Dynamics of Local Vibrational Modes in Semiconductors

LPC Meeting, Jefferson Lab

May 16th, 2007

Colleagues & Collaborators

Our group:

Erik Spahr

Pjerin Luli

Dr. Baozhou Sun

Collaborators:

Norman Tolk, Vanderbilt University

Leonard Feldman, Vanderbilt University

Michael Stavola, Lehigh University

Matthew McCluskey, Washington State University

Supported by: NSF, DoE, Jeffress Foundation

Outline

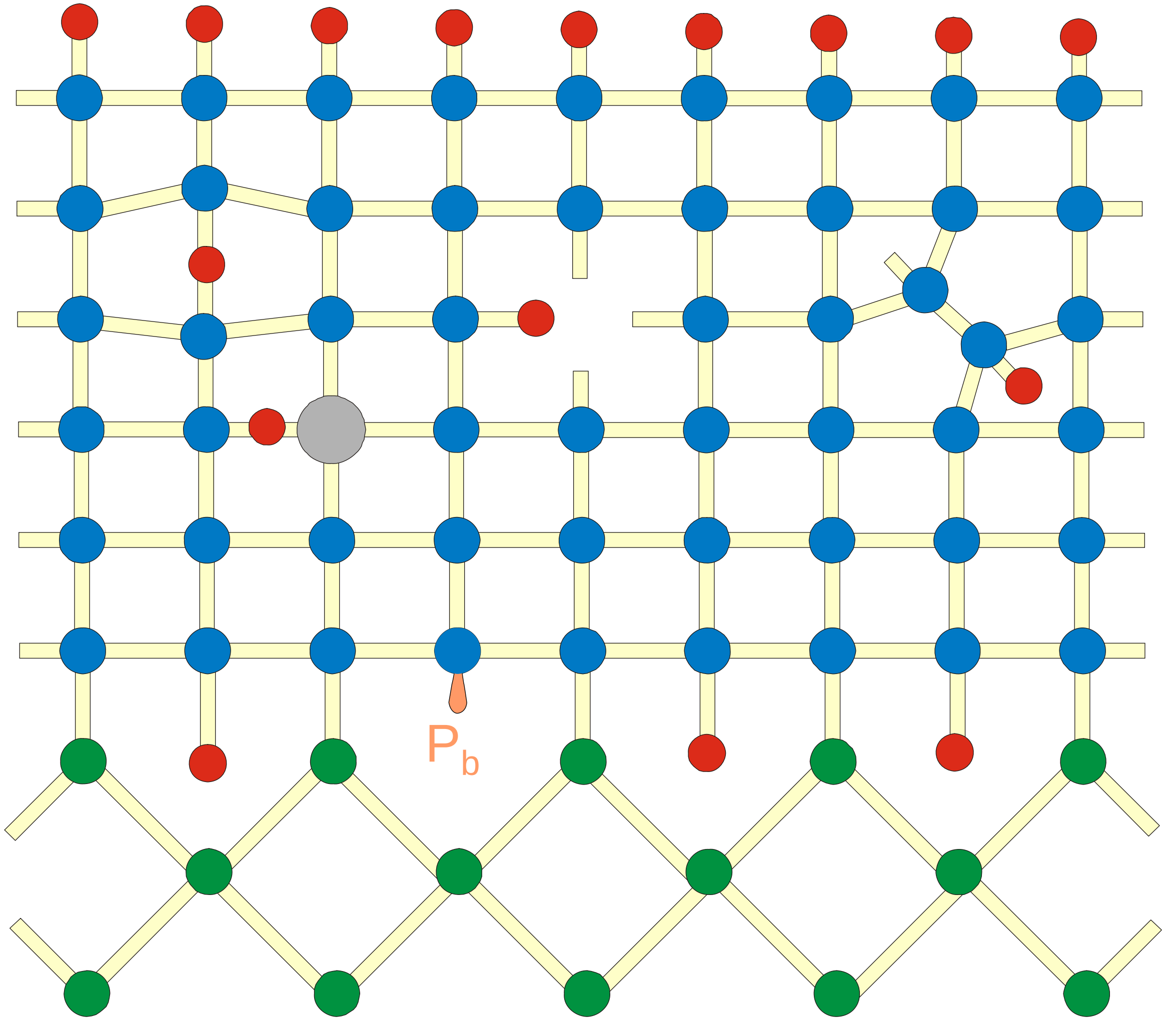
I. Summary of Previous Work: Vibrational Lifetime Study of H- and O-related Stretch Modes in Si and Ge

II. Vibrational Lifetimes of H-related Bend Mode in Si and other semiconductors

III. Future Work

O-H complexes in ZnO, MgO, etc.

