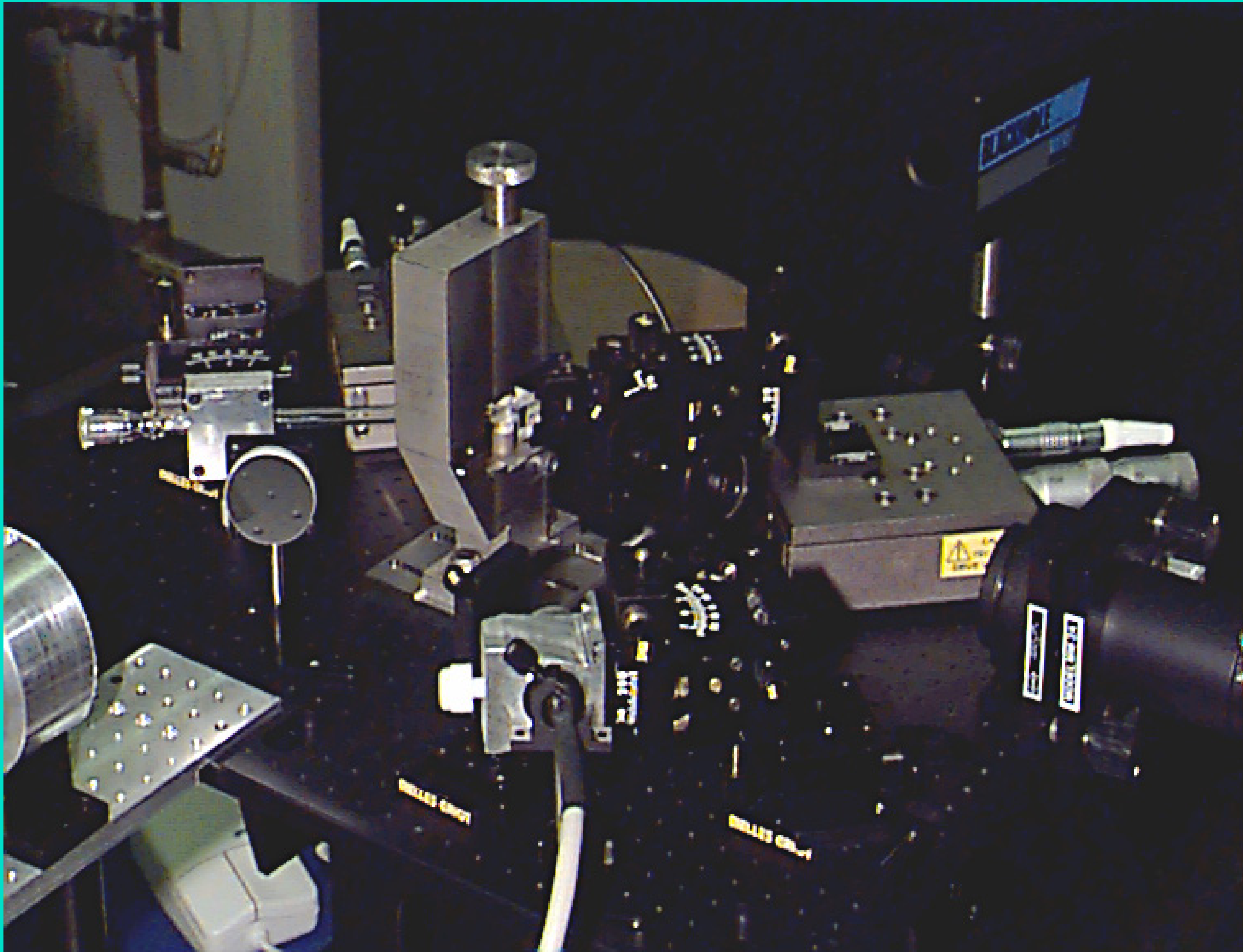
All TIR gives broad bandwidth.

Convex facet imparts stability.

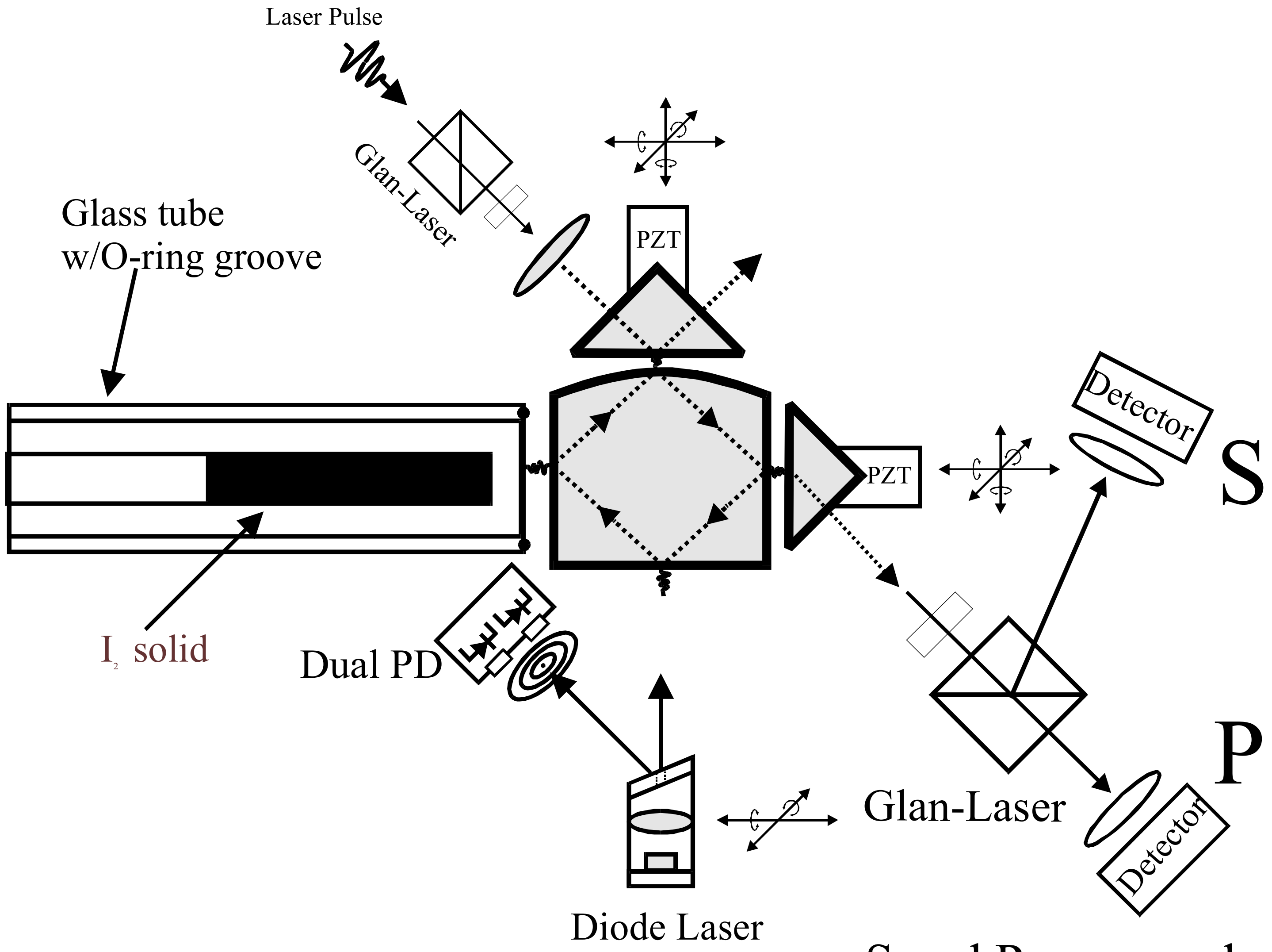
Input/Output coupling by photon tunneling.

Material - selected fused silica: Loss ~

200 ppm/cm	450 nm
50 ppm/cm	550 nm
7 ppm/cm	1400 nm
3 ppm/cm	1200 nm&1600 nm
1 ppm/cm	1550 nm



