Dynamics of Hydrogen Defects in Silicon

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Technological Importance

- Degradation of MOSFETs [1]
- STM-induced H desorption from Si:H surfaces [2]
- UV-induced Si_{Ga}-H depassivation in GaAs [3]

Giant H/D isotope effect

↓

Vibrational heating model

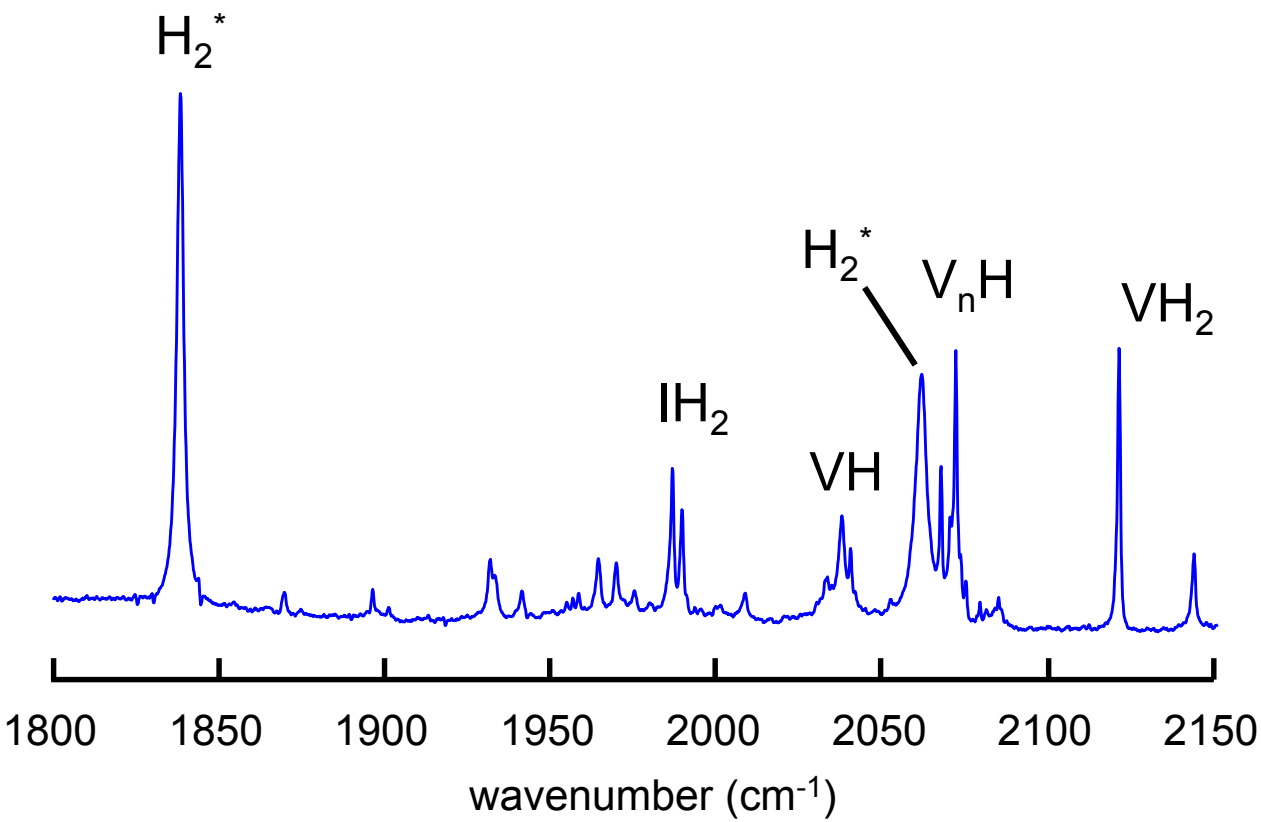
[1] J. W. Lyding *et al*, Appl. Phys. Lett. **68**, 2526 (1996)

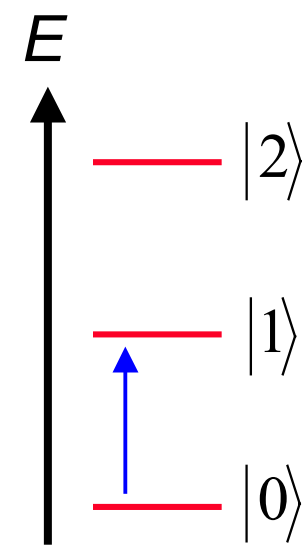
[2] T.-C. Shen *et al*, Science **268**, 1590 (1995)

[3] J. Chevallier *et al*, Appl. Phys. Lett. **75**, 112 (1999)