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

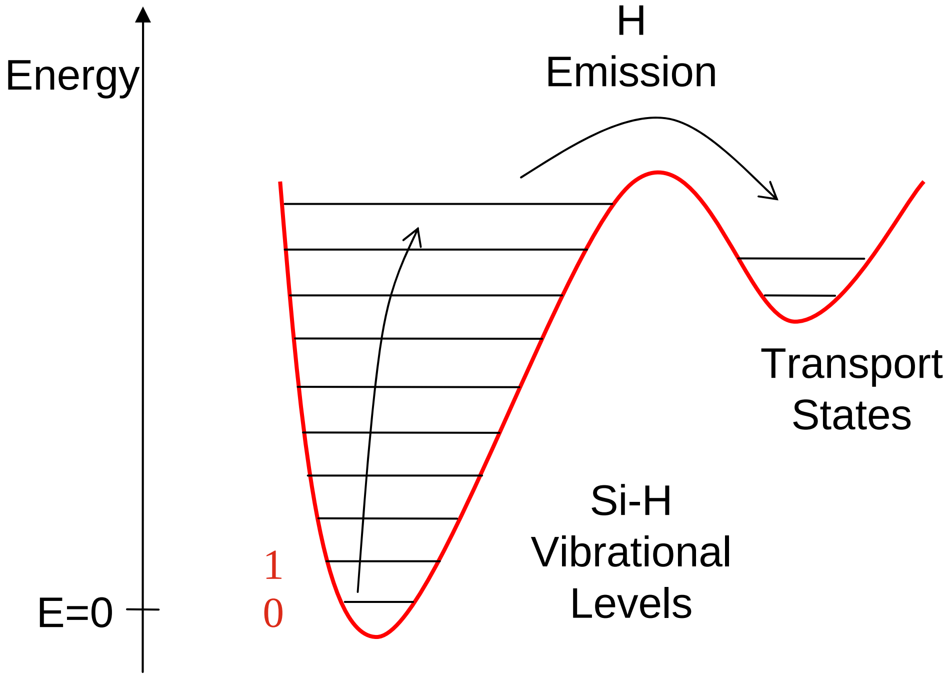
[1] J. W. Lyding *et al*, Appl. Phys. Lett. **68**, 2526 (1996)

[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)
C. G. Van de Walle *et al*. APL 68, 2526(1996)

Summary of Previous Study

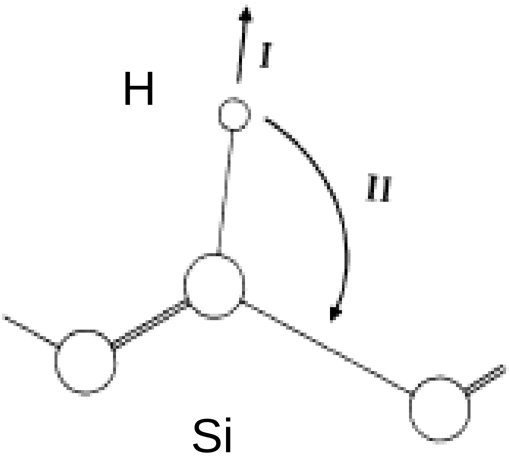
- Lifetime measurements of Si-H and Si-D stretch modes in Si
  - Time and frequency domain consistent
  - Strong structural dependence (4.2 ps for H_2^* & 295 ps for H_2V_2)
  - Lifetimes of Si-D modes are typically longer
  - Lifetime depends on the existence of lower-lying LVMs, pLVMs
- Lifetime measurements of Si-O stretch modes and the isotope effects in Si and Ge.
  - $^{17}O_i$ mode in Si lies in the highest density of three-phonon states (2TO+TA phonons), which gives rise to a shorter lifetime (T_1= 4.5 ps) than for the $^{16}O_i$ and $^{18}O_i$ modes (T_1~10 ps).
  - $^{16}O_i$ modes in Ge show much longer lifetime, T_1=125 ps, than in Si, resulting from different infrared activities of decay channels

What determines the lifetime?

Four factors:

1. Order of decay channel: Energy of Si-H is larger than Si-D(~$\sqrt{2}$), the number of accepting modes is larger for Si-H, strength of coupling constant is smaller, so Si-H lifetime is longer than Si-D. (Frequency-Gap Law)
2. Density of states of accepting phonon modes
3. Anharmonicity: The decay of the LVM into other modes is an anharmonic effect. If the amplitude is smaller, the anharmonicity is smaller which gives rise to longer lifetime. (Pajot, PRB, 48,17776 (1993))
4. IR vs. Raman activity of the accepting modes

Dissociation Pathways of Si-H Bonds



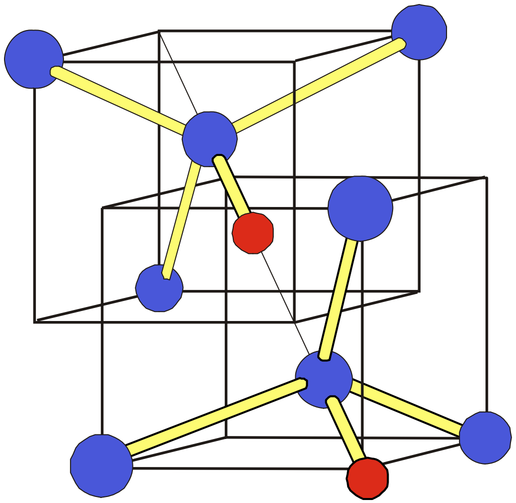
(a) The barrier of path I is much higher than path II.