TIR-ring resonator: Experimental details

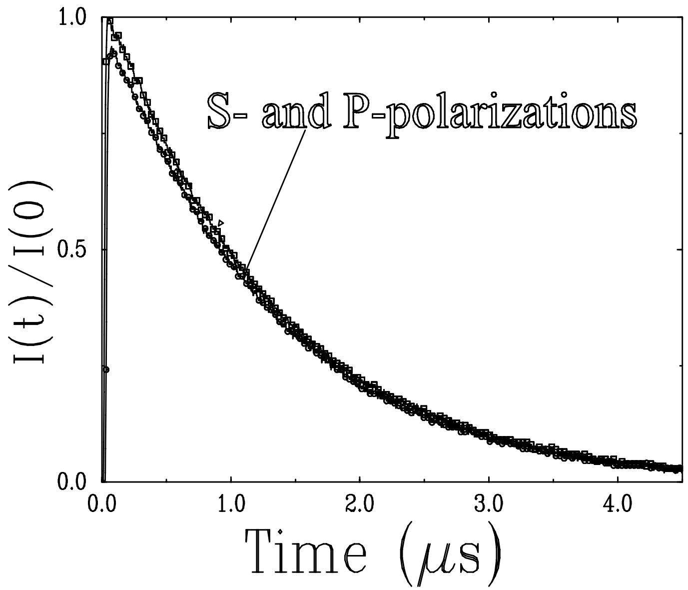


S and P measured simultaneously

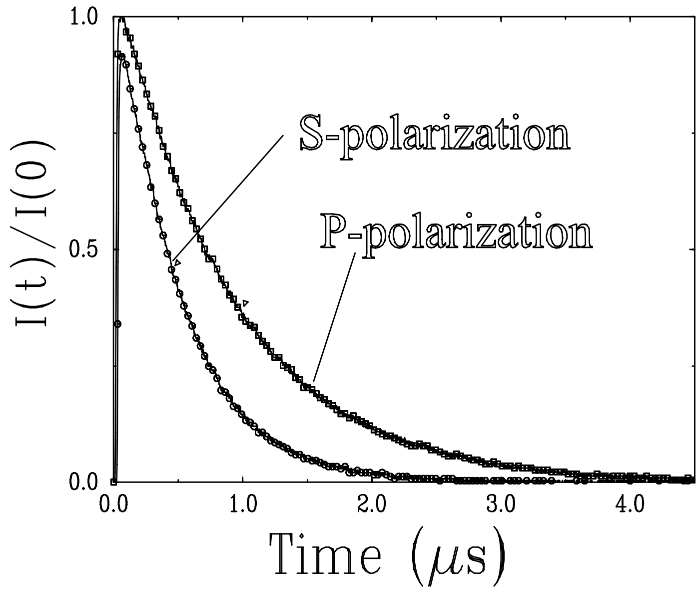
Extinction Ratio ~10^{-5}

Molecular Orientation Measurement

Before I_2 adsorption



After I_2 adsorption

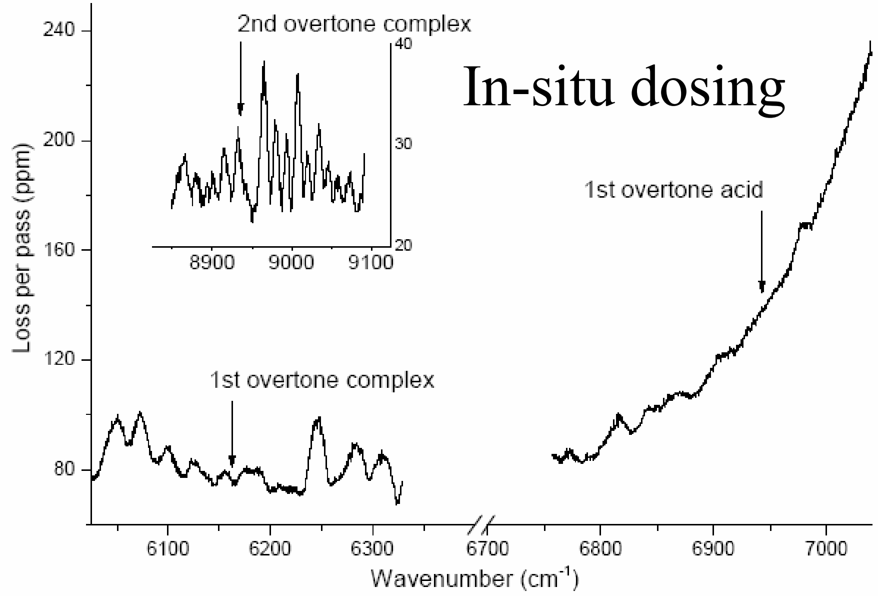


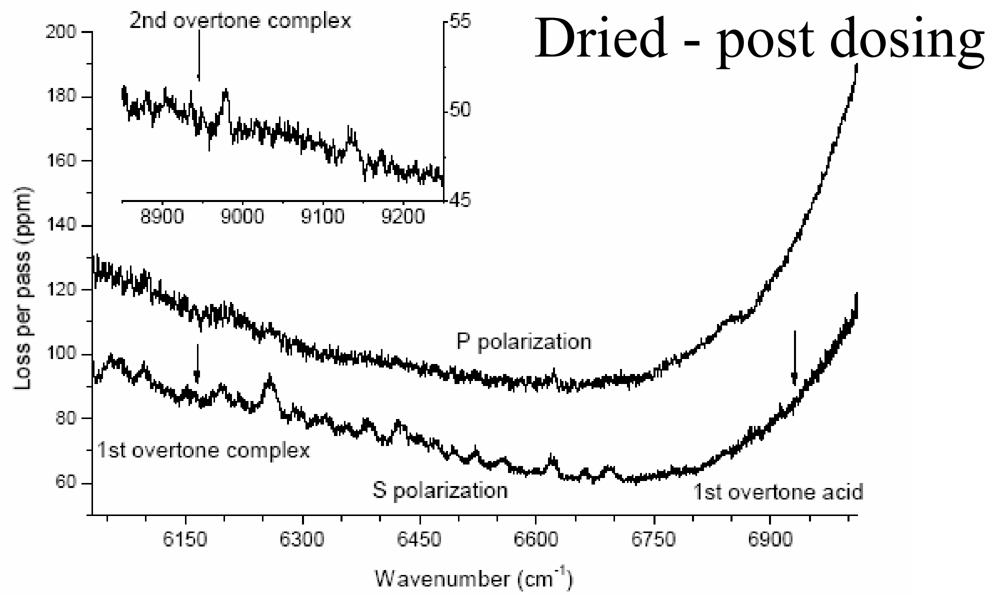
Large difference in Loss for S- vs P-polarization.

E-field: $\mathbf{I_z}$~ 7 (normal to surface) $\mathbf{I_y}$~ 4 and $\mathbf{I_x}$~ 0.2 (in-plane)

Results indicate I_2 molecules lay flat on average.

Overtones of adsorbed HNO_3





> 2vOH and 3vOH regions for HNO_3 adsorbed on SiO_2

> Demonstrates ~1000 cm^{-1} of bandwidth in the near IR.

> Tunneling gap-width held constant.

> A predominance of HNO_3:H_2O complex is observed.

Evaluating the Detection Limit for EW-CRDS

$$MDA = L_0(\Delta\tau/\tau) = \Gamma_y \mathbf{N_s} \sigma_s(\omega) \sec(\theta_i)$$

Γ_y = effective field enhancement (Need Θ_{avg})

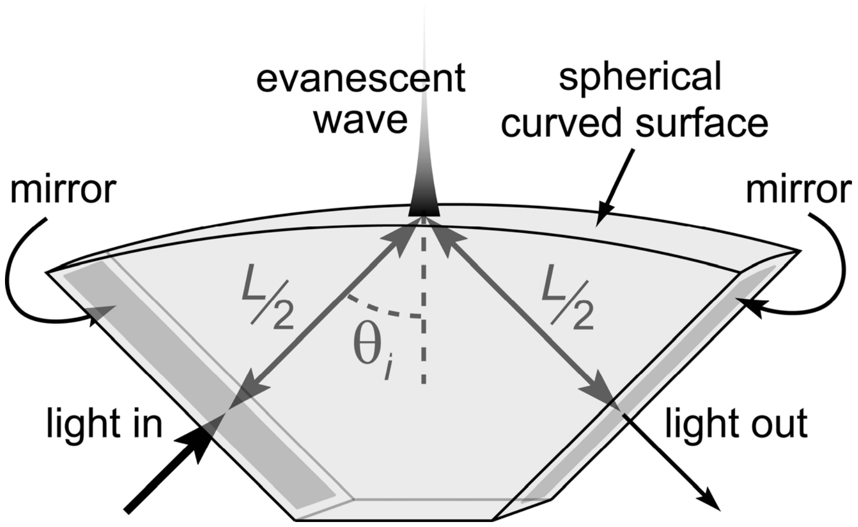
$\sigma_s(\omega)$ = surface cross section