Hydrogen in Crystalline Silicon

Example: Proton-implanted Si

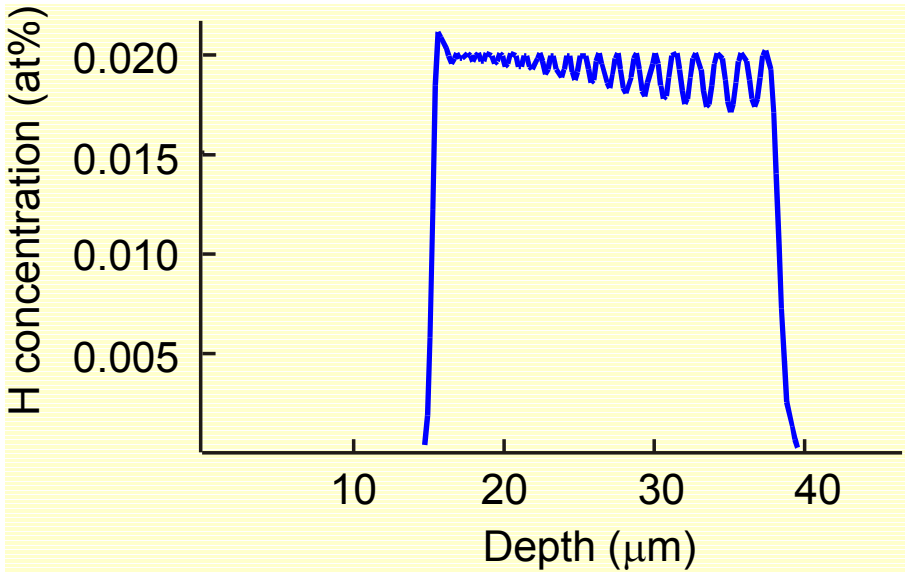




Experimental

Sample preparation

- Energies = 1.0 - 1.8 MeV
- [H] = 0.02 at%
- Temp = 80 K



Characterization

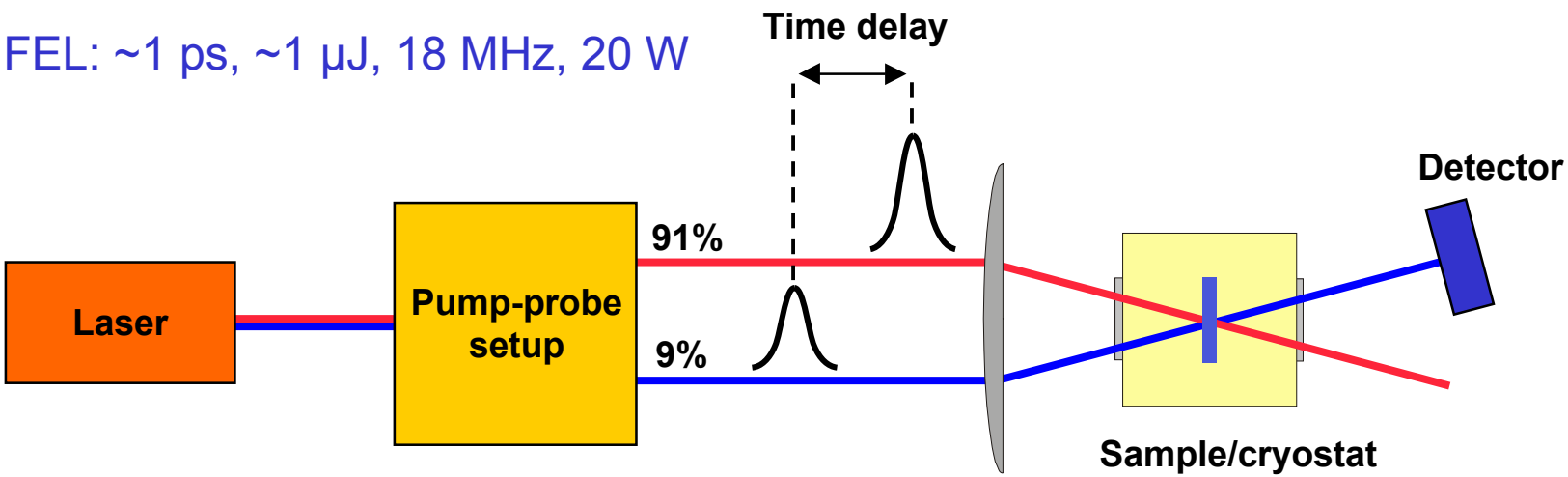
- *In-situ* FTIR
- 5 - 160 K

Time-resolved spectroscopy

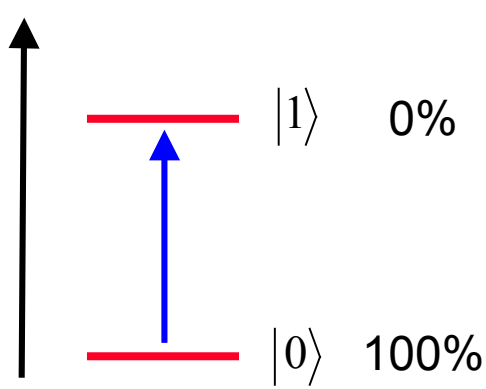
- *In-situ* transient-bleaching spectroscopy
- 5 - 160 K