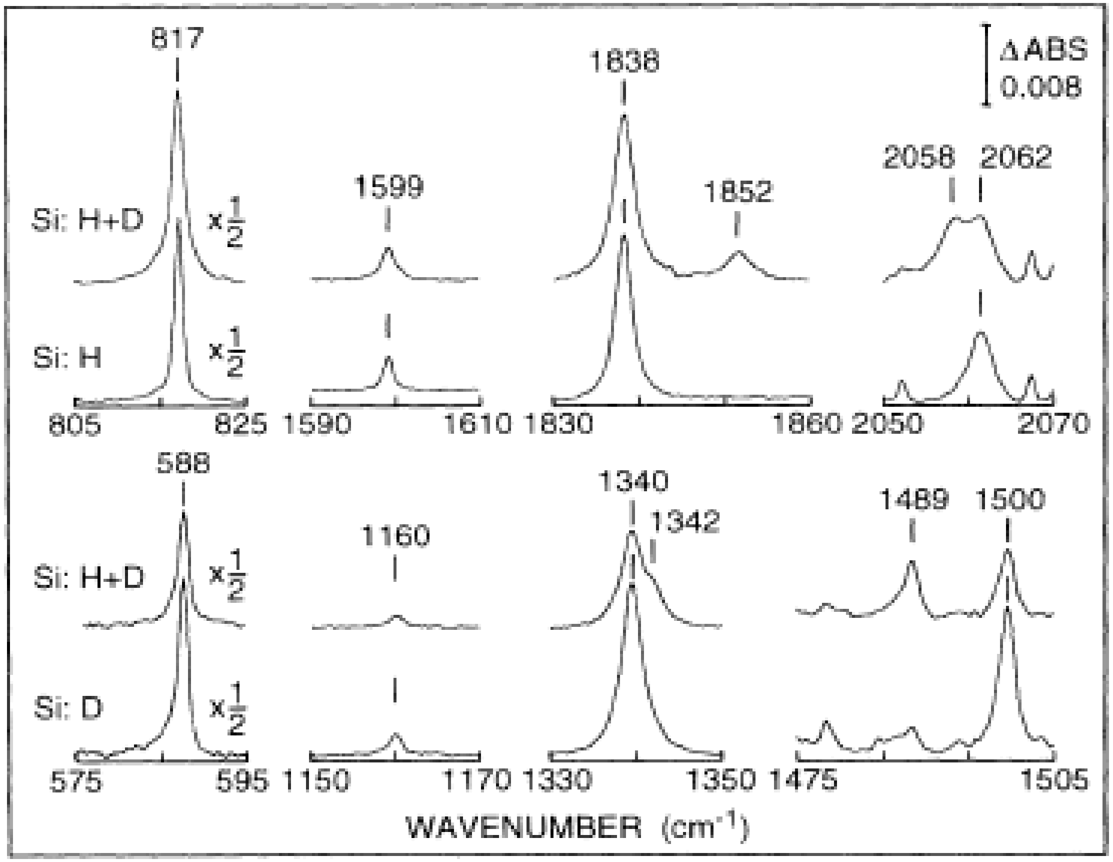
(b) Path II leads to a H position near the BC site, which is more stable.

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

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

Bend Mode in H_2^*





Four absorption modes:

817 cm^{-1} Bend mode

1599 cm^{-1} Overtone

1838 cm^{-1} Stretch (AB)

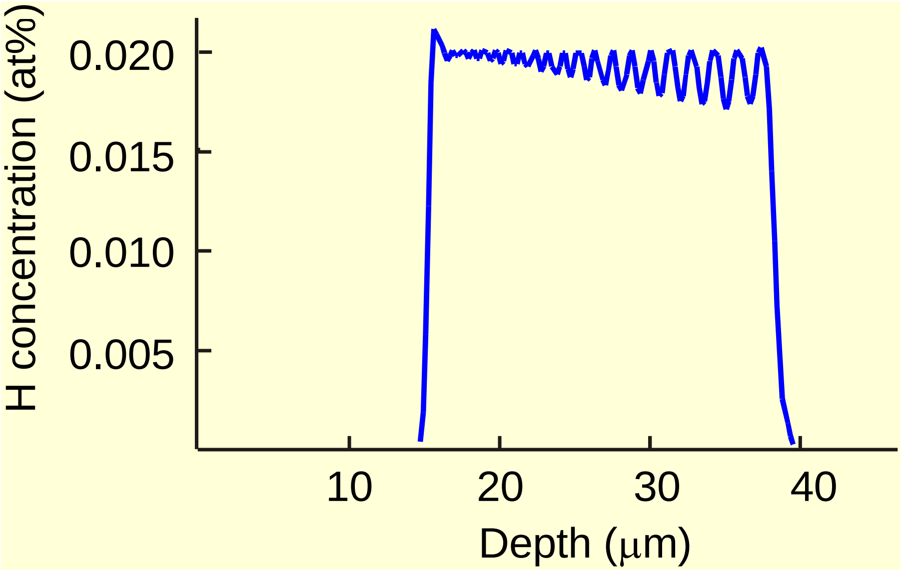
2062 cm^{-1} Stretch (BC)