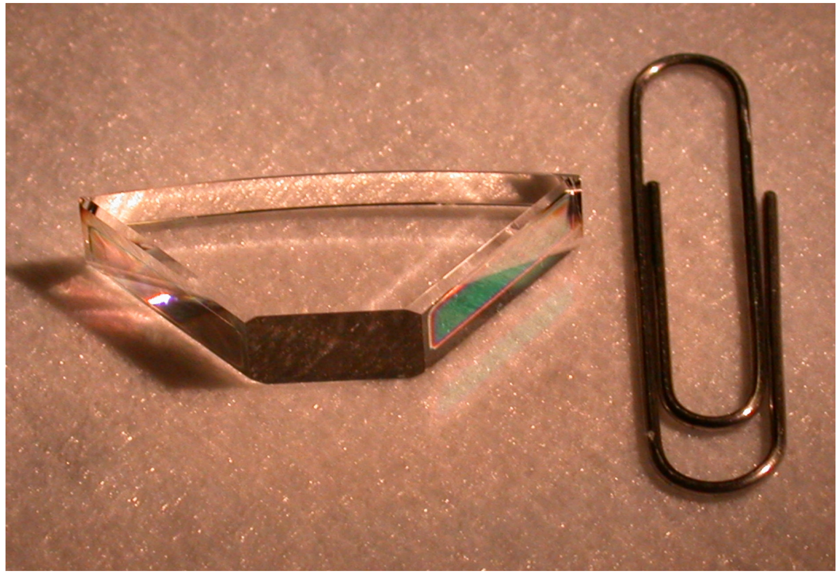
N_s = surface density

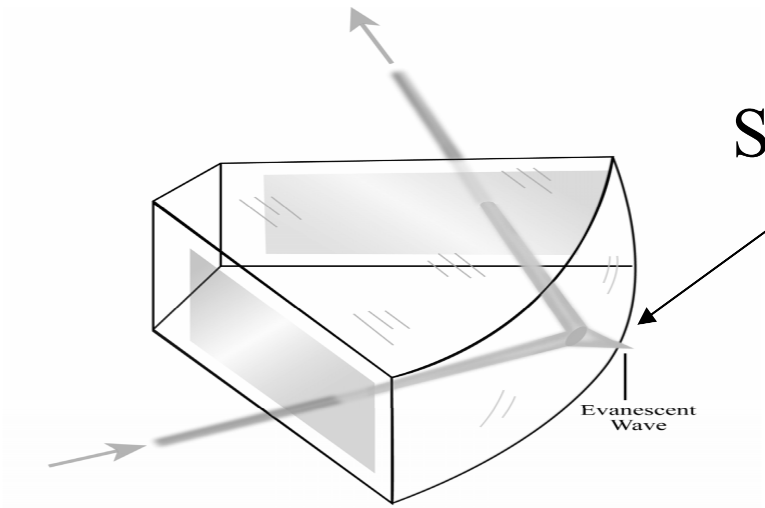
θ_i = angle of incidence

		$(\mathbf{N_s})_{min}$	$(\text{Coverage})_{min}$
I_2:	$\sigma_s(\omega) \sim 10^{-18}\ \text{cm}^2 \Rightarrow$	$N_s \sim 10^{10}/\text{cm}^2$	or 60 ppm ML
Dye:	$\sigma_s(\omega) \sim 10^{-16}\ \text{cm}^2 \Rightarrow$	$N_s \sim 10^{8}/\text{cm}^2$	or <1ppm ML
3vOH:	$\sigma_s(\omega) \sim 10^{-22}\ \text{cm}^2 \Rightarrow$	$N_s \sim 10^{13}/\text{cm}^2$	or 1% ML

Monolithic Folded Resonator







Sample area at apex: 85x99 μm

Center Wavelength = 1205 nm

Base loss = 18 ppm/pass (coating limited)

Bulk loss < 5 ppm (L/2 =2 cm)

MDA= $3x10^{-8}$ 5.3 μs ring-down time

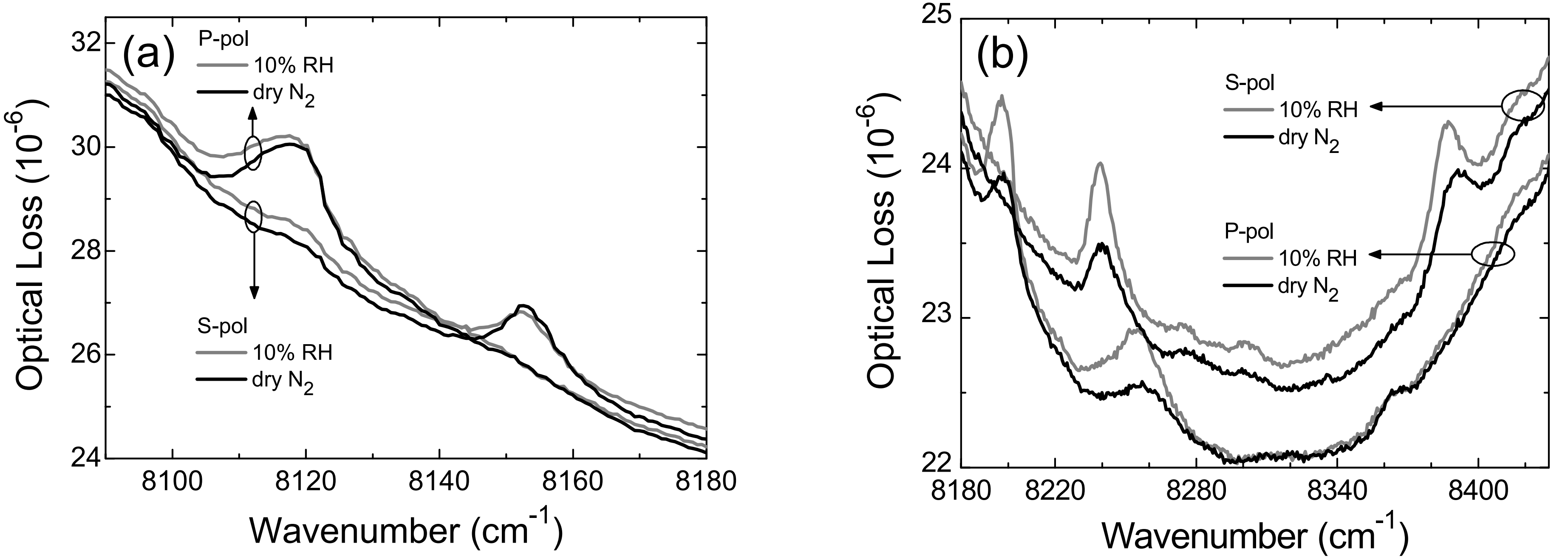
Applications of the Folded Resonator

1. Spectroscopy of the intrinsic surface OH groups and H_2O adlayer.

2. Absolute surface coverage measurement using the C-H stretching overtone.

3. Kinetics of “dangling bond” defect creation and healing in a-Si.

Spectroscopy of Atomically Smooth SiO_2



Left: $2\nu OH + \delta OH$ modes of SiOH Right: $2\nu OH + \delta OH$ modes of adsorbed H_2O

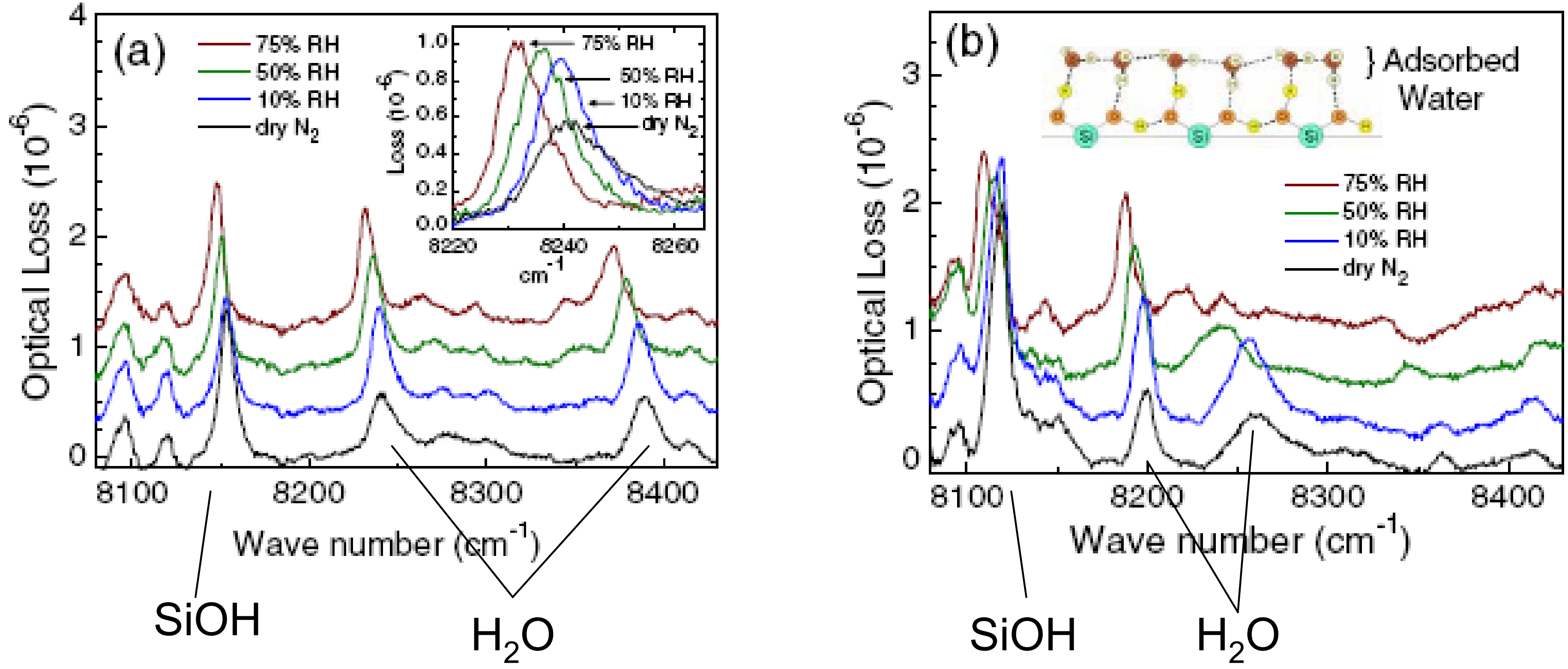
> Highly polarized and relatively sharp features

> Black plots: Under dry N_2 for several weeks.

