Vibrational Lifetimes and Decay Channels of Hydrogen-related Modes in Semiconductors

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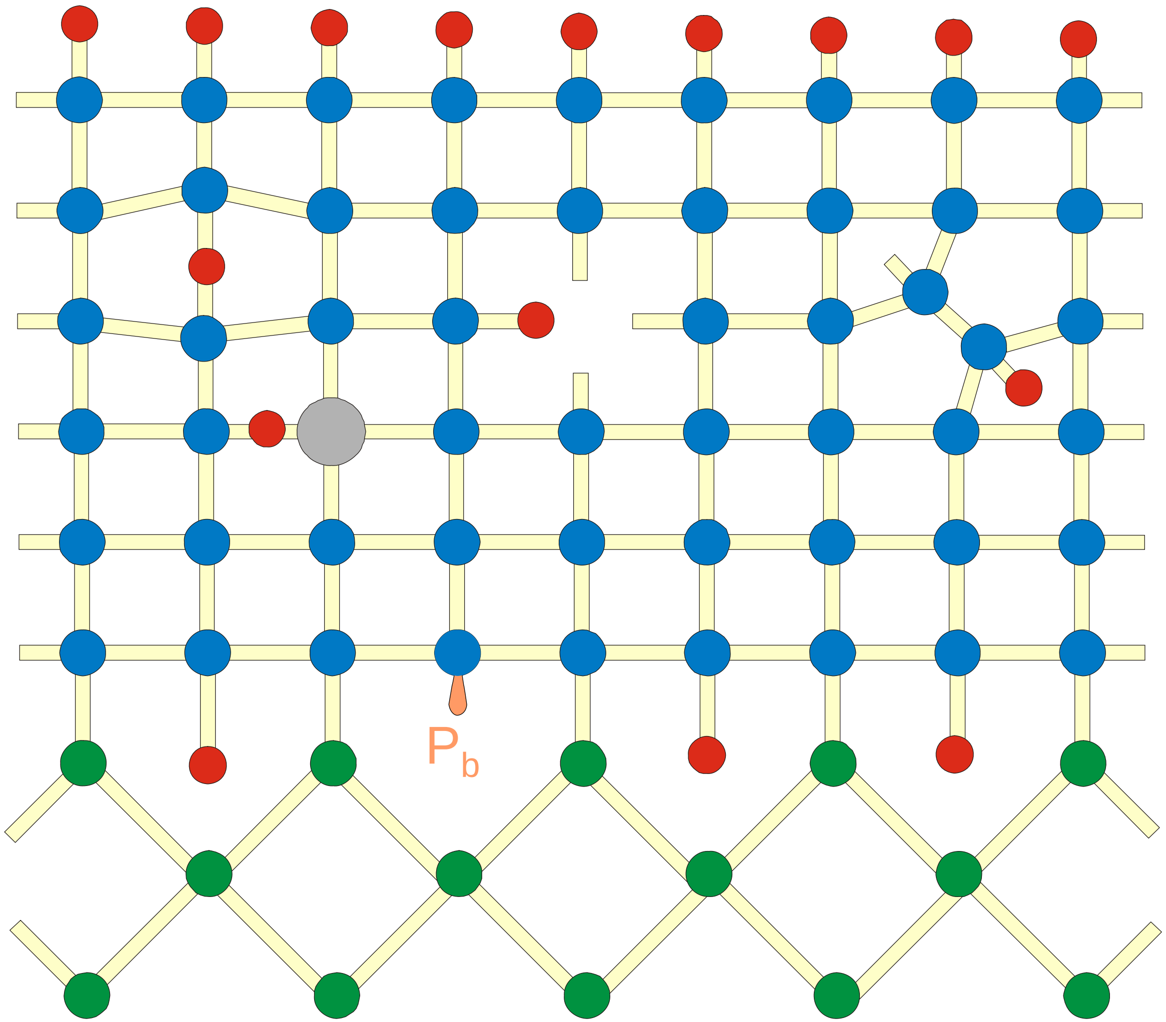
Hydrogen in Semiconductors



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

↓

Multiple Vibrational Excitation

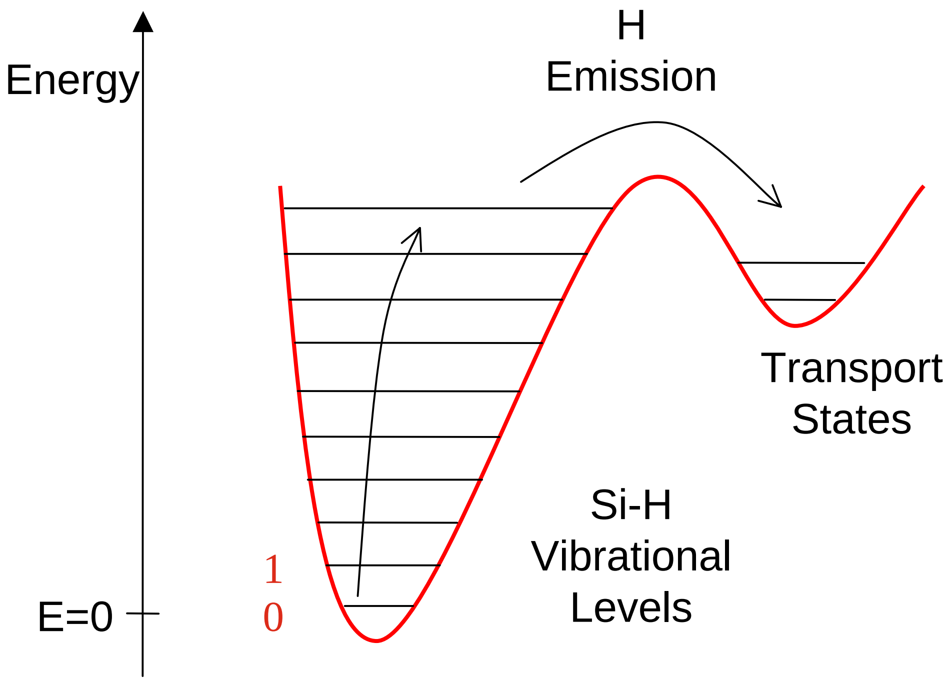
[1] J. W. Lyding *et al*, Appl. Phys. Lett. **68**, 2526 (1996)

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

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

Multiple Vibrational Excitation Mechanism

Truncated harmonic oscillator



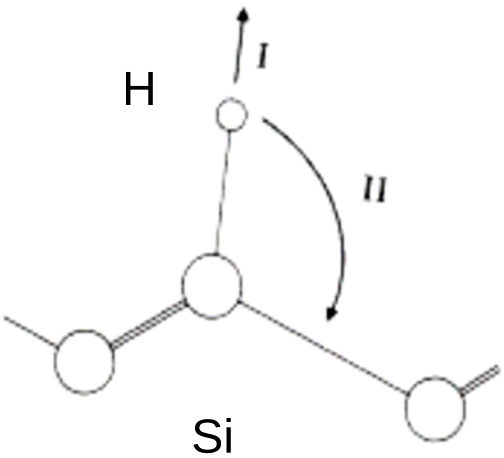
Dissociation rate:

$$R \sim \frac{(N_{\max}+1)}{T_1}\left(\frac{\Gamma_{exc}}{\Gamma_{exc}+1/T_1}\right)^{(N_{\max}+1)}$$

Dissociation rate extremely dependent on vibrational lifetime

B. N. J. Persson *et al*, Surf. Sci. **390**, 45 (1997)
E. T. Foley *et al*, Phys. Rev. Lett. **80**, 1336 (1998)

Dissociation Pathways of Si-H Bonds



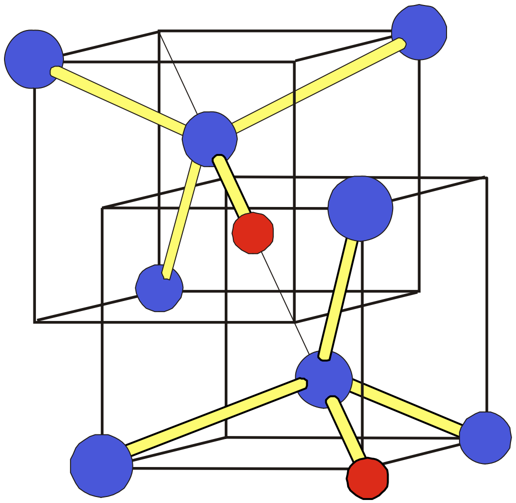
(a) The barrier of path I is much higher than path II.