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

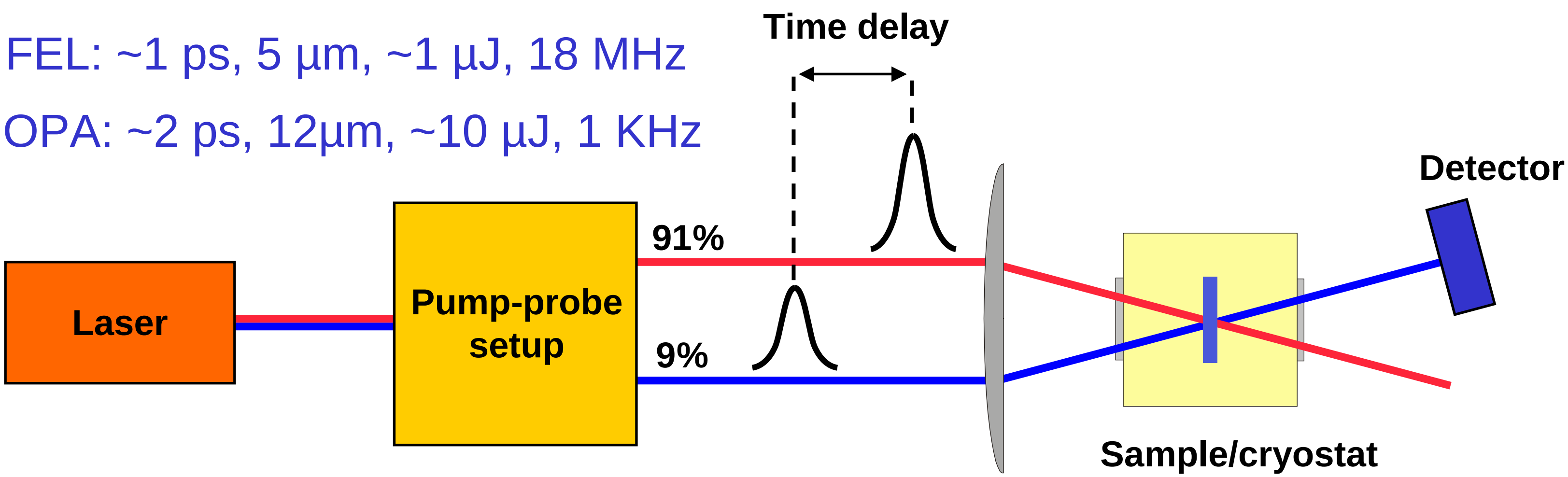
Time-resolved spectroscopy

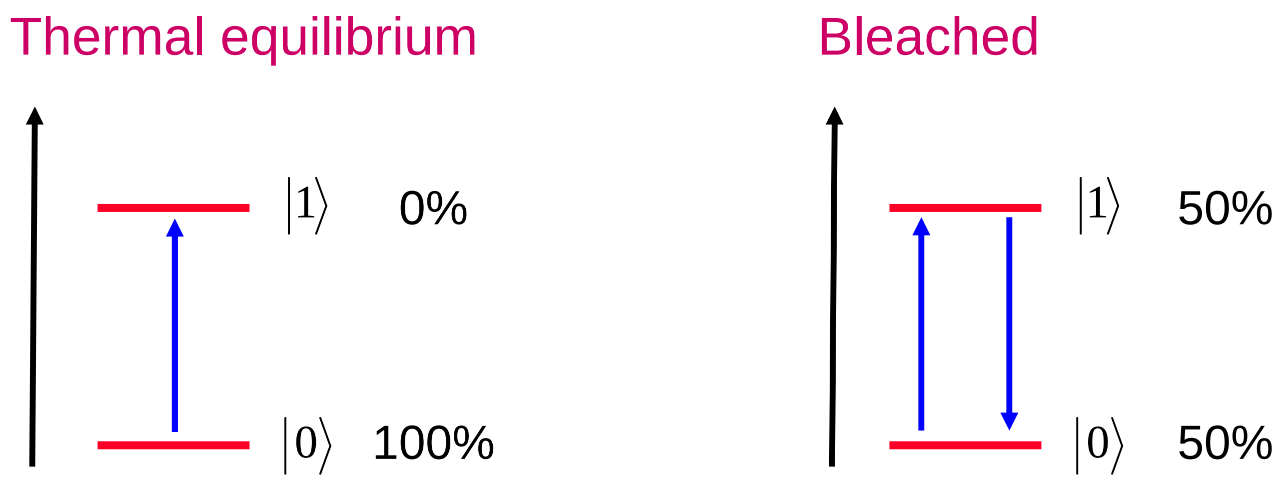
- *In-situ* transient-bleaching spectroscopy
- 5 - 290 K