> Grey plots: Under 10% Relative Humidity

A three-quantum process: 2 stretching quanta + 1quantum bending excitation

The H_2O peaks saturate…

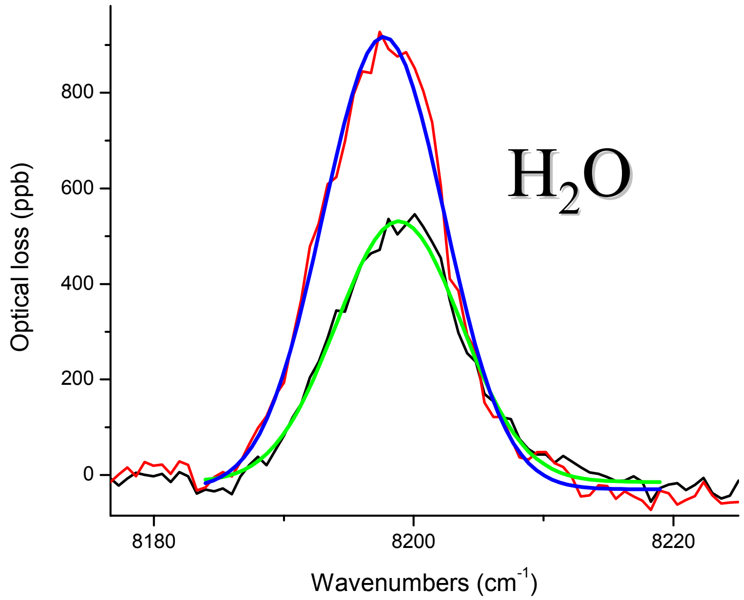


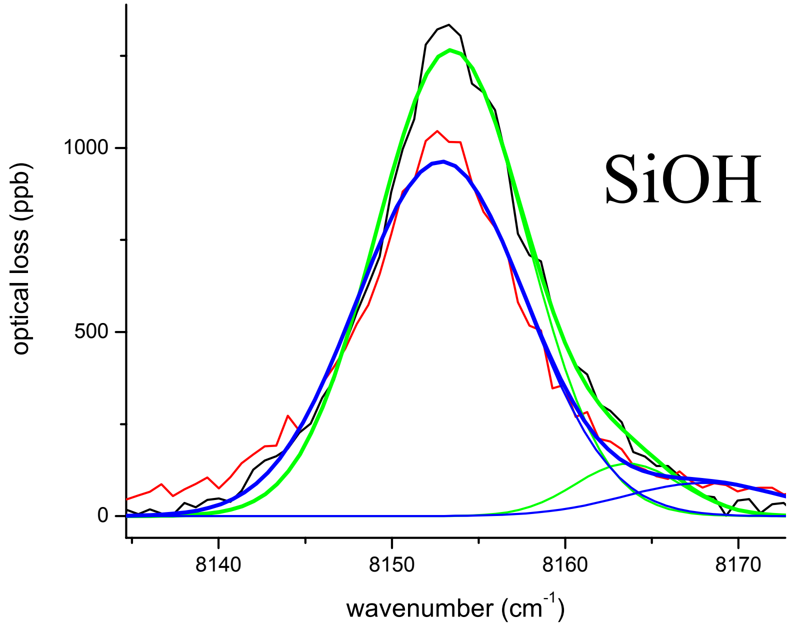
Baseline corrected data for different relative humidity (RH) levels.

SiOH peaks (2) are close to literature values; SiOH peaks are oppositely polarized.

Three H_2O peaks out of 4 show saturation with increasing RH: First monolayer is distinct.

The H_20 lines also sharpen...





FWHM: 11.3 cm^{-1} → 10.4 cm^{-1}

Area: 61% increase

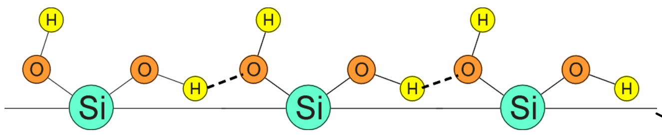
FWHM: 10.2 cm^{-1} → 11.5 cm^{-1}

Area: 15% decrease

- H_2O peaks sharpen; SiOH peaks broaden
- Increased ordering seems a likely explanation

Interpretation: A quasi-ice layer

SiO_2 surface is quasi-crystalline:

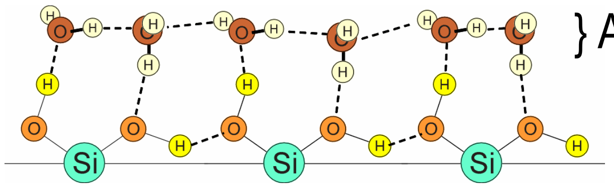


Geminal hydroxyls

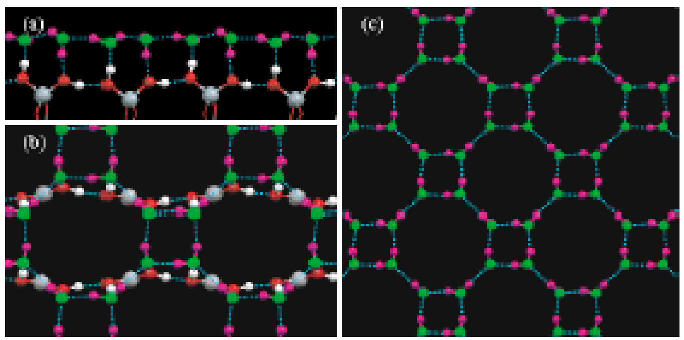
1. SiOH peaks are highly polarized
2. SiOH peaks are relatively sharp
3. Related observations in the literature
4. Consistent with (100) facet of cristobalite

   (Two peaks; oppositely polarized)

H_2O layer H-bonds to SiOH forming a quasi-ice layer:



} Adsorbed Water



"Ice Tessellation"

From Yang et al.

PRL 92(14), 2004

1. H_2O peaks are highly polarized.
2. H_2O peaks are relatively sharp.
3. H_2O peaks saturate as a function of RH.
4. H_2O peaks sharpen at a full monolayer.

Role of dipolar coupling?

>ALSO - SiOH groups show similar thermal stability to OH groups on Al(0001)

Absolute Coverage Measurement

- Why measure absolute coverage?

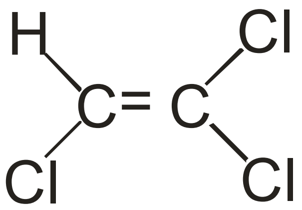
  1. Fundamental to surface science
  2. Absolute surface reaction rate constants
  3. For understanding sensor response

- Procedure for absolute coverage measurement:

  1. Measure absolute (integrated) intensity in a reference state.
  2. From EW-CRDS spectra, obtain average orientation.
  3. Use conservation of the integrated intensity:

$$\mathbf{N_s} = \frac{2\cos\theta_i \int L_{abs,TE}(\omega)\, \omega^{-1} d\omega}{3 I_y \sin^2(\Theta_{avg}) \int \sigma_0(\omega)\, \omega^{-1} d\omega}$$

Absolute Coverage Measurement for TCE



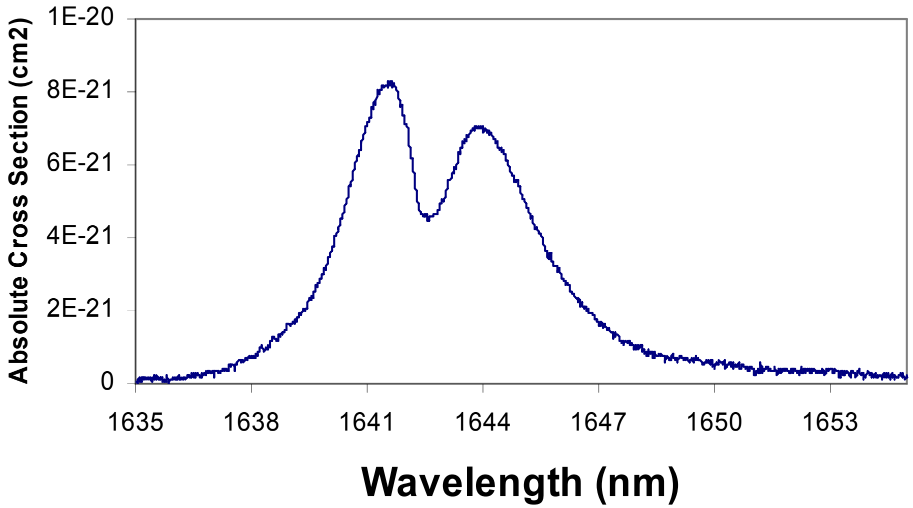
1. Gas-phase reference state:
   a. Use a calibrated diffusion vial
   b. Mass-flow controller

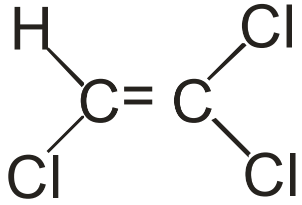
Yields a Primary Standard Traceable coverage Measurement!