Transient Bleaching Spectroscopy

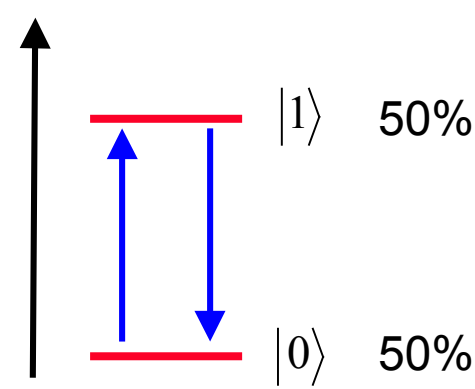
FEL: ~1 ps, ~1 μJ, 18 MHz, 20 W



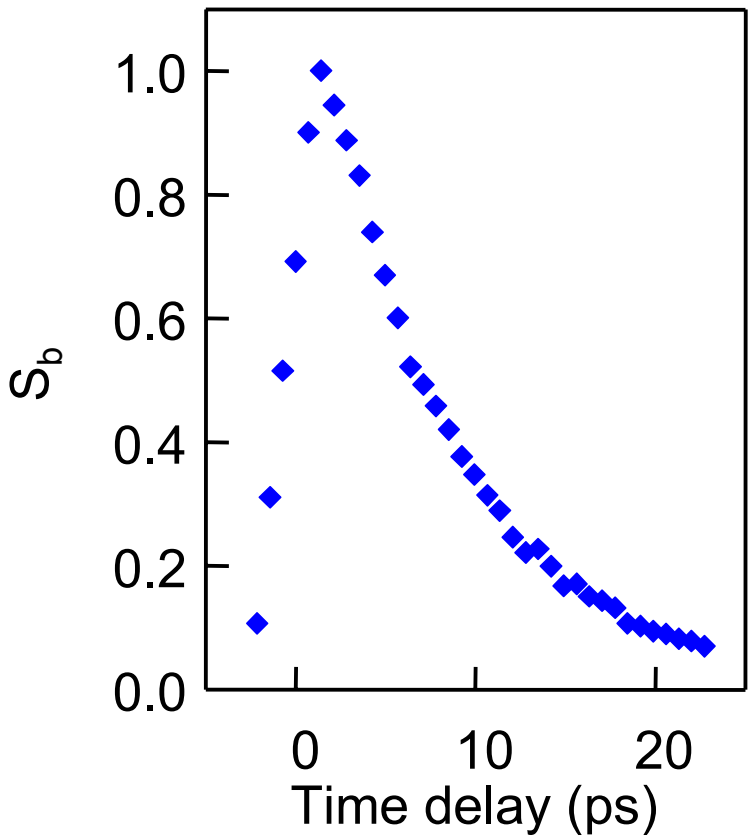
Thermal equilibrium

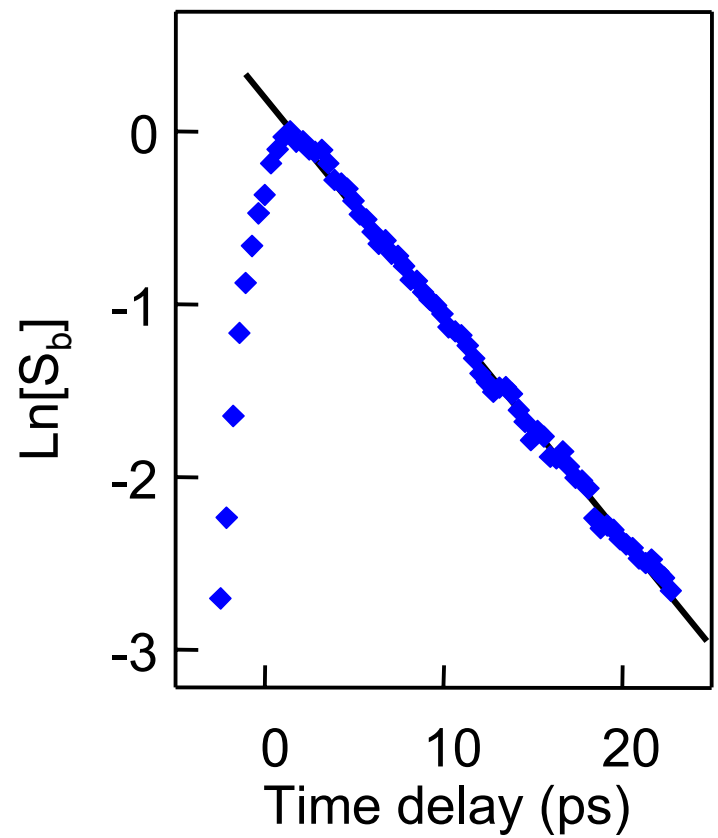


Bleached



Vibrational Lifetime of H_{BC} Stretch

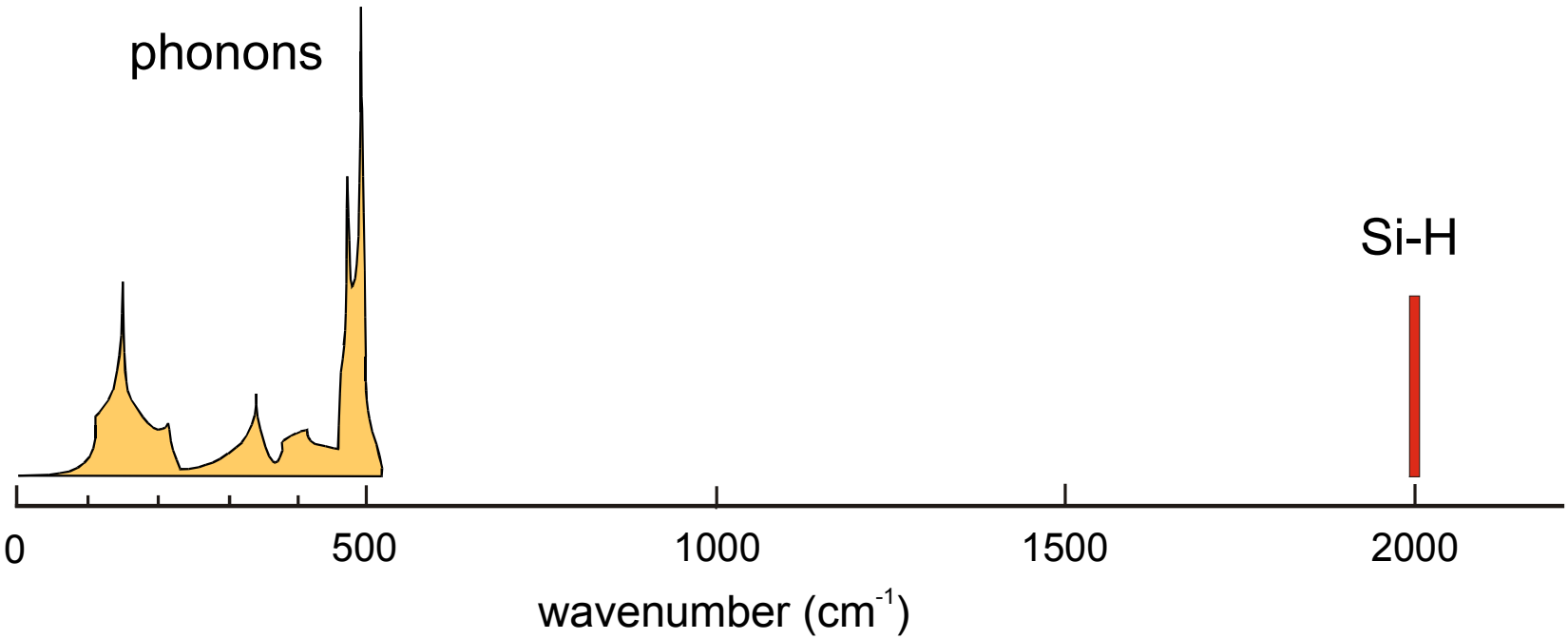