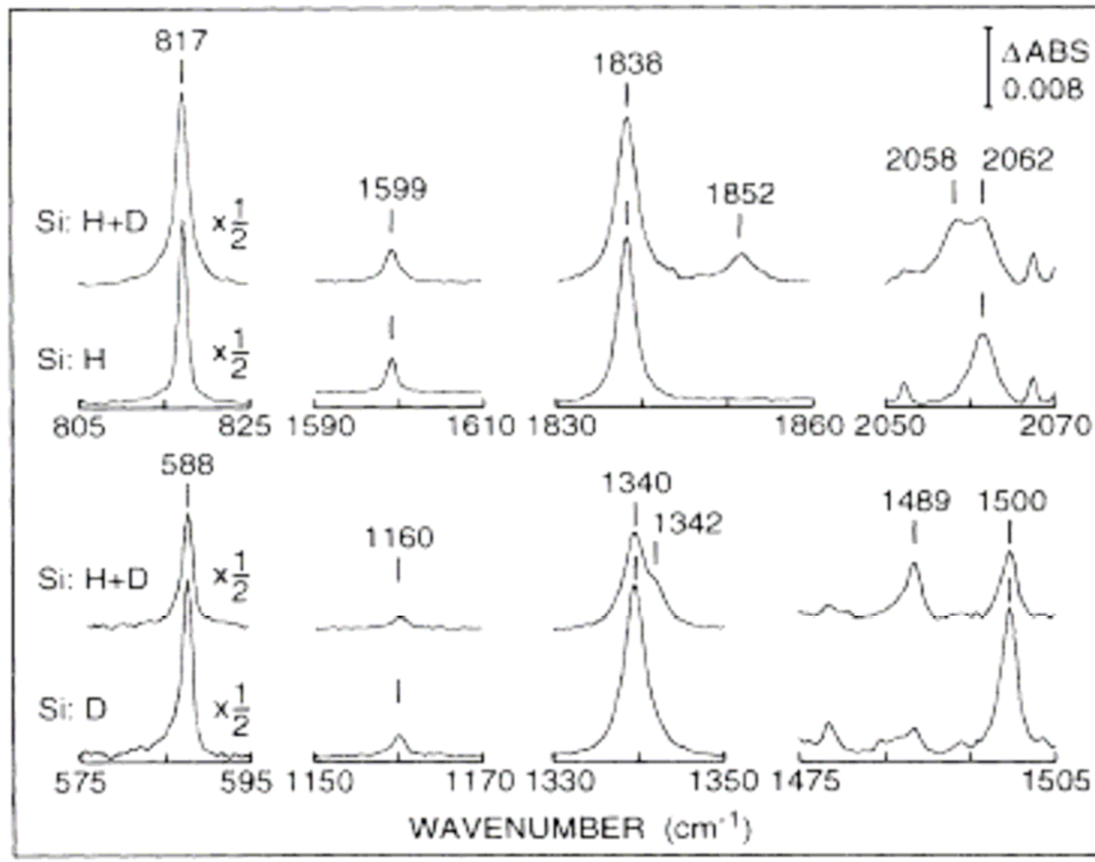
(b) Path II leads to a H position near the BC site, which is more stable.

Dissociation of Si-H bonds is controlled by the bending mode

C. G. Van de Walle *et al*. PRB 49, 14776 (1994)

Bending Mode of H_2^*





Four absorption modes:

817 cm^{-1} Bending mode

1599 cm^{-1} Overtone

1838 cm^{-1} Stretch (AB)

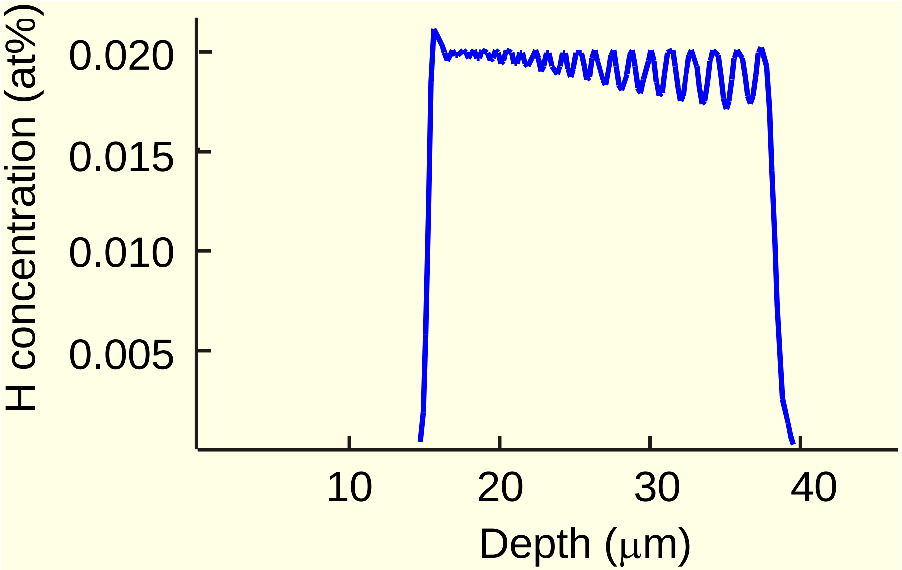
2062 cm^{-1} Stretch (BC)

J. D. Holbech *et al,* PRL 71, 875 (1993)

Experimental

Sample preparation

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



Characterization

- *In-situ* FTIR
- 5 - 290 K

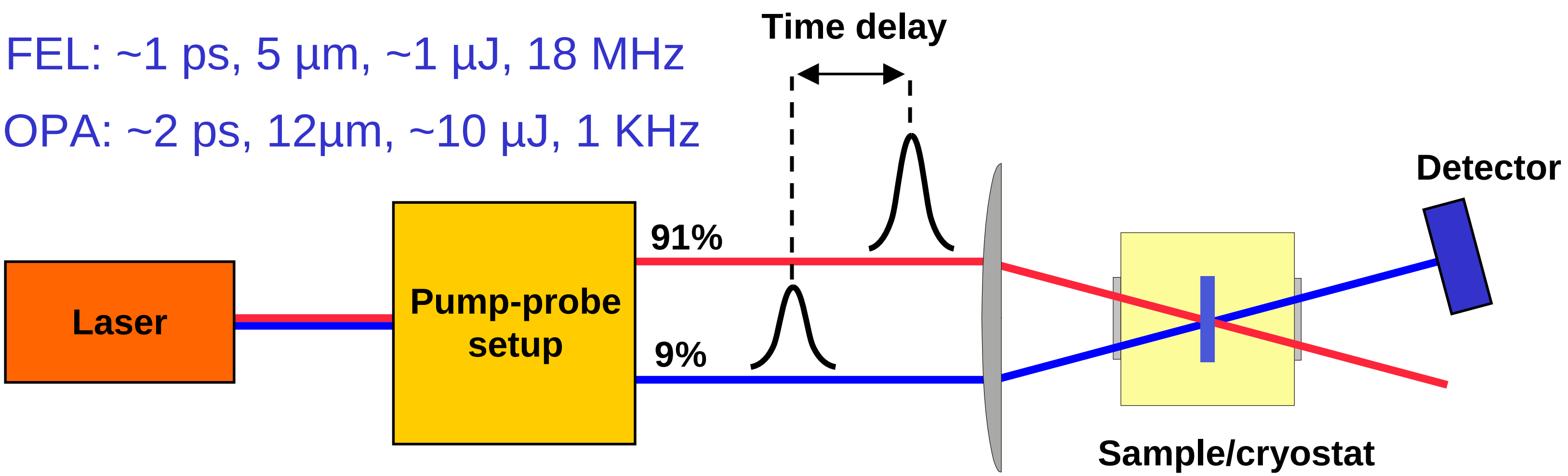
Time-resolved spectroscopy

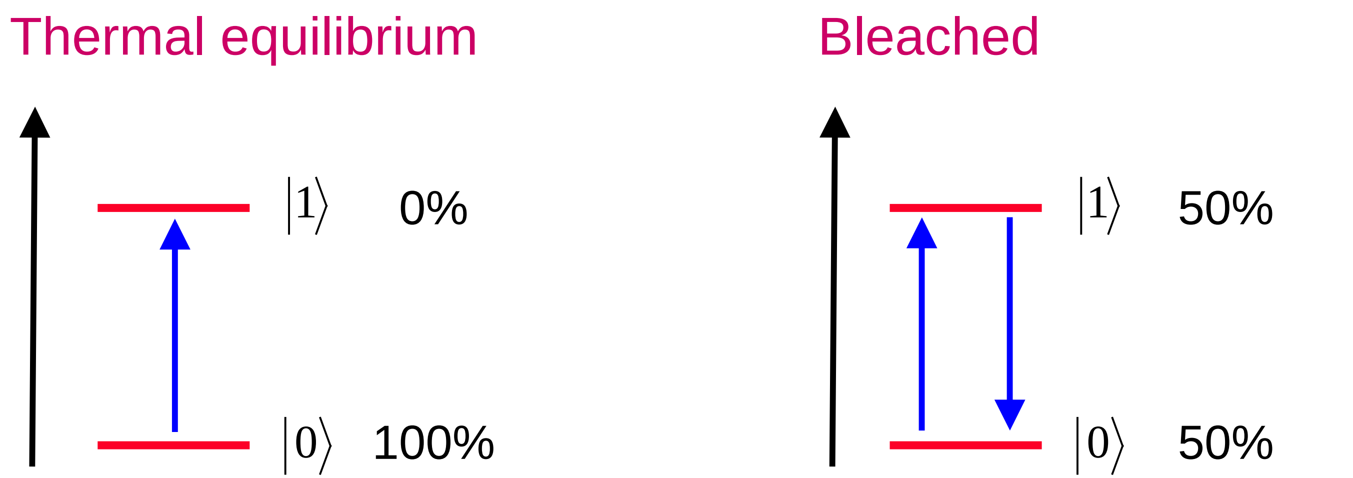
- *In-situ* transient-bleaching spectroscopy
- 5 - 290 K