2. $\sigma_{abs}(\omega) = L_{abs}(\omega)/(\text{Path length*Number density})$

3. Peak cross section is 8.3×10^{-21} cm^2/molecule

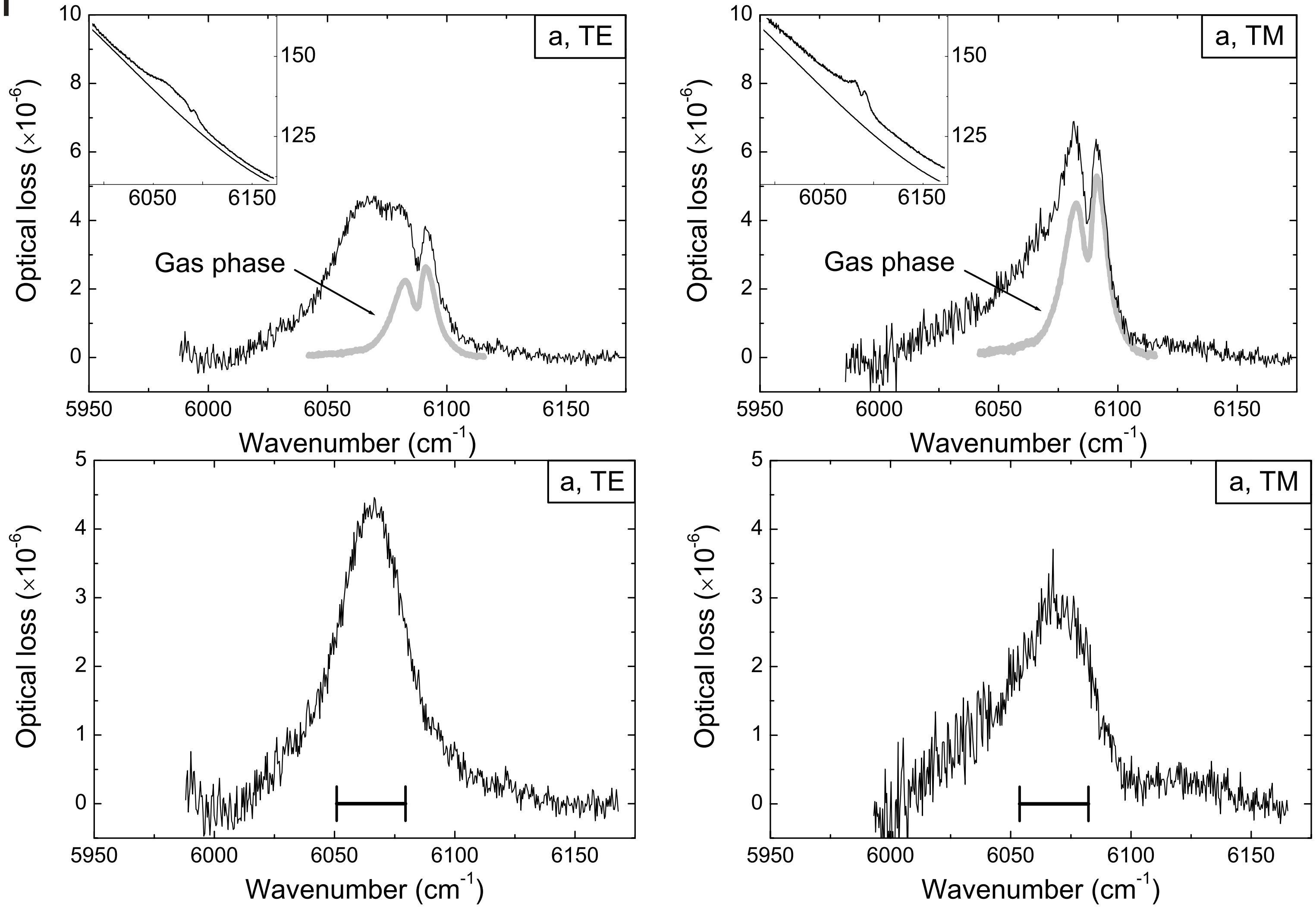
4. Integrated cross-section $\int\sigma(\omega)d\omega$ is conserved.



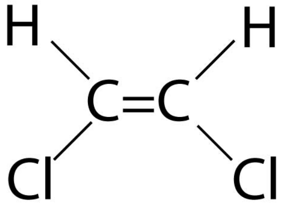


C_s

EW-CRDS spectra of TCE

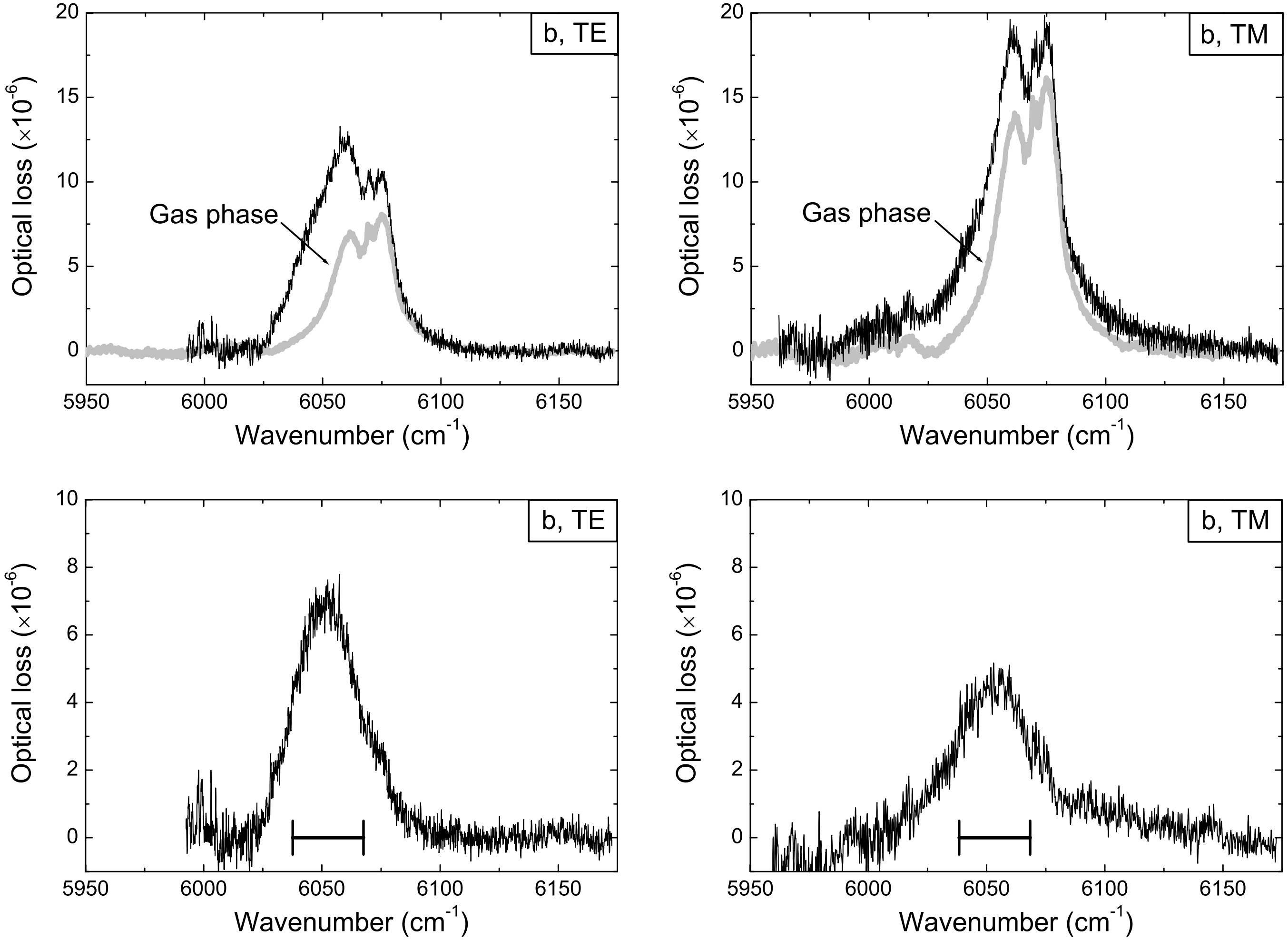


N_s=1.41x10^{14} molecules/cm^2 and Θ=(74±2)^o

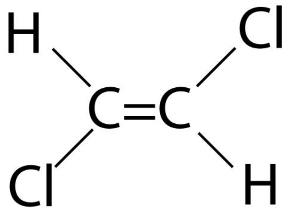


cis-DCE (dichloroethylene)