Transient Bleaching Spectroscopy

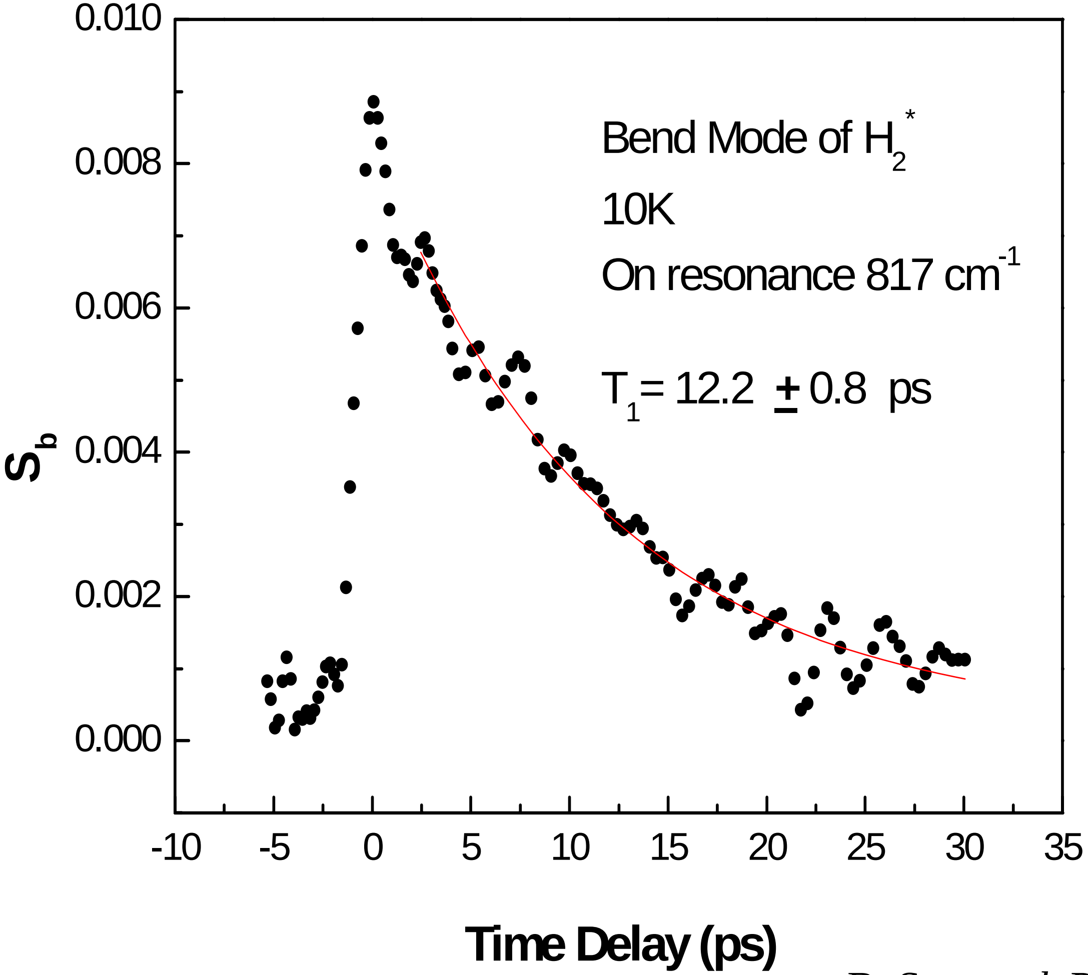
FEL: ~1 ps, 5 µm, ~1 µJ, 18 MHz

OPA: ~2 ps, 12µm, ~10 µJ, 1 KHz





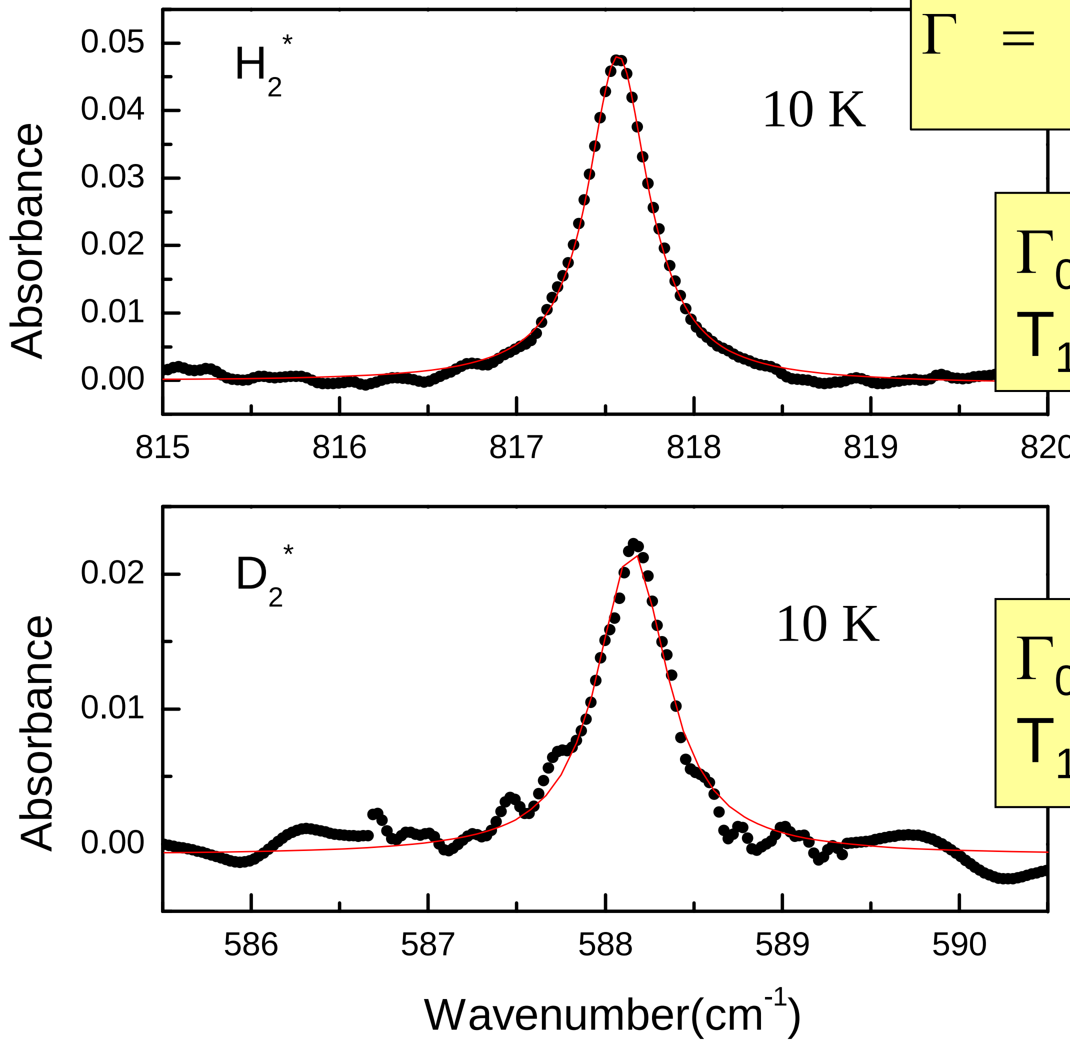
Vibrational Lifetime of H_2^* Bending Mode