Transient Bleaching Spectroscopy

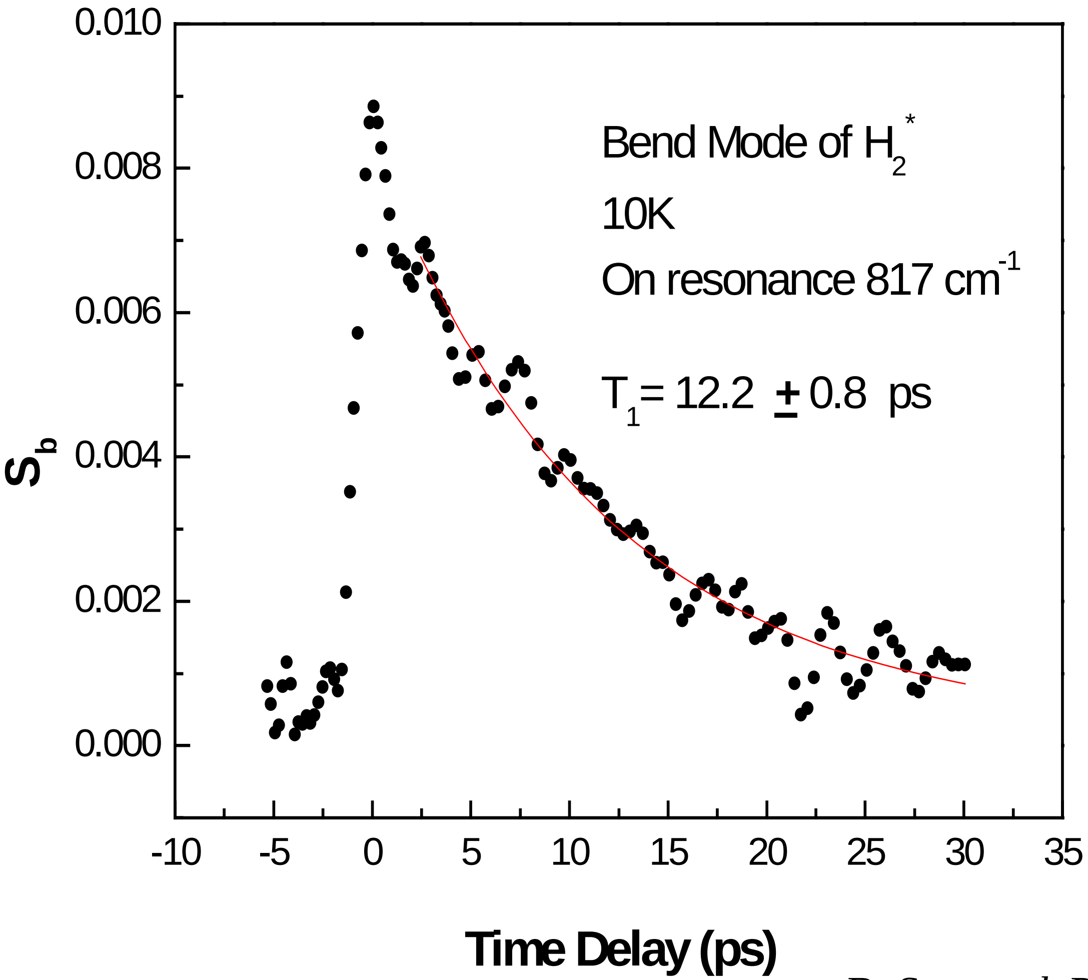
FEL: ~1 ps, 5 µm, ~1 µJ, 18 MHz

OPA: ~2 ps, 12µm, ~10 µJ, 1 KHz





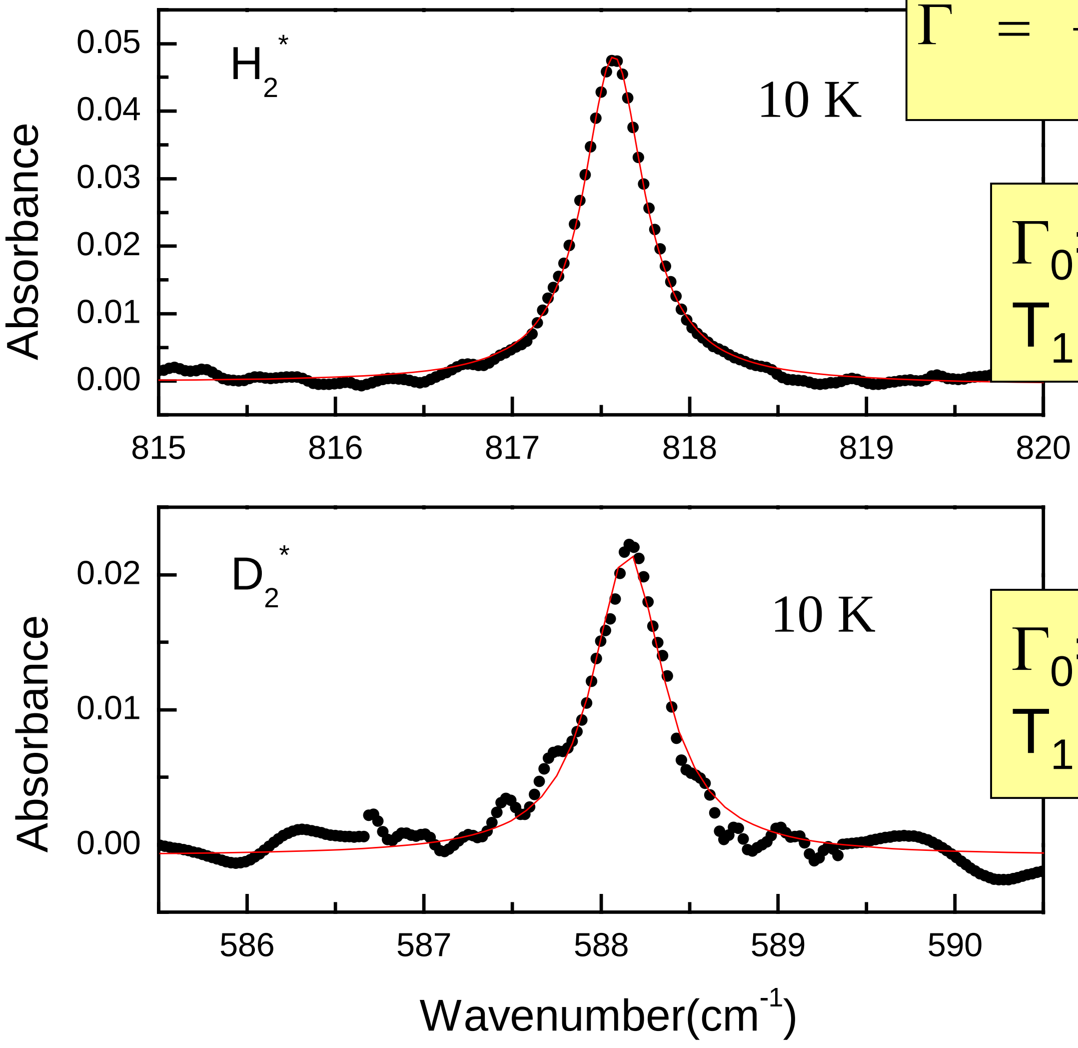
Vibrational Lifetime of H_2^* Bending Mode