C_{2v}

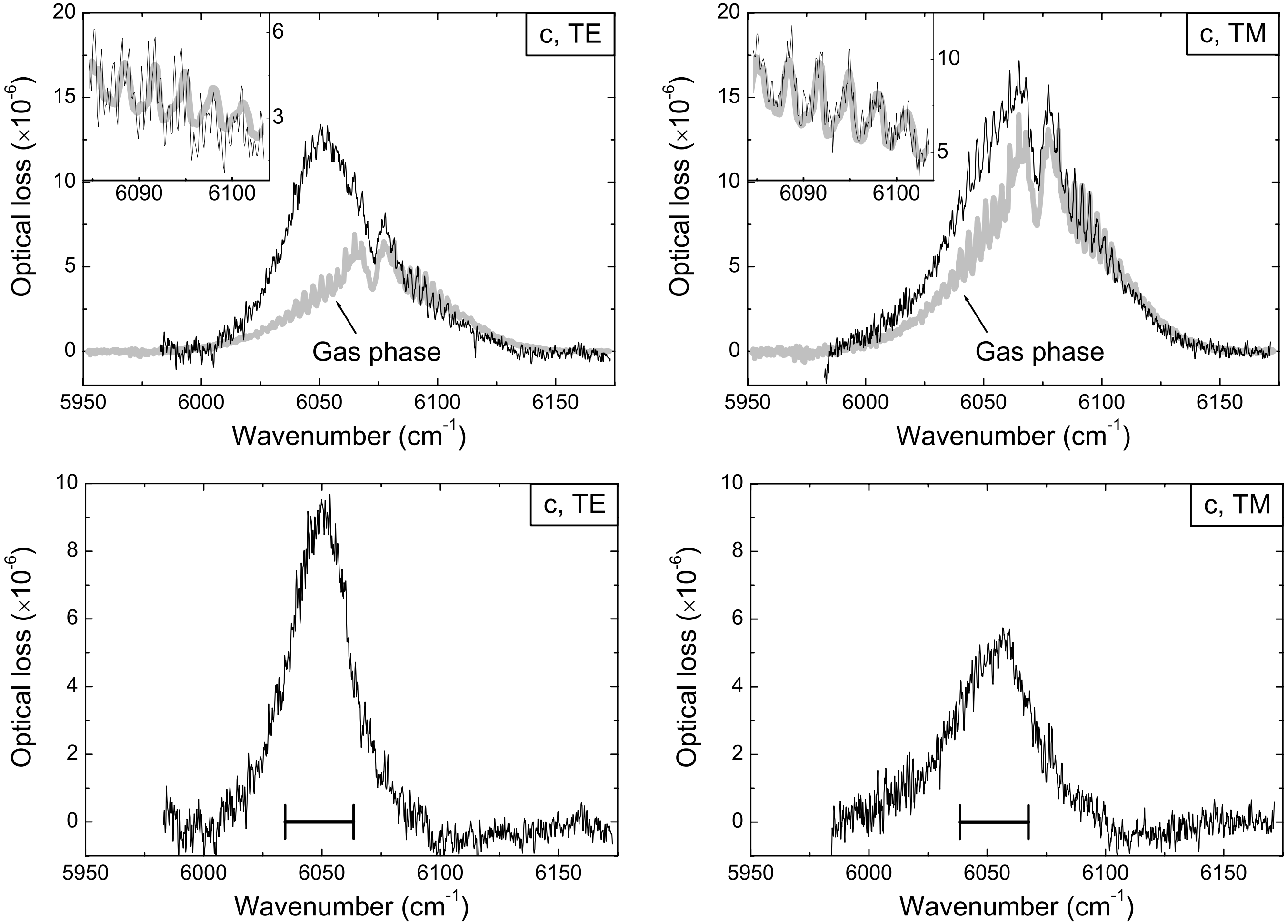


N_s=1.40x10^{14} molecules/cm^2 and Θ=(75 ±2)^o



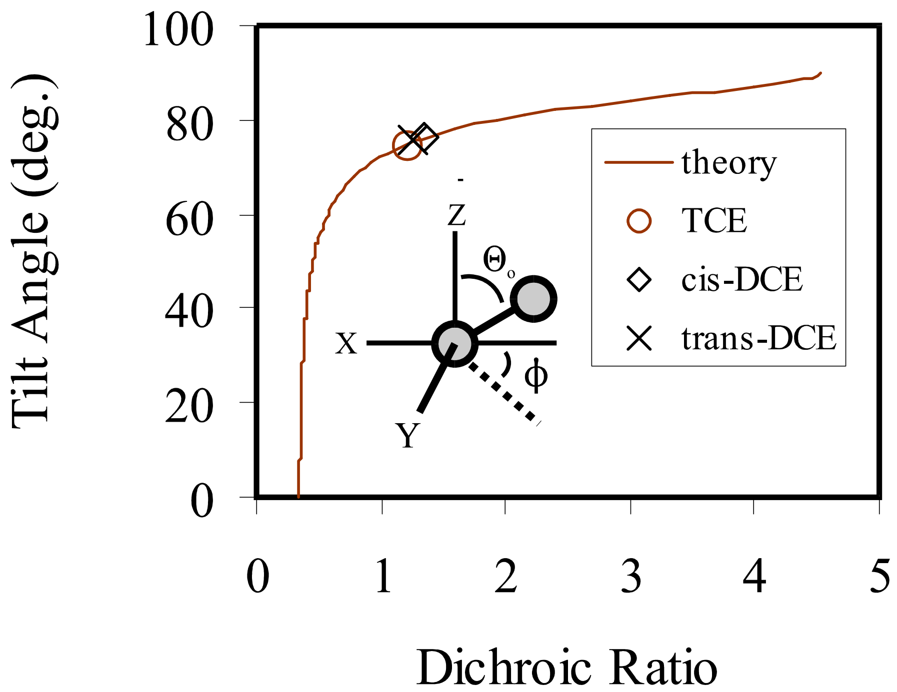
trans-DCE

D_{2h}



$N_s = 1.59 \times 10^{14}$ molecules/cm^2 and $\Theta = (76 \pm 2)^o$

Surface Orientation of TCE, c-DCE, and t-DCE



- Similar coverage: TCE 31% c-DCE 31% t-DCE 35%
- Orientation: Planar molecules lie flat at sub-ML coverage
- Major error source: Orientation

Limitations of a Molecular Orientation Measurement

1. Linear dichroism measures *average* orientation only.

2. If the dichroic ratio is expanded in spherical harmonics:

$$\rho(\Theta) = A_s/A_p = \Sigma_{lm}\, d_{lm} Y_{lm}$$

only $d_{20}(\Theta)$, the "order parameter" is obtainable:

$$d_{20}(\Theta_{avg}) = (3\cos^2(\Theta_{avg})-1)/2$$

where Θ_{avg} is average tilt angle of the transition moment.

3. Orientation distribution is unknown but can often be inferred.

4. "Flat" orientation has minimal error.

H-atom-induced defects in amorphous Si

The Problem (so-called Staebler-Wronski effect):

Solar cells made from a-Si:H degrade rapidly from 12% to 8% efficiency

The effect is reversed by heating to 150 °C

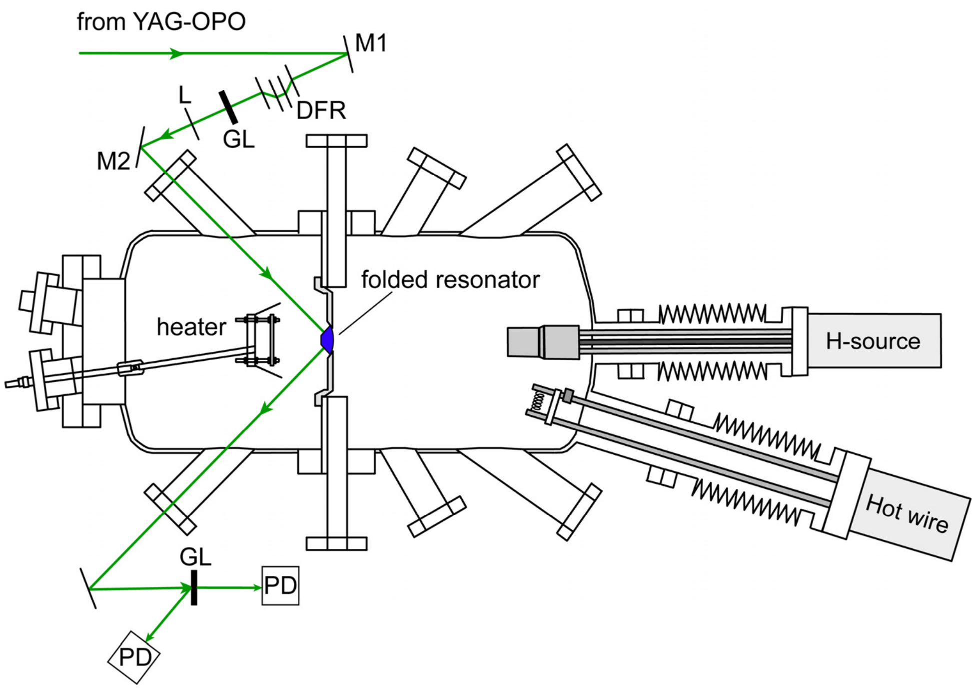
Proposed mechanism:			
		a-Si:H + hv → e- + h+	Electron/hole pair created
		Si-H + e-/h → Si• + H •	Recombination generates H•
	k_i	H• + Si-Si → Si• + Si-H	H atoms are very mobile
	k_r	Si• + Si• ↔ Si-Si + H_2*	"Dangling bond" defect is paired with H-atom and is also mobile

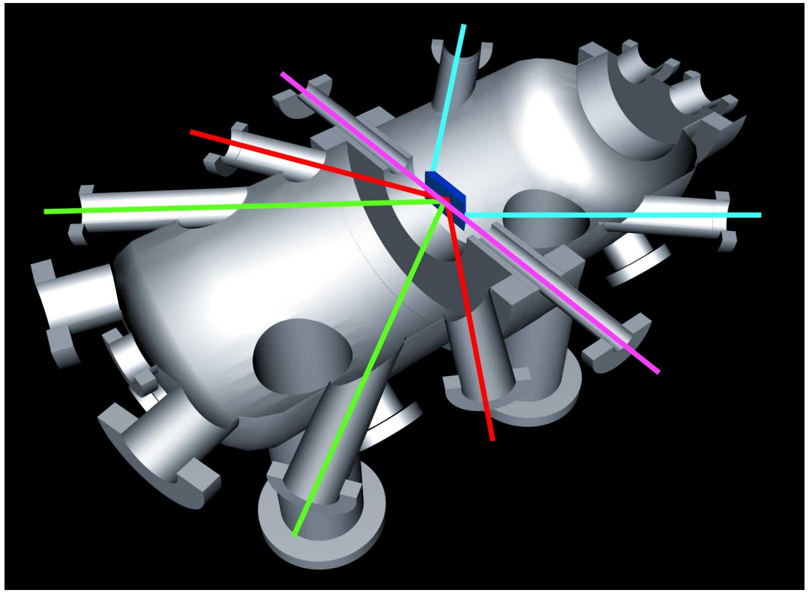
We apply a well-characterized H-atom beam to an a-Si:H film on a folded resonator

This decouples the H-atom generation step from the H-atom reactions.