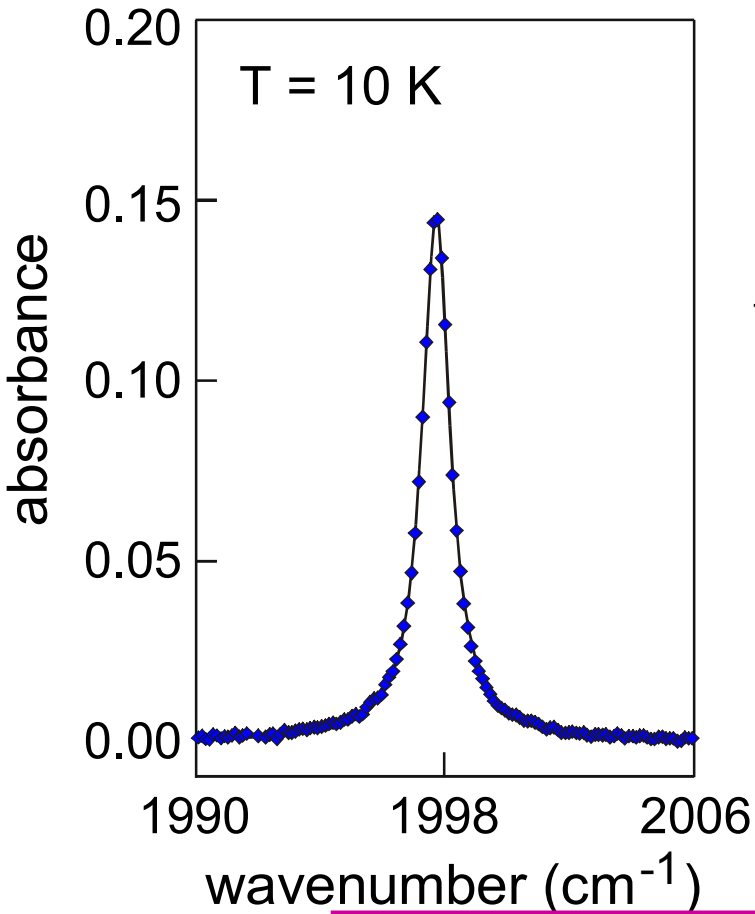
$T_1 = 7.8 \pm 0.2$ ps

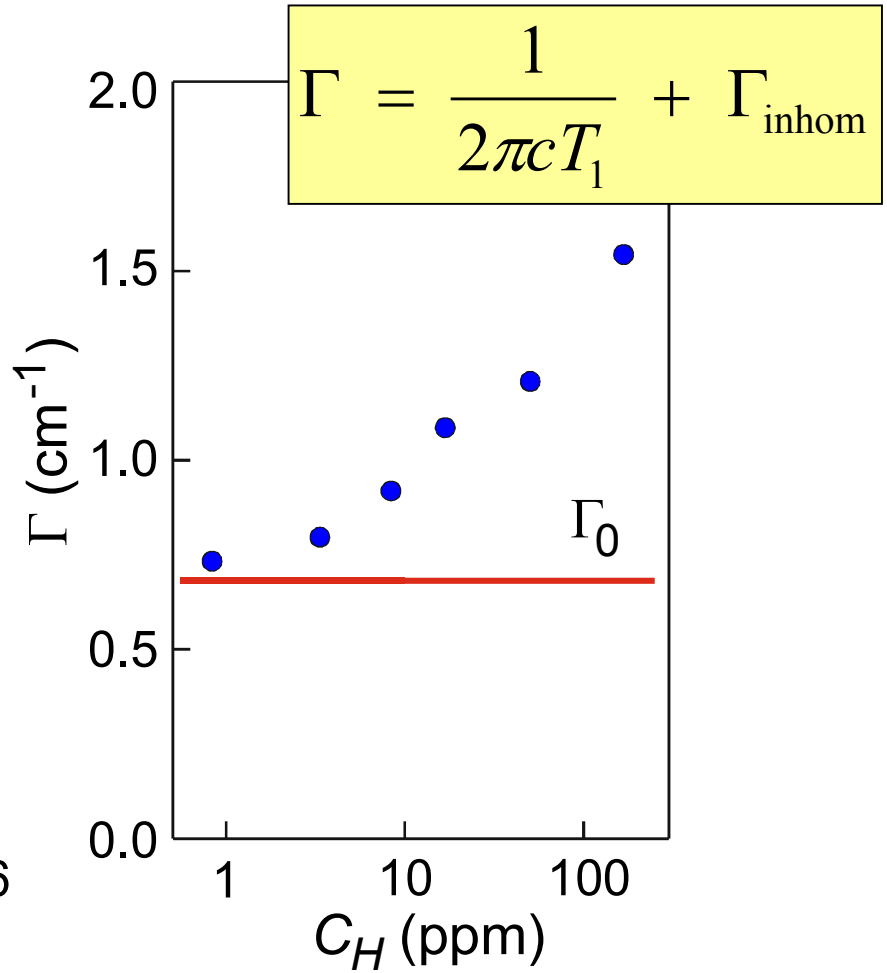
Decay Mechanism

- Radiative: No, $T_{1,IR}$~ 2 ms
- Electronic: No, donor level of $H_{BC}^{(+)}$ is unoccupied and > 0.25 eV from valence band
- Vibrational: Yes, but requires emission of ≥ 4 phonons