B. Sun *et al*, PRL 96, 35501 (2006)

Natural Linewidth of Bending Modes

$$\Gamma = \frac{1}{2\pi c T_1} + \frac{1}{\pi c T_2} + \Gamma_{inhom}$$

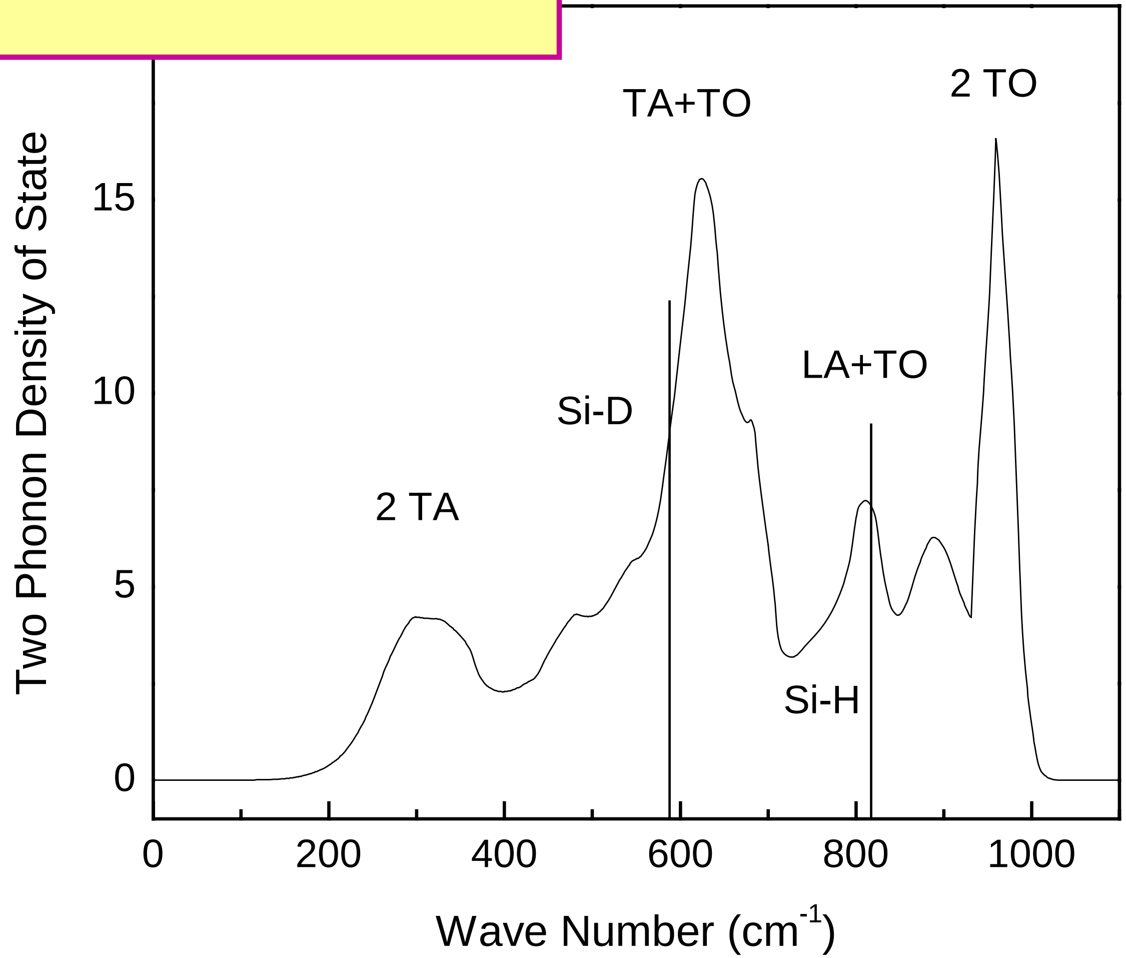


Γ_0= 0.42 ± 0.01 cm^{-1}
T_1 =12.6 ± 0.4 ps

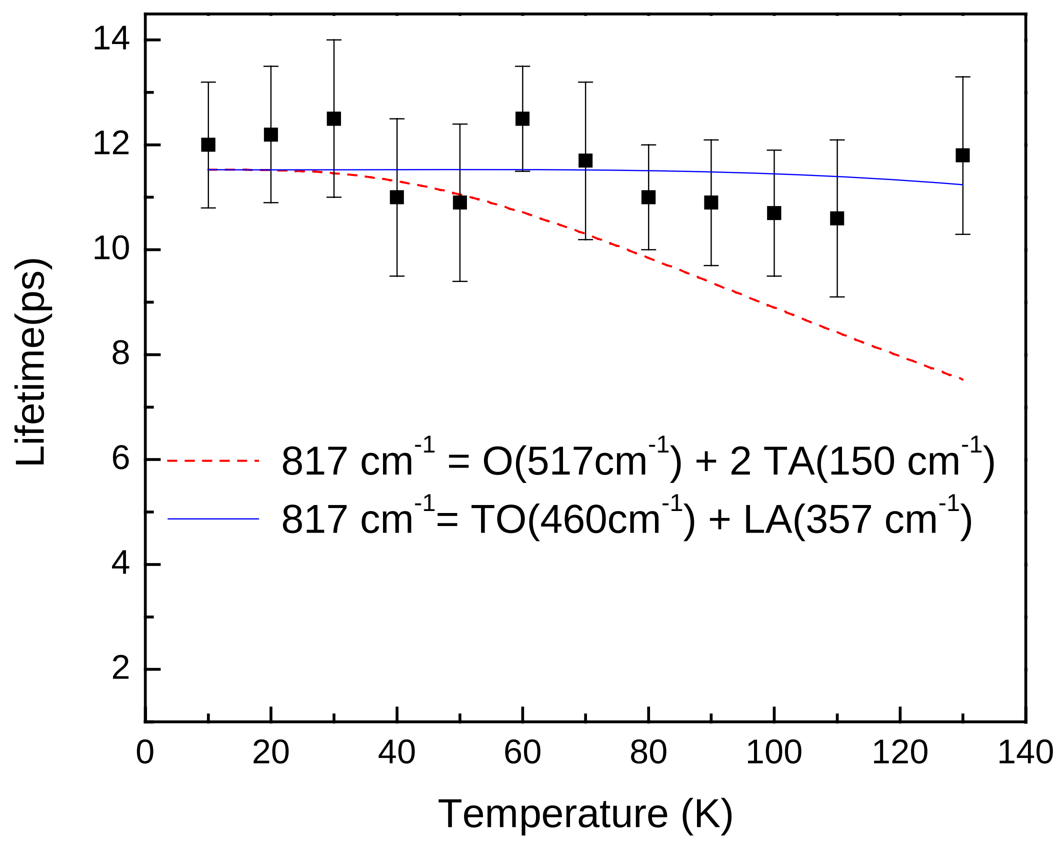
Γ_0= 0.51 ± 0.02 cm^{-1}
T_1 =10 ± 0.6 ps

Two-phonon Density of States in Si

$$\rho^{(2)}(\omega) = \int d\omega_1 \rho^{(1)}(\omega - \omega_1)\rho^{(1)}(\omega_1)$$

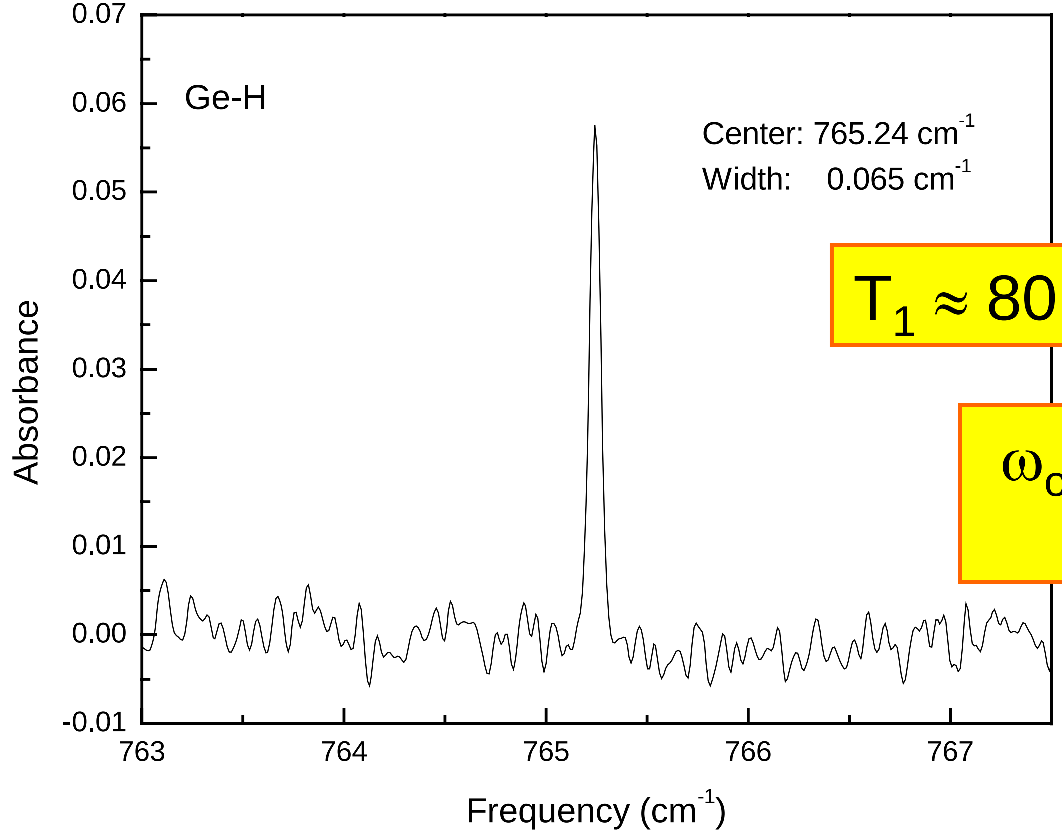


Temperature Dependence of Lifetime



H_2^* bending mode decays by lowest-order (two) phonon process

Ge-H bending mode of H_2* in Ge



$T_1 \approx 80$ ps

$\omega_{op} = 306$ cm^{-1}
N = 3

Decay Mechanism and Frequency Gap Law

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

The coupling constant $|G_{\{\nu\}}|$ decrease fast with increasing order *N* of the multiphonon process