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

Natural Linewidth of Bending Modes

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



$\Gamma_0 = 0.42 \pm 0.01\ cm^{-1}$

$T_1 = 12.6 \pm 0.4$ ps

$\Gamma_0 = 0.51 \pm 0.02\ cm^{-1}$

$T_1 = 10 \pm 0.6$ ps

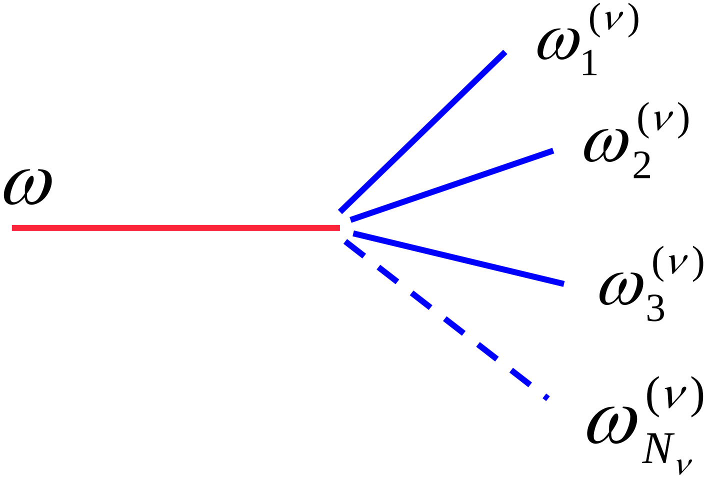
Multiphonon Relaxation

Decay of LVM into "phonon" bath:

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

Each channel ν:

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



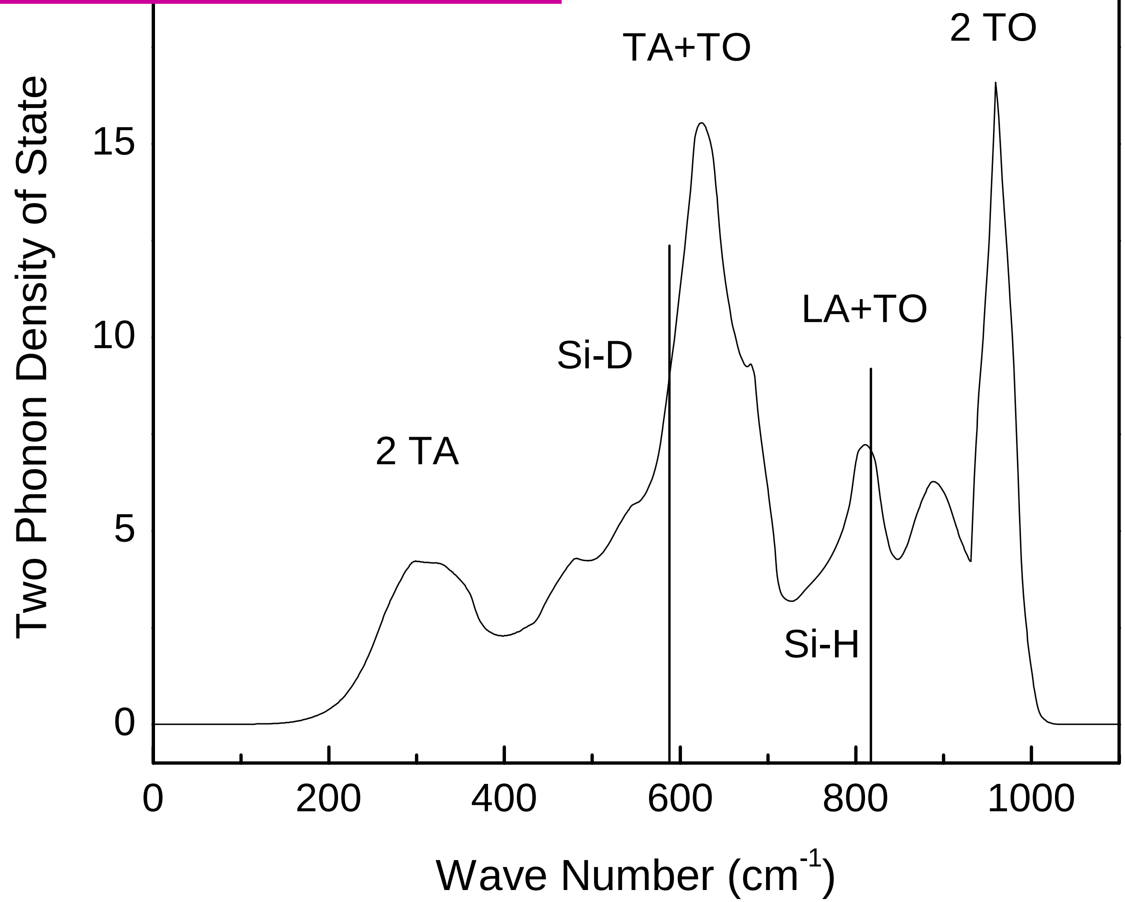
$$n_{\{\nu\}} = \frac{\exp(\hbar\omega / k_B T) - 1}{\prod_{j=1}^{N_\nu} [\exp(\hbar\omega_j^{(\nu)} / k_B T) - 1]}$$