Natural Line Shape





Time and frequency domain consistent

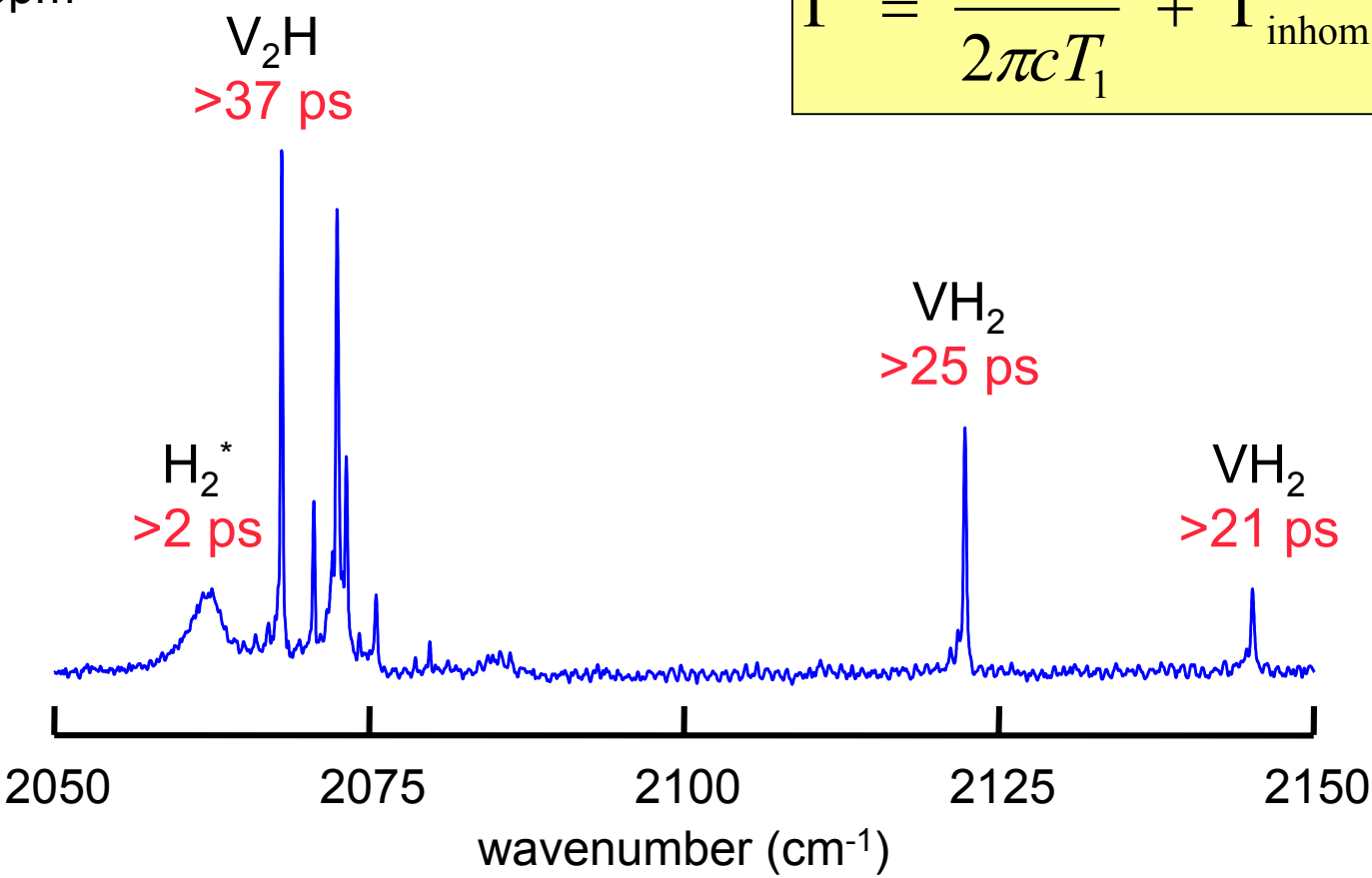
Structural Dependence

Implanted range = 1200 μm

C_H = 7.3 ppm

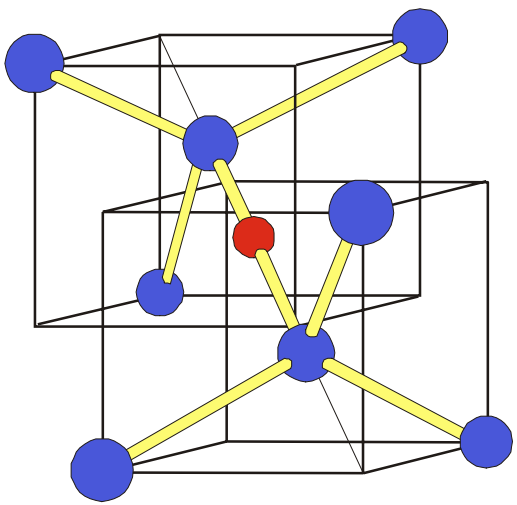
T = 10 K

$$\Gamma = \frac{1}{2\pi c T_1} + \Gamma_{inhom}$$



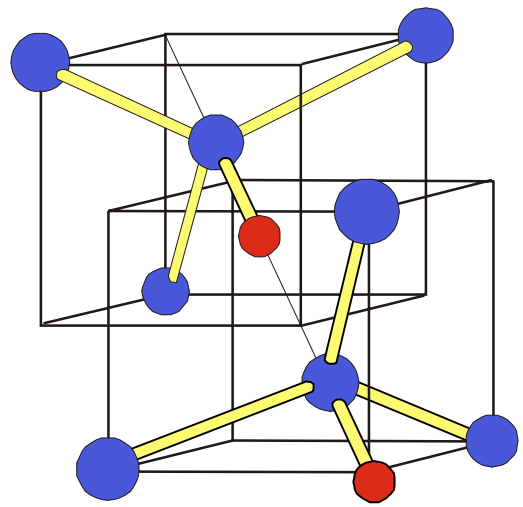
Defects identified by B. Bech Nielsen *et al*