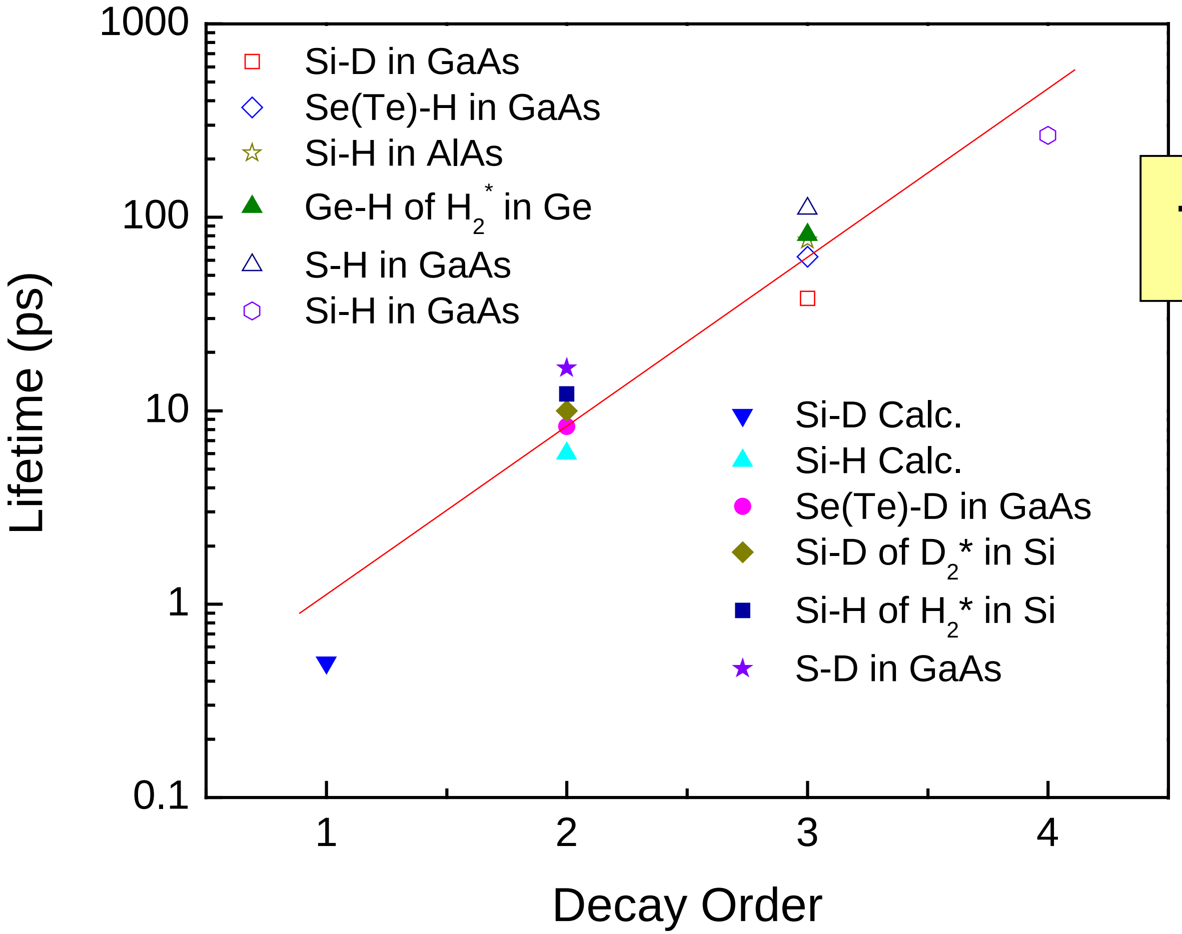
$$\gamma = \frac{1}{T_1} = 2\pi |G|^2 n\rho$$

$$G \cong A\delta^N \ ,0 < \delta << 1$$

Frequency Gap Law:	$\gamma(0) \propto \delta^{2N}$

Nitzan *et al*, J. Chem. Phys. **60**, 3929 (1974)
Egorov *et al*, J. Chem. Phys. **103**, 1533 (1995)