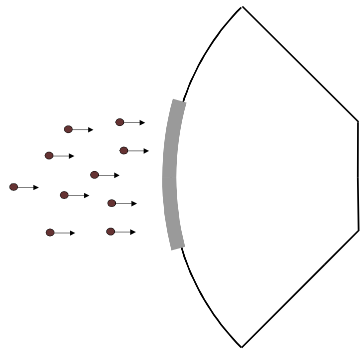
Using EW-CRDS, we obtain absolute values of k_i, k_r, and D, the diffusion coefficient.

Experimental Details

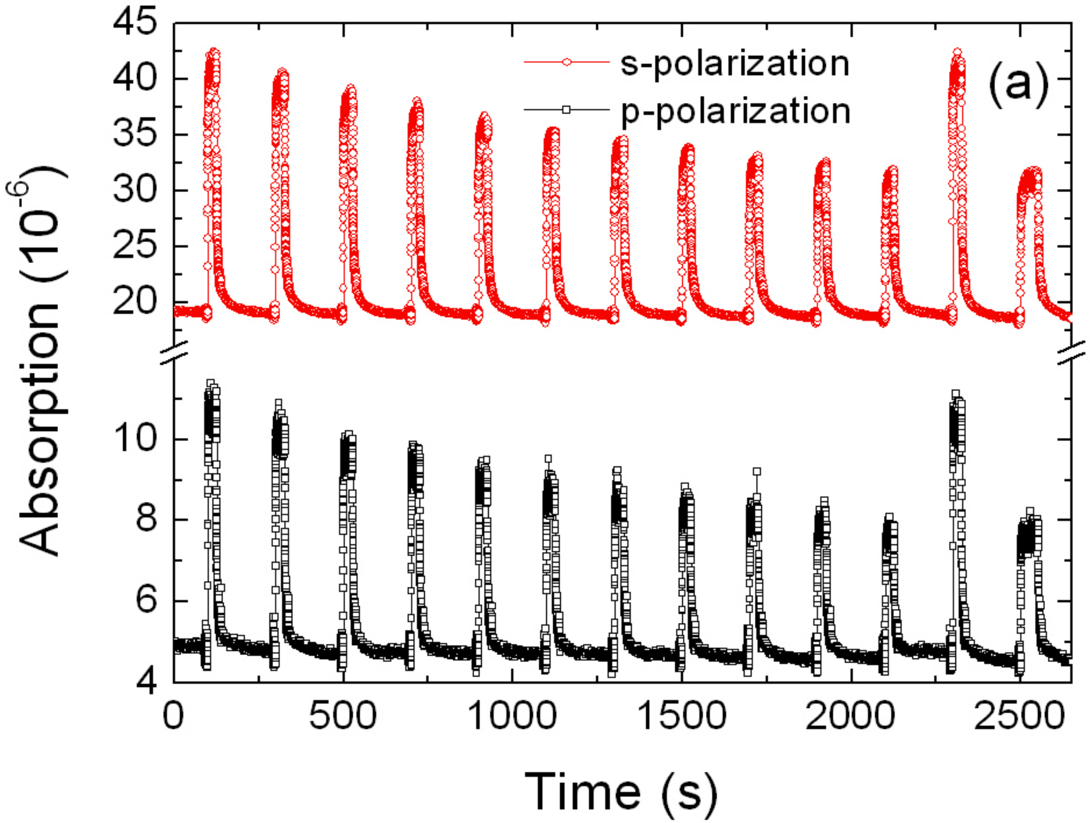


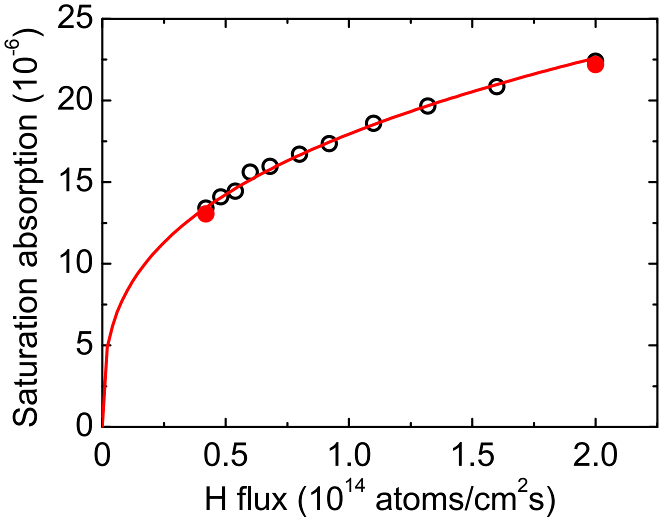


- Hot-wire CVD is used to grow a-Si:H from SiH_4
- Heated tube with stable H_2 flow creates the H-atom beam
- H-atom flux varies with film-source distant
- Film thickness = 60 nm ; Temp fixed at 150 °C



Measured Results





$$(N_{db})_{ss} \sim (F_H)^{1/3}$$

Flux dependence

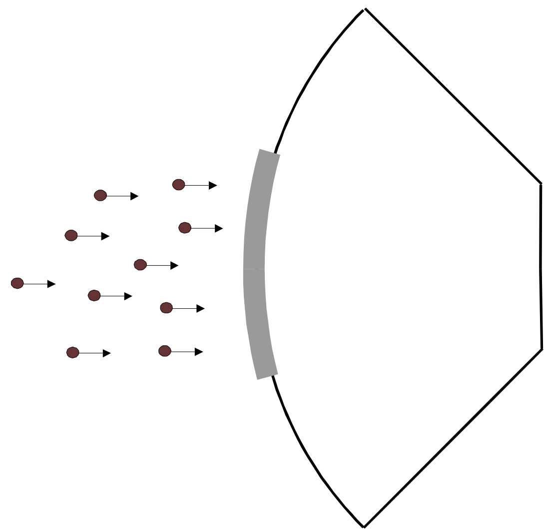
Each exposure has a different H-atom flux.

Top plot is S-polarization; Bottom plot is P-polarization.

Last two fluxes recheck first and last case.

Note S-polarized > P-polarized absorption

Qualitative Physical Picture (that emerges from the data)



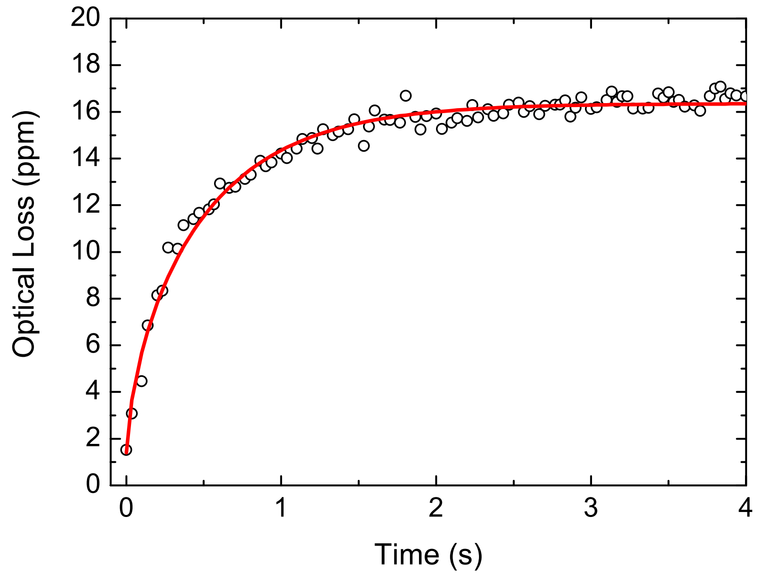
1. H-atoms diffuse rapidly, reaching a uniform density in ~ 1 sec.

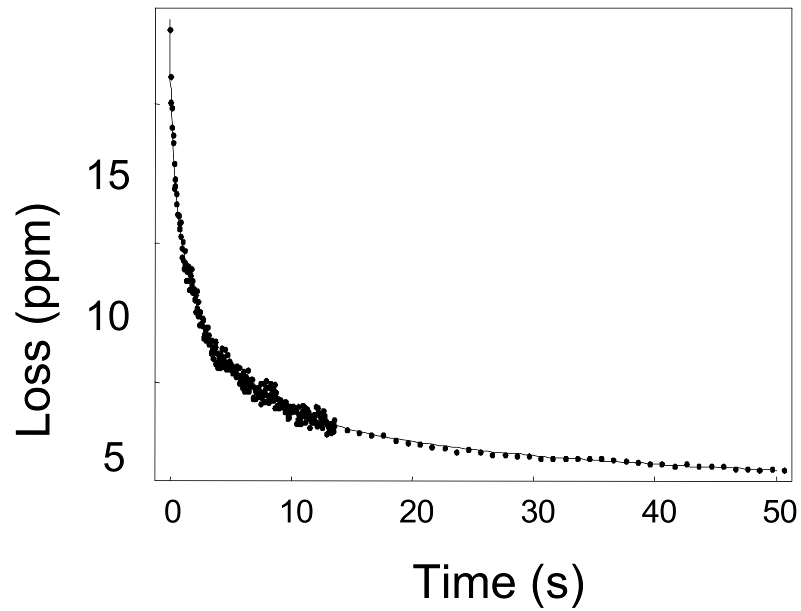
2. Only a small fraction react (~1%). The majority simply diffuse out.