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

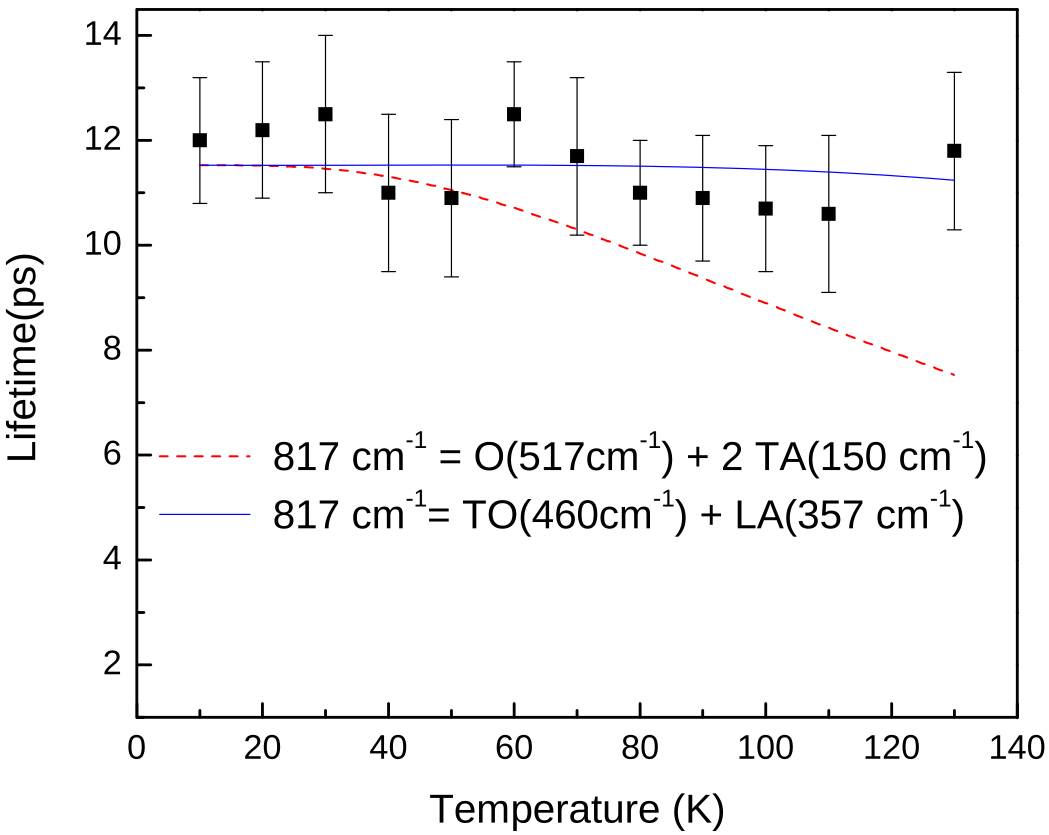
A. Nitzan *et al*, J. Chem. Phys. **60**, 3929 (1974)

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

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

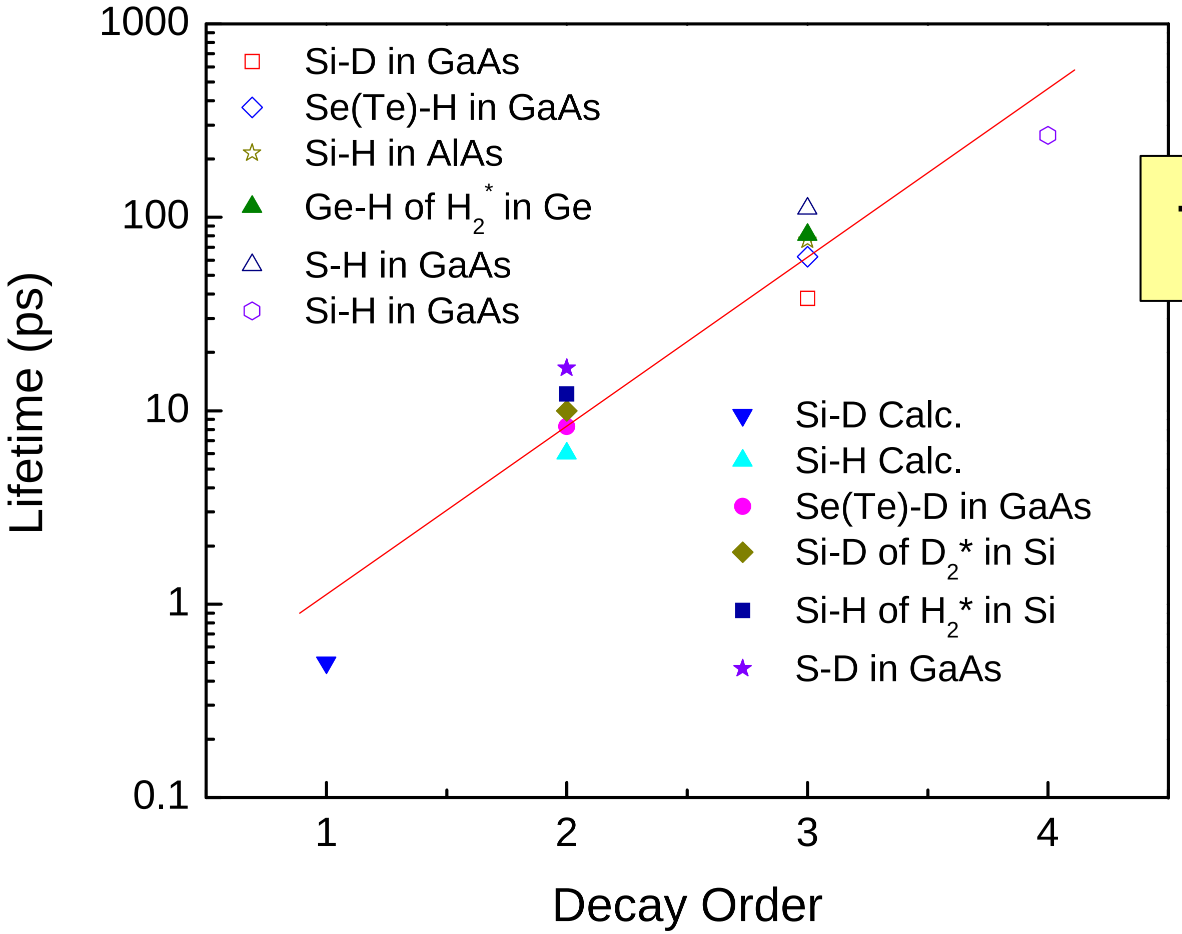
$$\gamma = \frac{1}{T_1} = 2\pi |G|^2 n\rho$$