Decay-Order Dependence of Lifetime



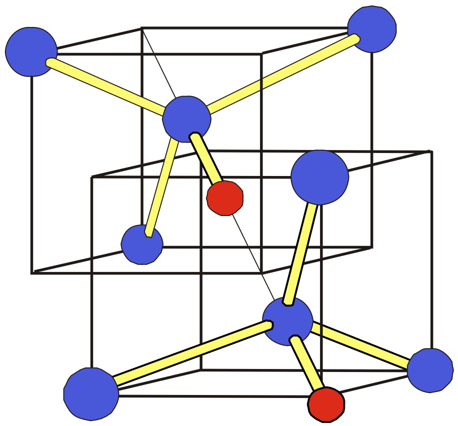
$$T_1 = A \cdot e^{B \cdot N}$$

A = 0.1 ps

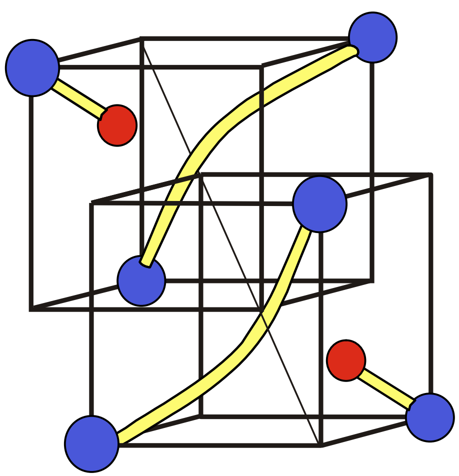
B = 2.0

Decay-order determines the lifetime of hydrogen bending modes

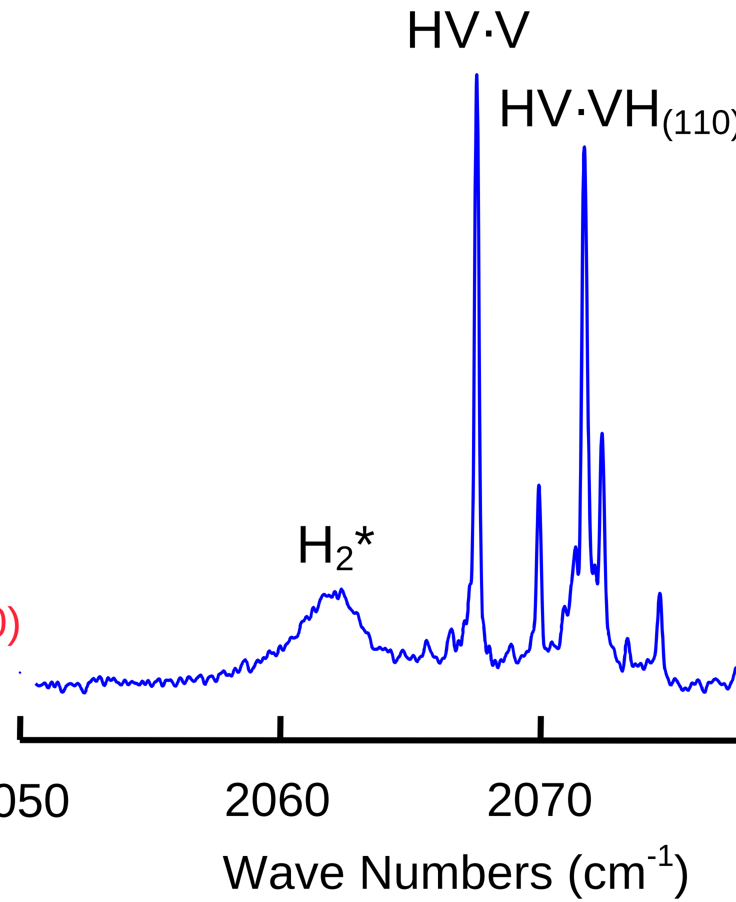
Structures and Absorption Spectroscopy



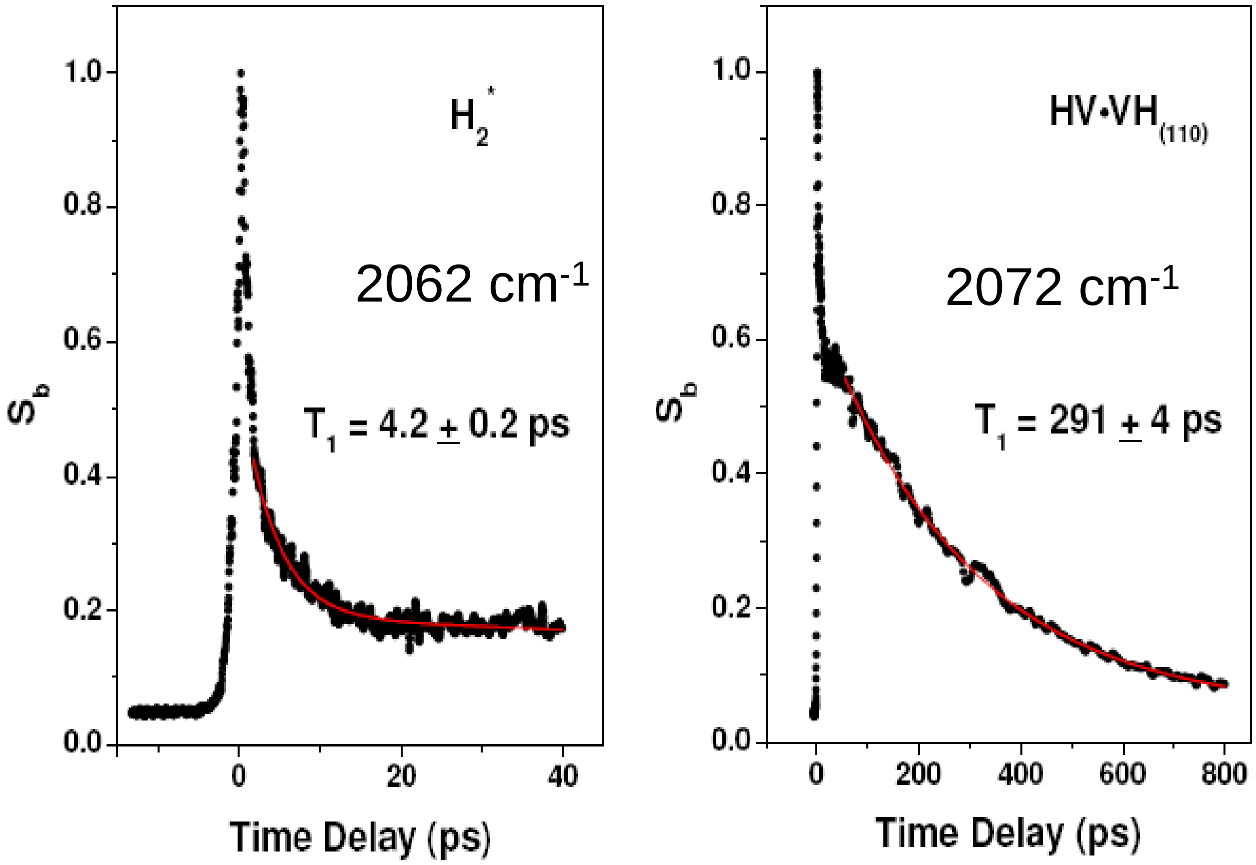
H_2^*



HV·VH(110)

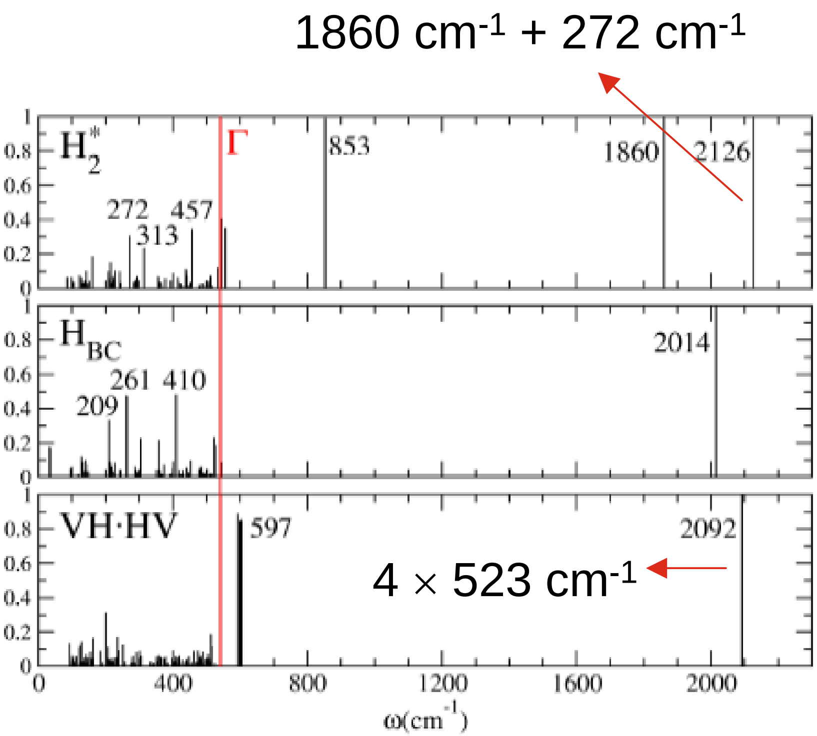


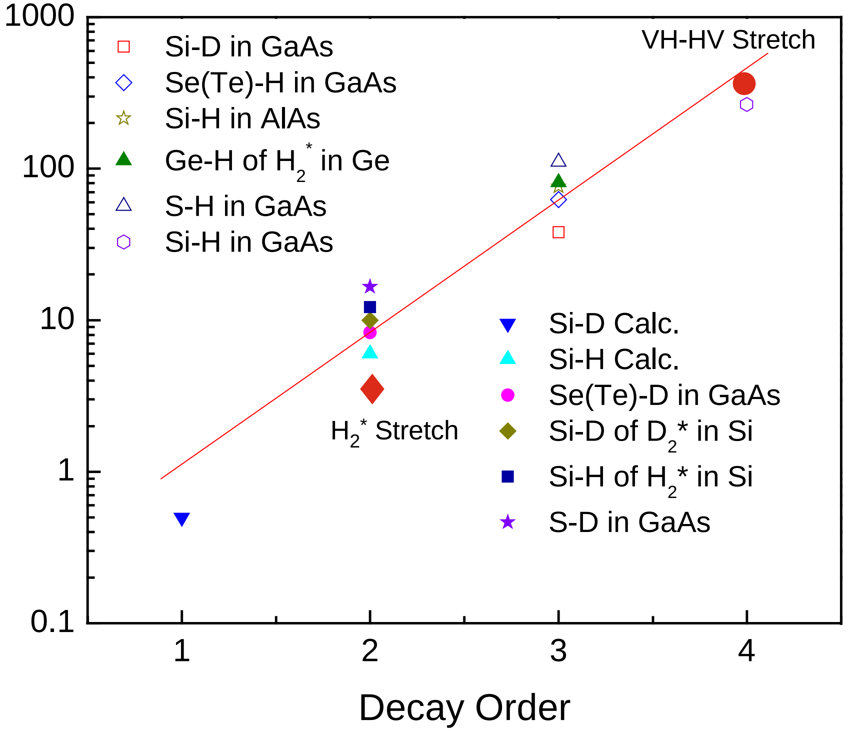
Vibrational Lifetime of H_2^* and HV·VH$_{(110)}$ Stretch



G. Lüpke *et al*, PRL 88, 135501 (2002)

MD Calculations of LVM Lifetimes





Stefan K. Estreicher *et al.*

The decay of high-frequency LVMs depends on the existence of lower-lying LVMs as well as pLVMs in the vibrational spectra of the defect.

Summary

- First measurements of the vibrational lifetime of H(D)-related bending modes in Si and Ge,
- Time and frequency domain consistent,
- H_2^* bending mode decays via the lowest order multi-phonon process,
- Vibrational lifetimes of H-related bending modes follow a universal frequency gap law,
- Molecular-dynamics calculations show that the decay of H-related stretch modes depends on the existence of lower-lying LVMs as well as pLVMs.