3. The small fraction insert into weak Si-Si bonds - but are still mobile.

4. The dB defects couple in a binary reaction that is reversible at 150 °C.

EW-CRDS Detection of H-atom Interactions





Uptake – Kinetics dominated process.

Average field in the film is used.

Both insertion and dB-dB coupling.

$$\frac{d\alpha(t)}{dt} = \sigma_{db}\int_0^h \Gamma(z)dz\left\{\frac{k_i[Si-Si]\gamma F_H}{N_b} - k_r N_{db}^2\right\}$$

$\Gamma(z)$ is the E-field enhancement

Decay is a diffusion dominated process.

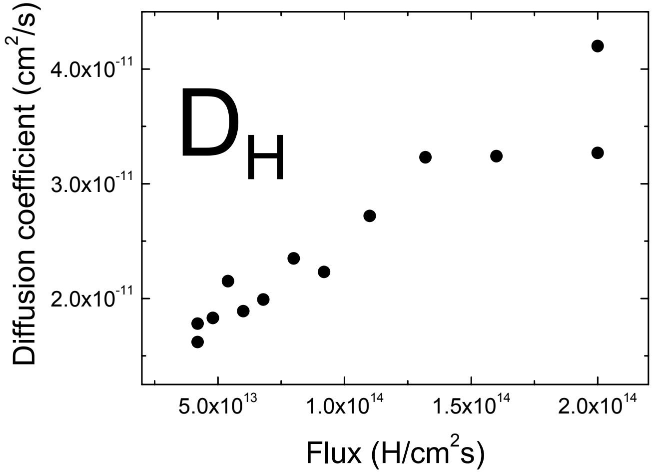
Spatial dependence of the field is used.

Only insertion is relevant; H-atoms vent.

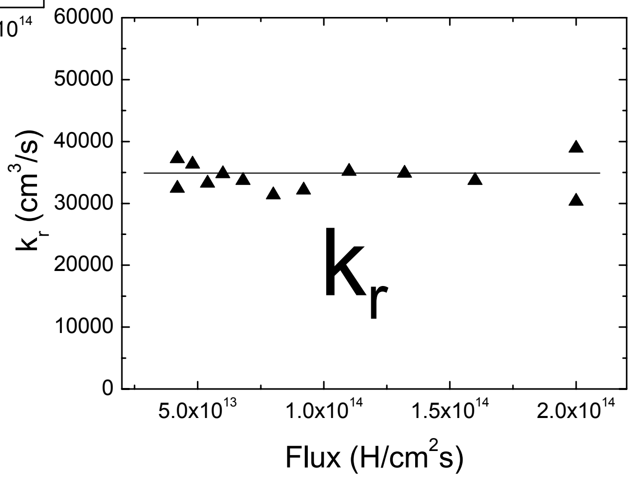
$$\frac{d\alpha(t)}{dt} = \sigma_{db}k\ [Si-Si]H_0\int_0^h \Gamma(z)f(z,t)dz$$

D_H

Diffusion coefficient, Db coupling, & Insertion rate constants

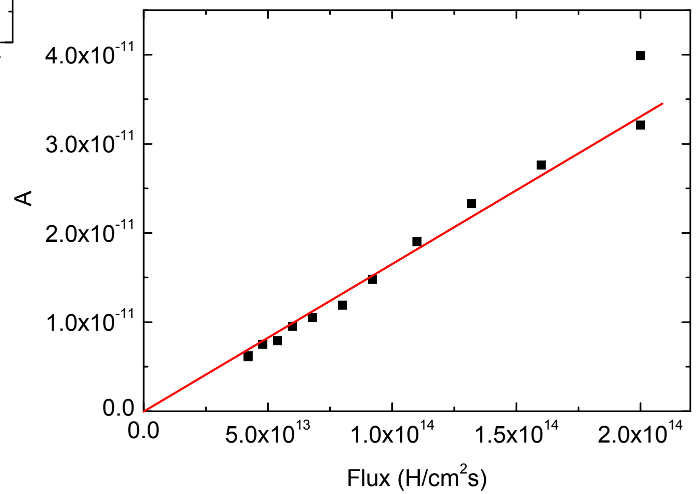


- A weakly flux-dependent D is found.
- Magnitude ~10^{-11} - neglect of diffusion in uptake.
- Similar values reported. More accurate?



$$A(\Phi_H) = k_i\left[Si - Si\right]\gamma F_H \sigma_{db}\int_0^h \Gamma(z)dz$$

Linear with F_H

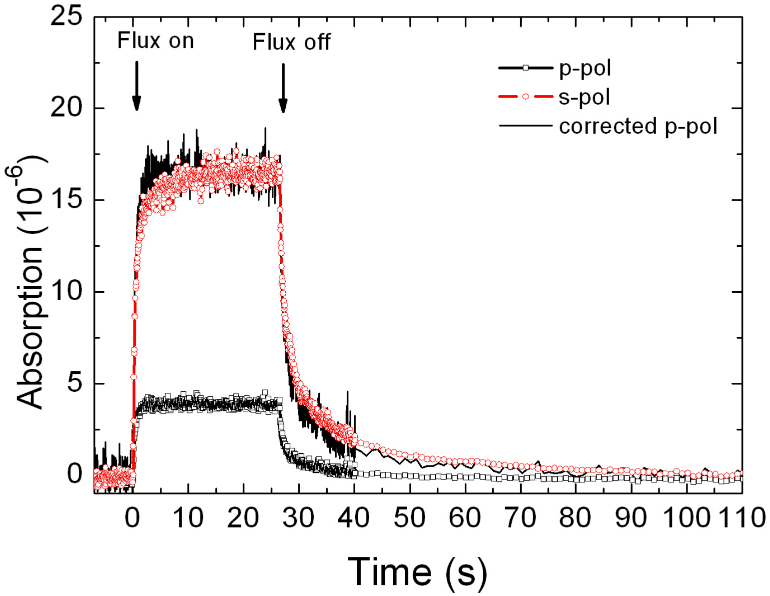


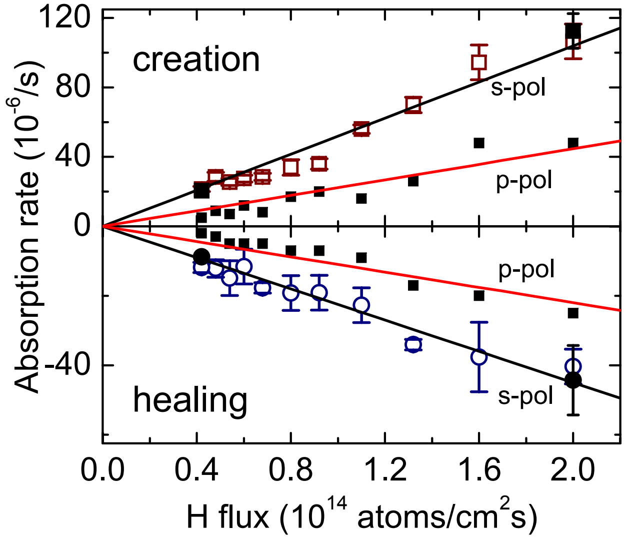
$k_i\left[Si - Si\right]H_0$

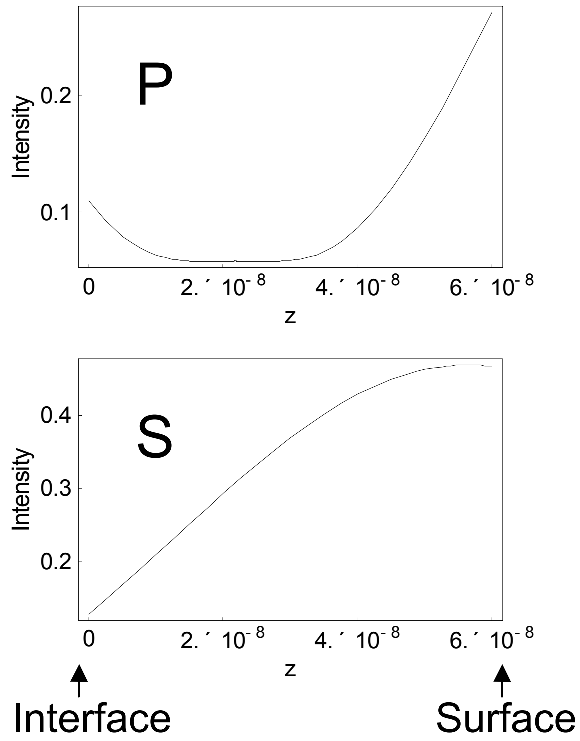
- H_0 from uptake DE
- k_i[Si-Si]=pseudo first order

1/k_i[Si-Si]=H-atom lifetime ~10 s

Bulk vs Surface Response?







We expected a surface contribution.

No sign of the 30:1 P:S surface polarization ratio.

Measured S&P signals overlap when corrected for BULK field differences.

Early time points overlap when corrected for shallow BULK field differences.

We think H- on the surface rearranges/accommodates rapidly between impacts.

Summary

<u>Monolithic resonators</u> provides many advantages:

- **High sensitivity**
- **Polarized measurements**
- **In-situ operation**
- **Design flexibility**

The Future:

- **Absolute surface reaction kinetics**
- **Spectroscopy, growth, and reactions of oxides**
- **Reactions in and on thin films**
- **Applications to:**
  - **Atomic layer deposition**
  - **Catalysis**
  - **Solar cells (cont.)**
  - **Biosensing**
  - **….**

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Thank you!