Interstitial-Type Defects



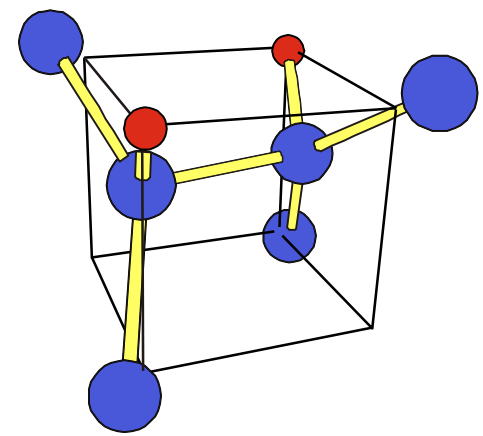
$H_{BC}^{(+)}$

ω (cm^{-1})	T_1 (ps)
1998	7.8



H_2^*

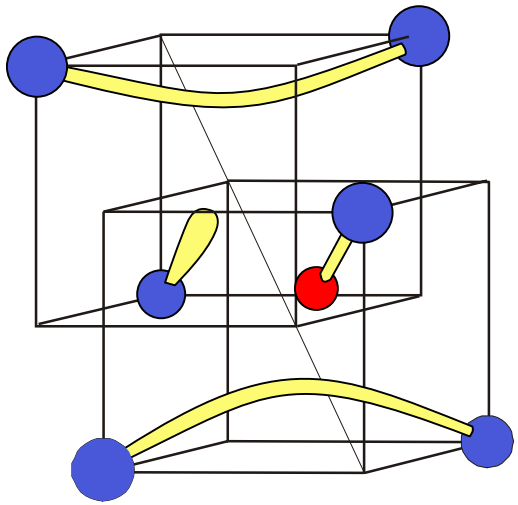
ω (cm^{-1})	T_1 (ps)
1838	~3
2062	~2

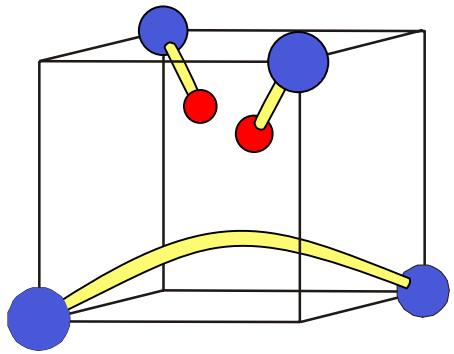


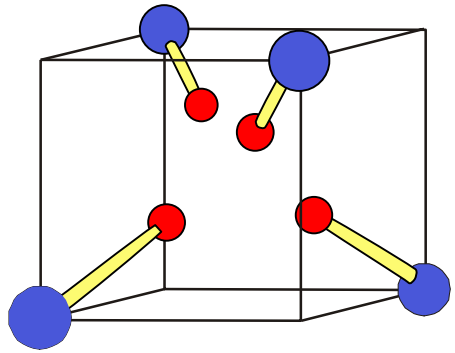
IH_2

ω (cm^{-1})	T_1 (ps)
1987	~8
1990	~8

Vacancy-Type Defects



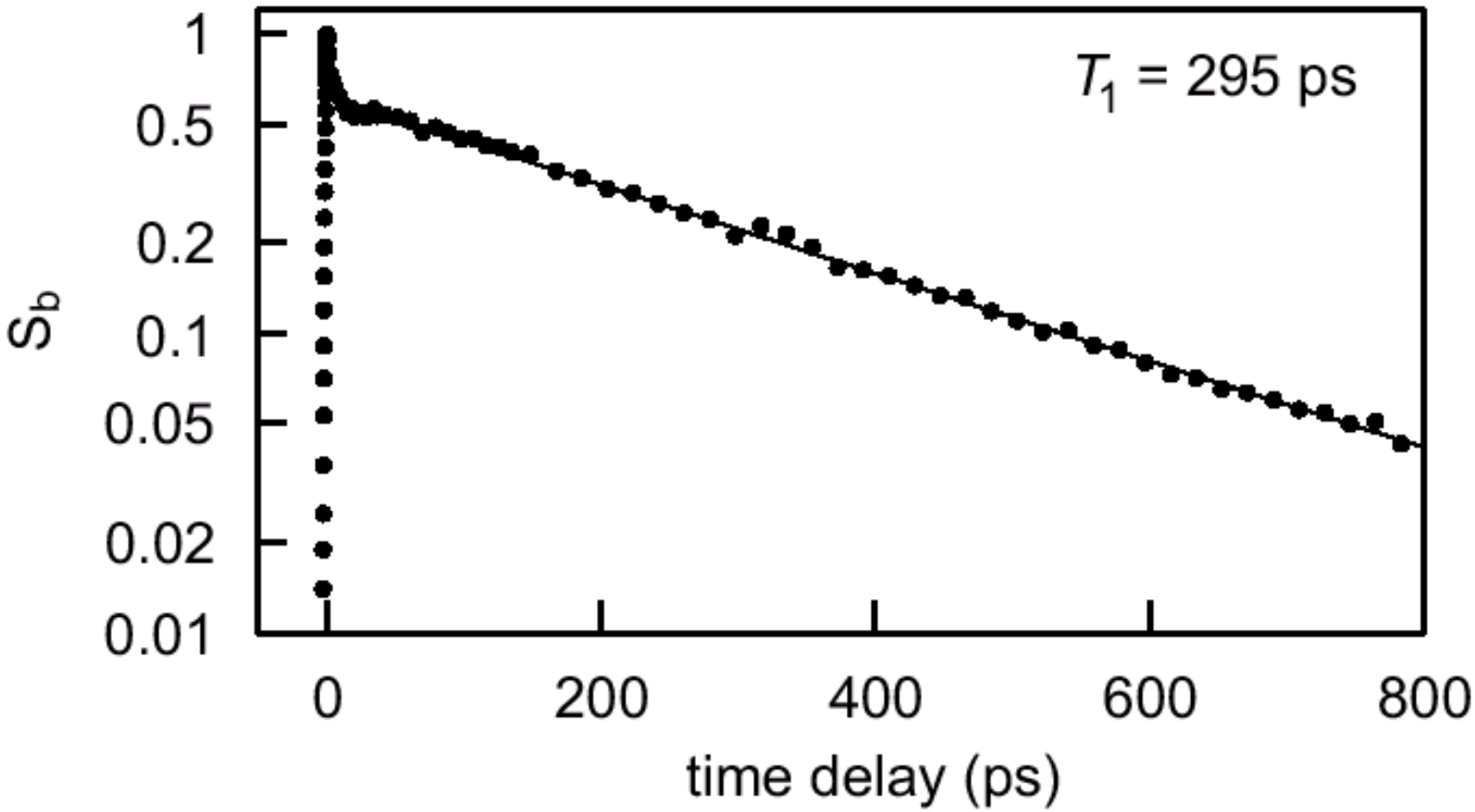




V_2H		VH_2		VH_4	
ω (cm^{-1})	T_1 (ps)	ω (cm^{-1})	T_1 (ps)	ω (cm^{-1})	T_1 (ps)
2068	> 37	2122	> 25	2223	> 48
		2145	> 21		

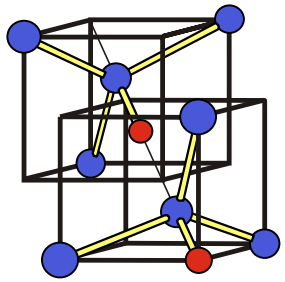
B. Pajot *et al*, Phys. Rev. B **59**, 7500 (1999)

Vibrational Lifetime of $HV \cdot VH_{110}$

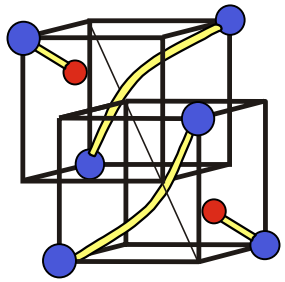


The transient bleaching spectrum was taken at the Jefferson Lab. FEL.

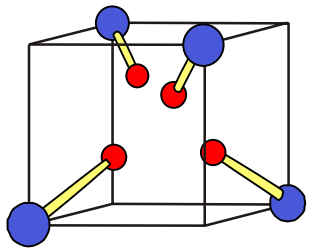
Absorbance Spectra of e-Irradiated, H-Doped Si



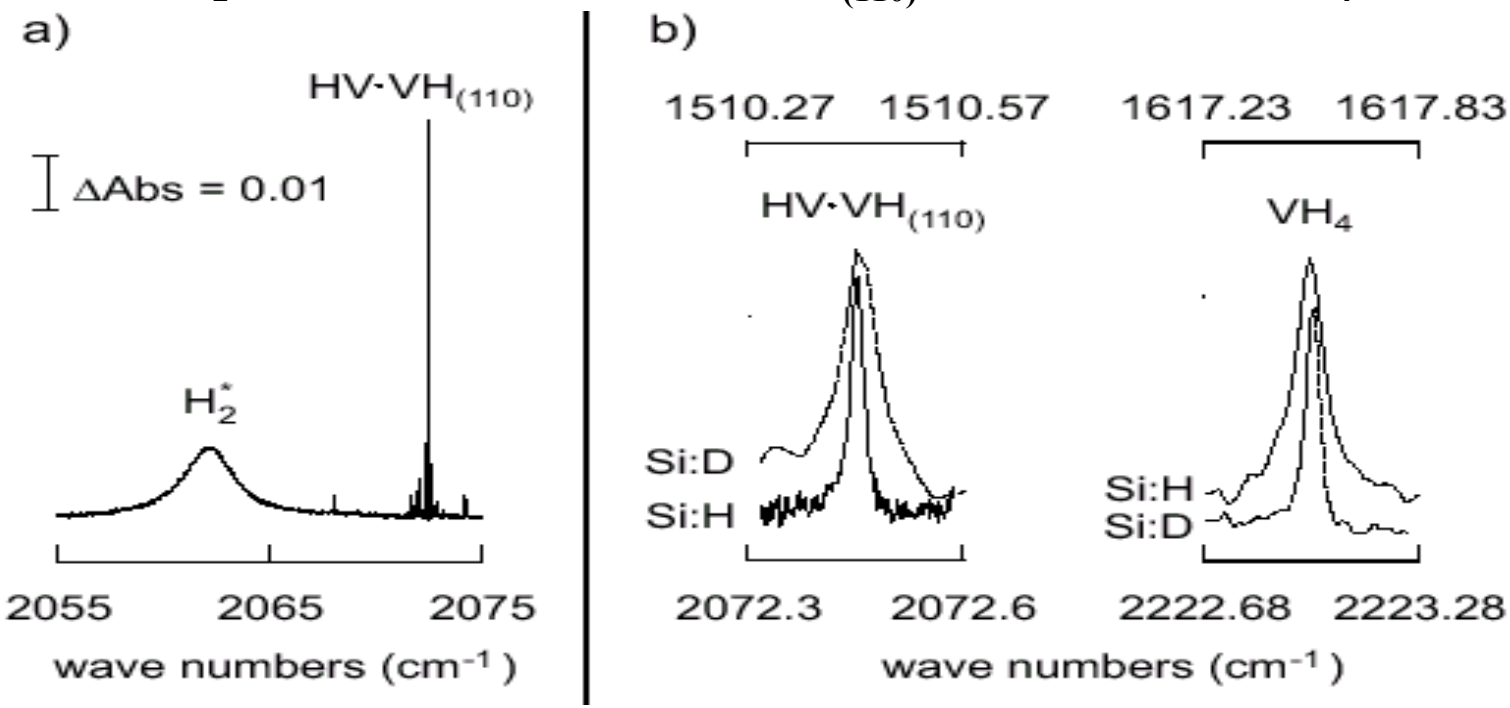
H_2^*



$HV{\cdot}VH_{(110)}$



VH_4



Lifetimes of Si-H and Si-D Stretch Modes

Defect	ω_H (cm^{-1})	T_1 (ps)	T_1 (ps)	ω_D(cm^{-1})
H_2*	2062.1	1.9	4.8	1500.1
IH_2	1987.1	12	20	1446.5
IH_2	1990.0	11	18	1448.7
VH_2	2122.3	60	70	1547.9
VH_2	2145.1	42	55	1565.1
VH_4	2223.0	56	143	1617.5
$HV{\cdot}VH_{(110)}$	2072.5	295	93	1510.4