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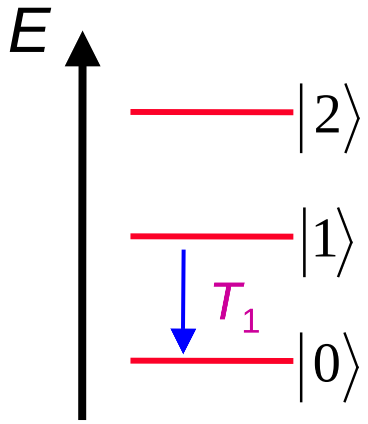
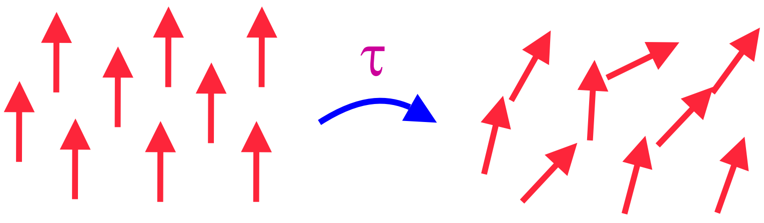
Dynamics of LVMs

Population relaxation



Characteristic time: T_1

Phase relaxation

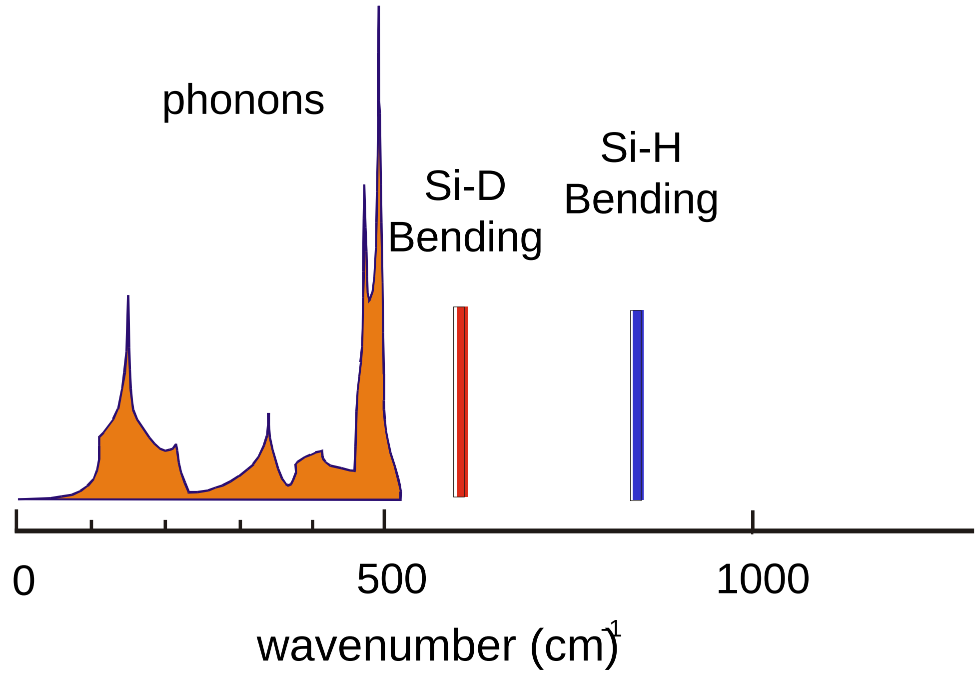


$$\langle \mu(\tau)\rangle = \langle \mu(0)\rangle \, e^{i\omega_{LVM}\tau} e^{-\tau/T_2^*}$$

Characteristic time: T_2^*

Decay Mechanism

- Radiative: No, $T_{1,IR}$~ 2 ms
- Electronic: No, H- or O-related defects studied here cannot introduce shallow electronic levels
- Vibrational: Yes, but requires emission of ≥ 2 phonons



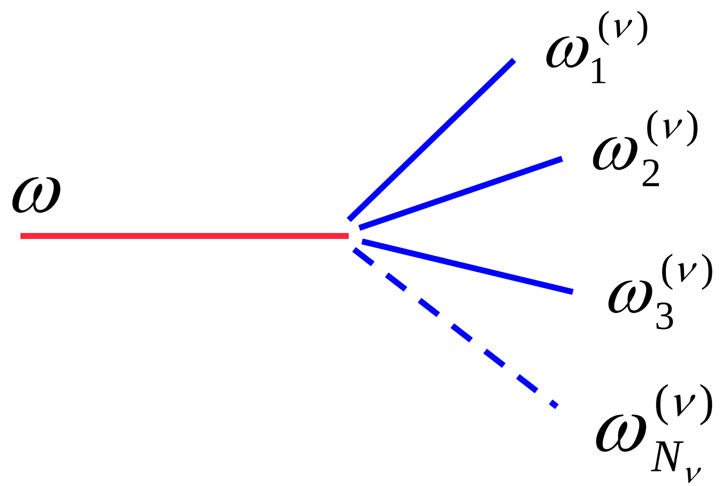
Multiphonon Relaxation

Decay of LVM into "phonon" bath:

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

Each channel ν:

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



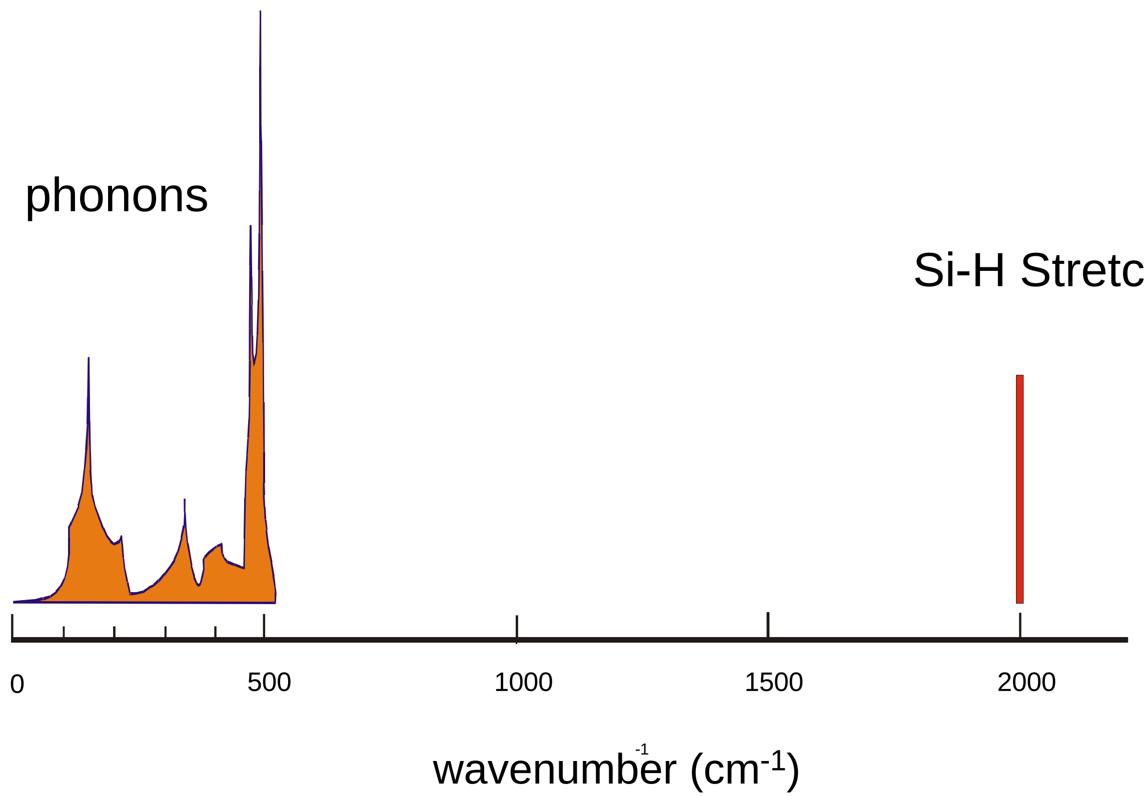
$$n_{\{\nu\}} = \frac{\exp(\eta\omega / k_B T) - 1}{\prod_{j=1}^{N_\nu} [\exp(\eta\omega_j^{(\nu)} / k_B T) - 1]}$$

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

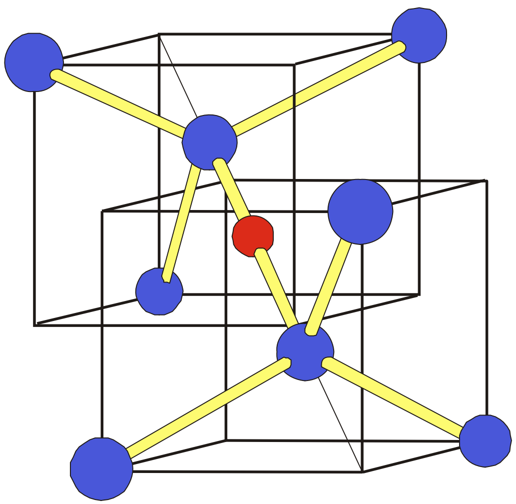
A. Nitzan *et al*, J. Chem. Phys. **60**, 3929 (1974)

Decay Mechanism

Since Si-H stretch modes are high-frequency modes, the decay mechanism is more complicated.

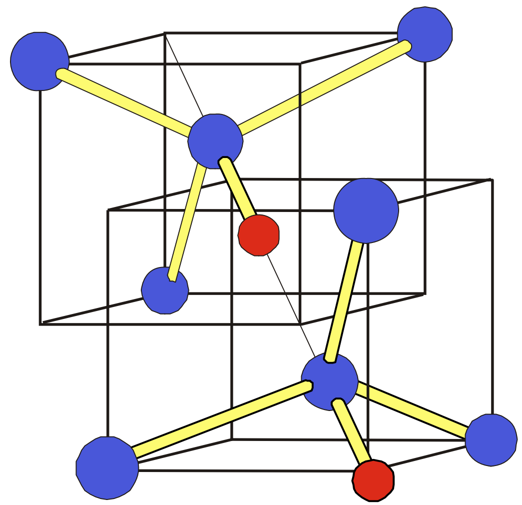


Interstitial-Type Defects



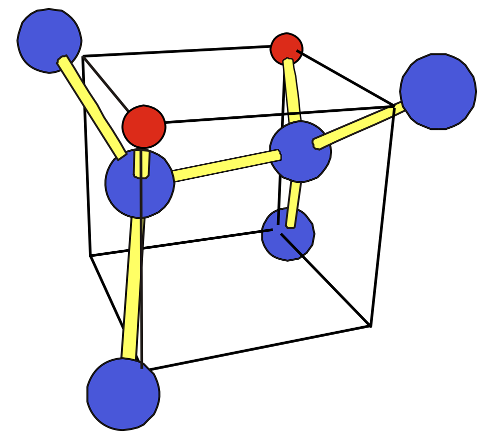
$H_{BC}^{(+)}$

ω (cm⁻¹)	T_1 (ps)
1998	7.8



H_2^*

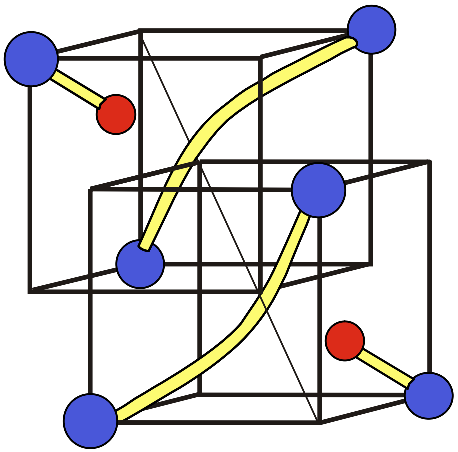
ω (cm⁻¹)	T_1 (ps)
1838	~3
2062	~4



IH_2

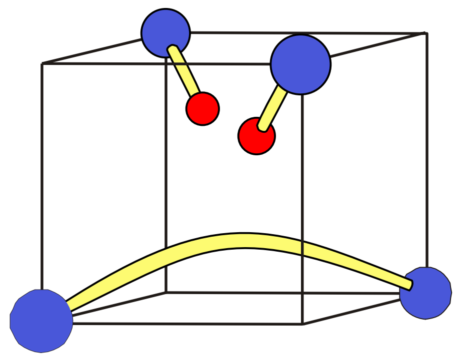
ω (cm⁻¹)	T_1 (ps)
1987	~12
1990	~11

Vacancy-Type Defects



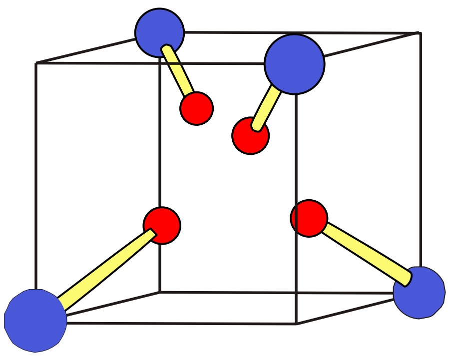
$HV{\cdot}VH_{(110)}$

ω (cm^{-1})	T_1 (ps)
2072	295



VH_2

ω (cm^{-1})	T_1 (ps)
2122	~ 60
2145	~42



VH_4

ω (cm^{-1})	T_1 (ps)
2223	~ 56

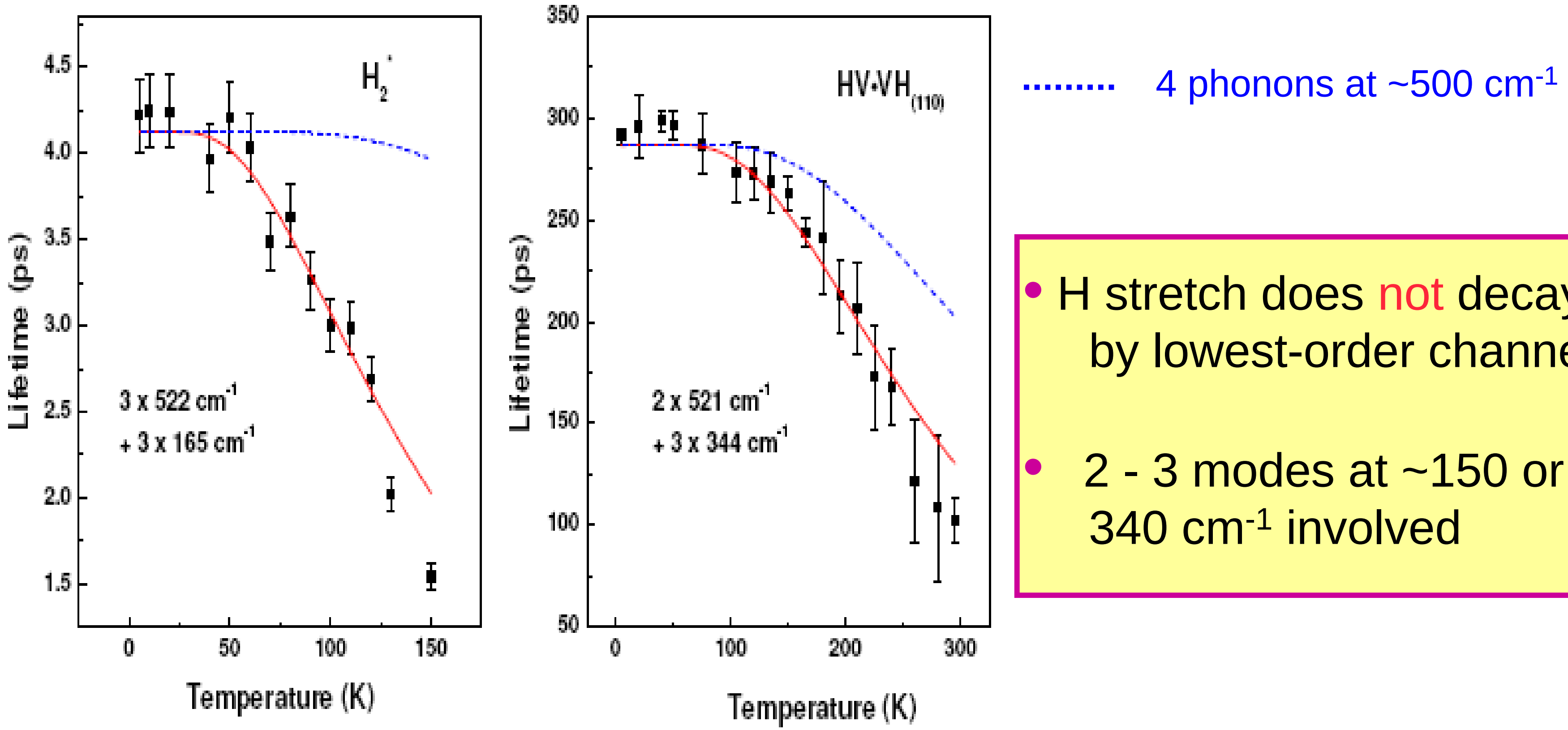
B. Pajot *et al*, Phys. Rev. B **59**, 7500 (1999)

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	4	5	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, *et al*. Phys. Rev. Lett. 87, 145501 (2001).

Temperature Dependence of T_1



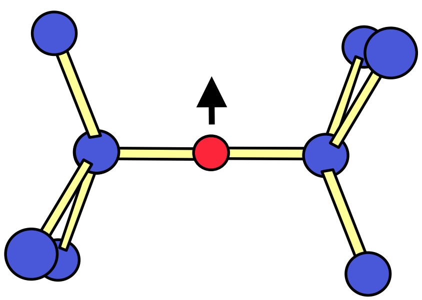
- H stretch does not decay by lowest-order channel
- 2 - 3 modes at ~150 or 340 cm^{-1} involved

G. Lüpke, X.Zhang, B. Sun, A. Fraser, N.H.Tolk, L.C.Feldman, Phys. Rev. Lett. 88, 135501 (2002).

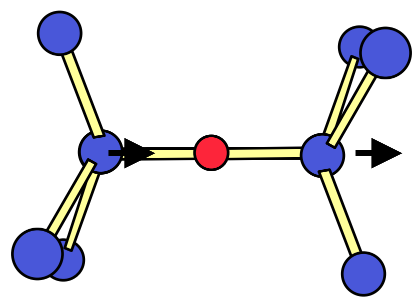
Exchange Modes

Vibrational dynamics of H-related Stretch determined by anharmonic coupling with Modes within phonon bands

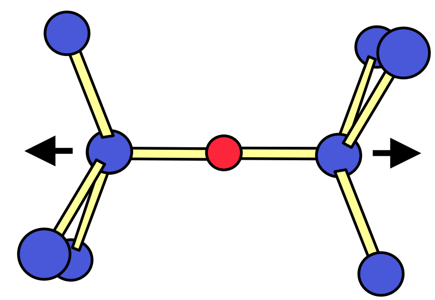
Candidates:



Si-H-Si bend



Perturbed acoustic phonon



Perturbed optic phonon