M. Budde, G. Lüpke, *et al.*, Phys. Rev. Lett. 87, 145501 (2001).

Decay Mechanism

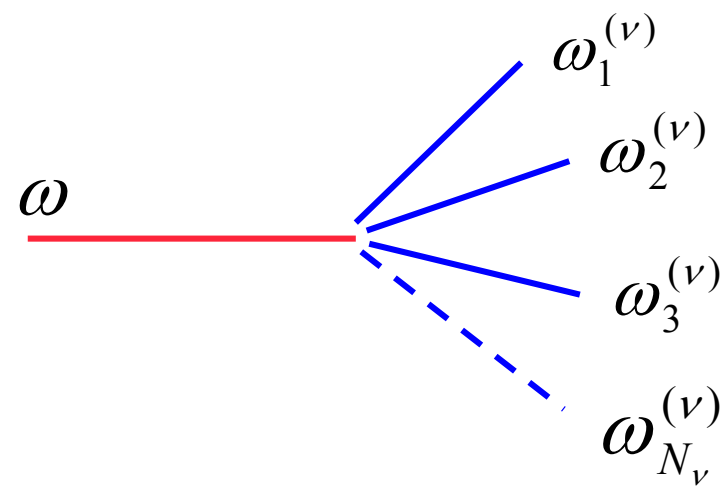
Decay of LVM into "phonon" bath:

$$\frac{1}{T_1} = 2\pi \sum_{\{\nu\}} |G_{\{\nu\}}|^2 \, n_{\{\nu\}} \rho_{\{\nu\}}$$

Each channel ν:

$$\omega = \sum_{j=1}^{N_\nu} \omega_j^{(\nu)}$$

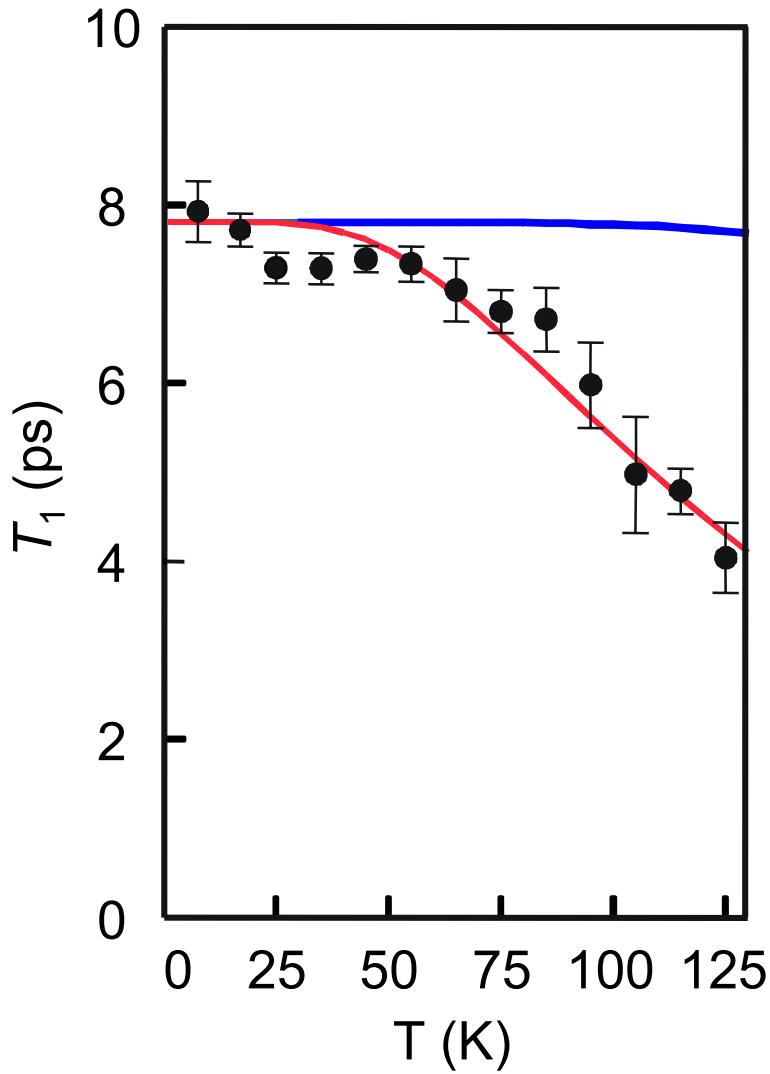
$$n_{\{\nu\}} = \frac{\exp(\hbar\omega / k_B T) - 1}{\prod_{j=1}^{N_\nu} [\exp(\hbar\omega_j^{(\nu)} / k_B T) - 1]}$$



$$\rho_{\{\nu\}} = \int d\omega_1^{(\nu)} \ldots \int d\omega_{(N_\nu - 1)}^{(\nu)} \rho_1^{(\nu)}(\omega_1^{(\nu)}) \cdots \rho_{N_\nu}^{(\nu)}(\omega_{N_\nu}^{(\nu)})$$

A. Nitzan *et al*, J. Chem. Phys. **60**, 3929 (1974)

Temperature Dependence



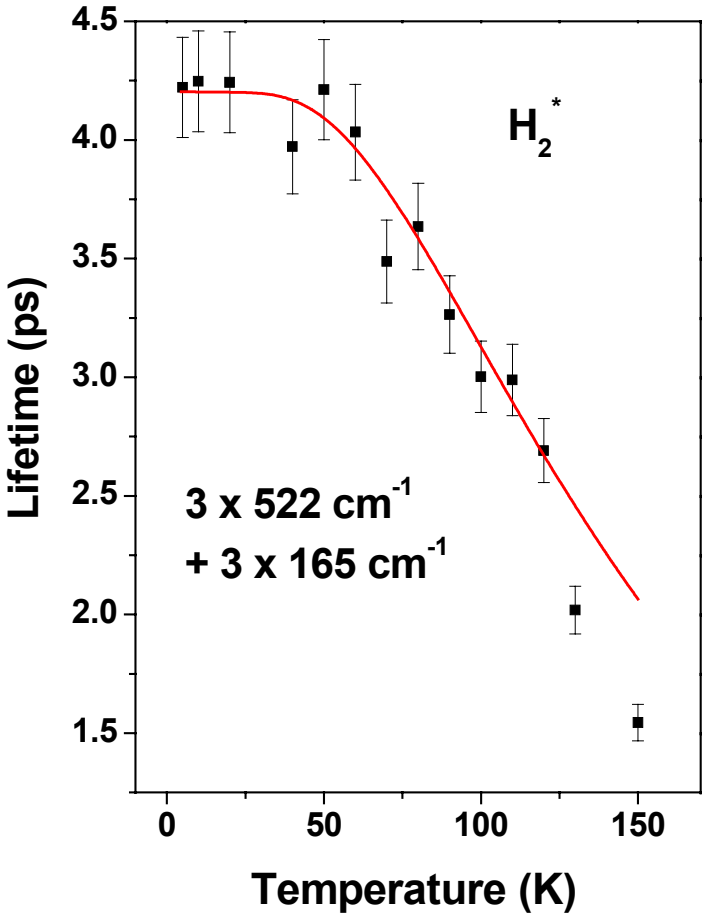
Decay channel:

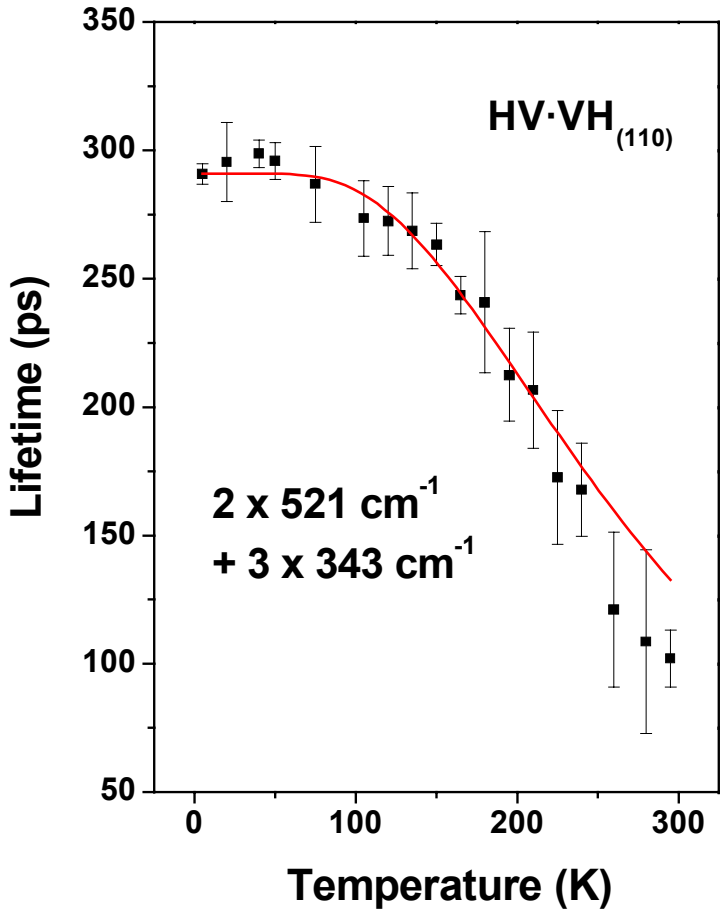
4 phonons at ~500 cm^{-1}

3 modes at ~150 cm^{-1}
+ 3 modes at ~500 cm^{-1}

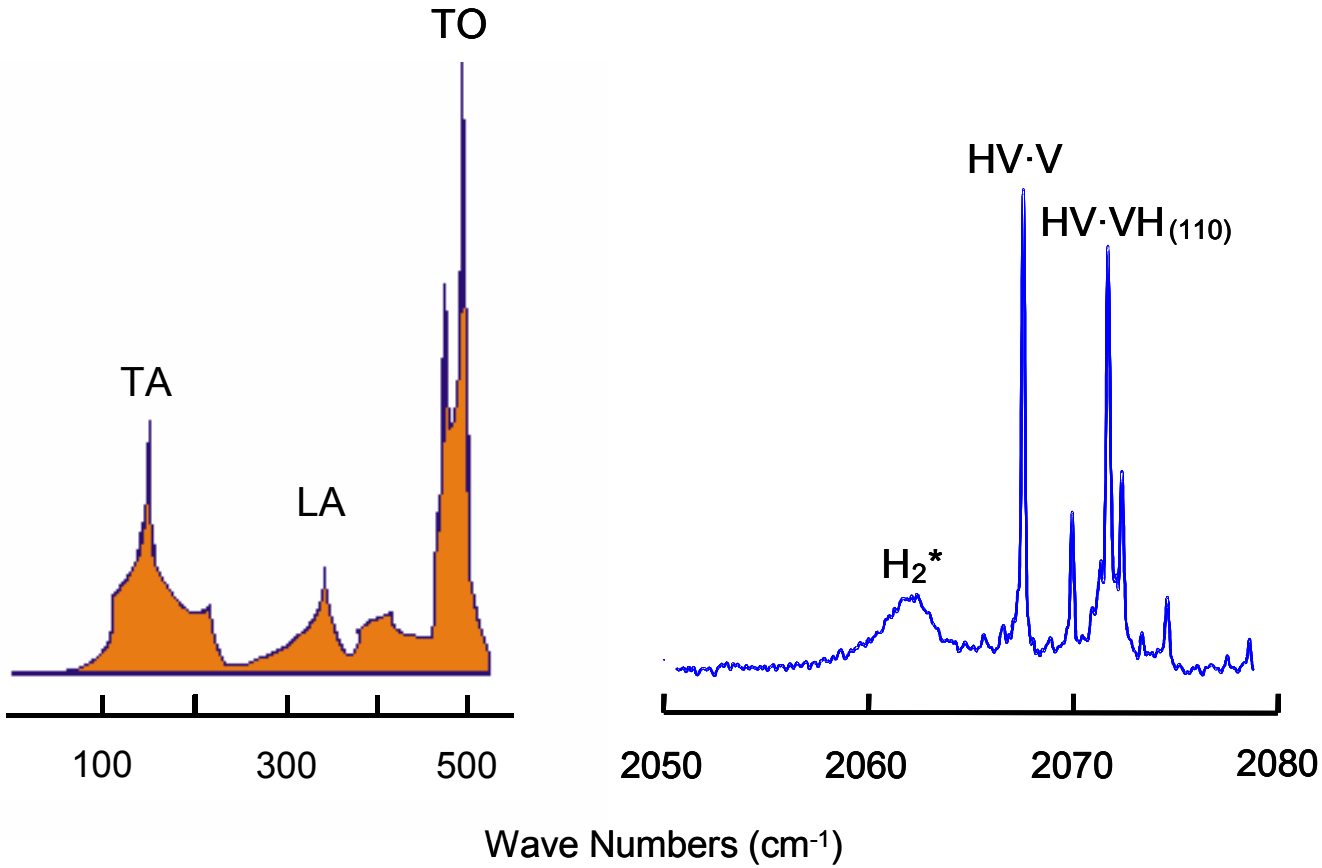
- $H_{BC}^{(+)}$ stretch does not decay by lowest-order channel
- 2 - 3 modes at ~150 cm^{-1} involved

Temperature Dependence of T_1





Phonon and Absorbance Spectrum of Si



Summary

- First measurements of Si-H and Si-D lifetimes
- Time and frequency domain consistent
- New insight into LVM lifetimes:
  - Does not decay via lowest-order channel
  - Strong structural dependence
  - Lifetimes of Si-D modes are typically longer