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

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



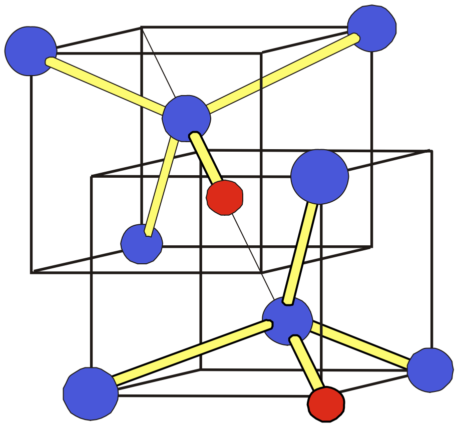
$$T_1 = A \cdot e^{B \cdot N}$$

A = 0.1 ps

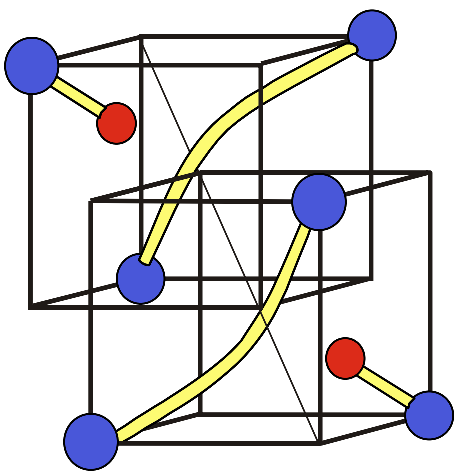
B = 2.0

Decay-order determines the lifetime of hydrogen bending modes

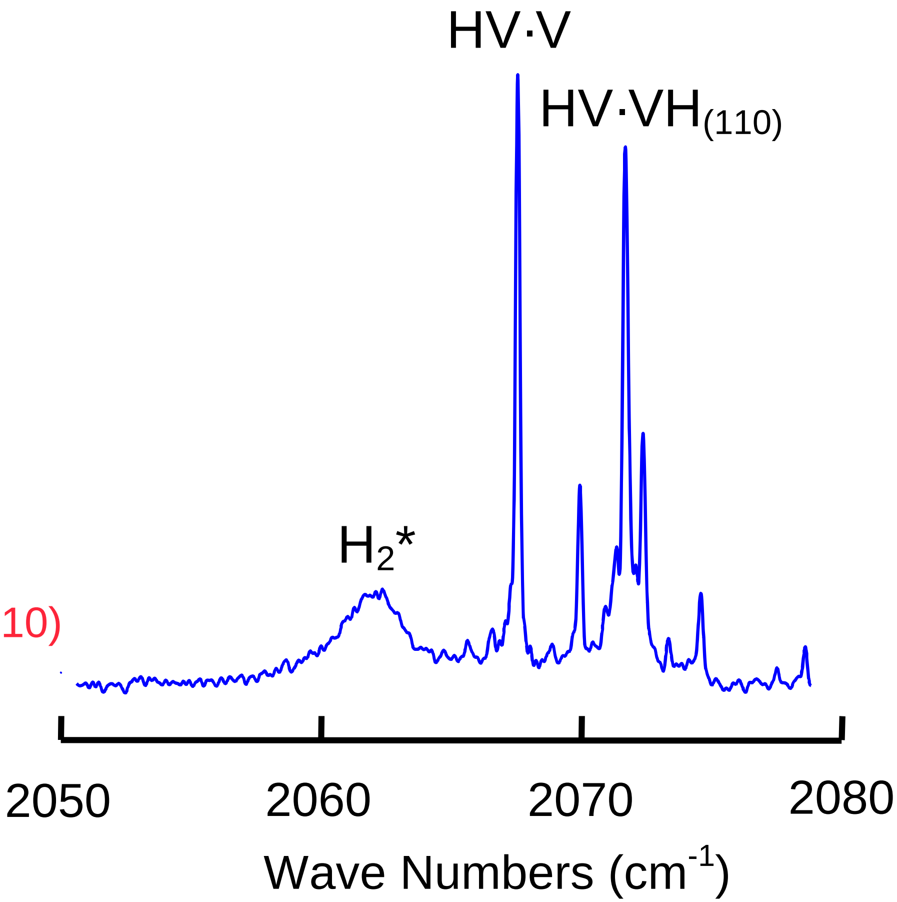
Does the Frequency-Gap Law hold for the Stretch Modes?



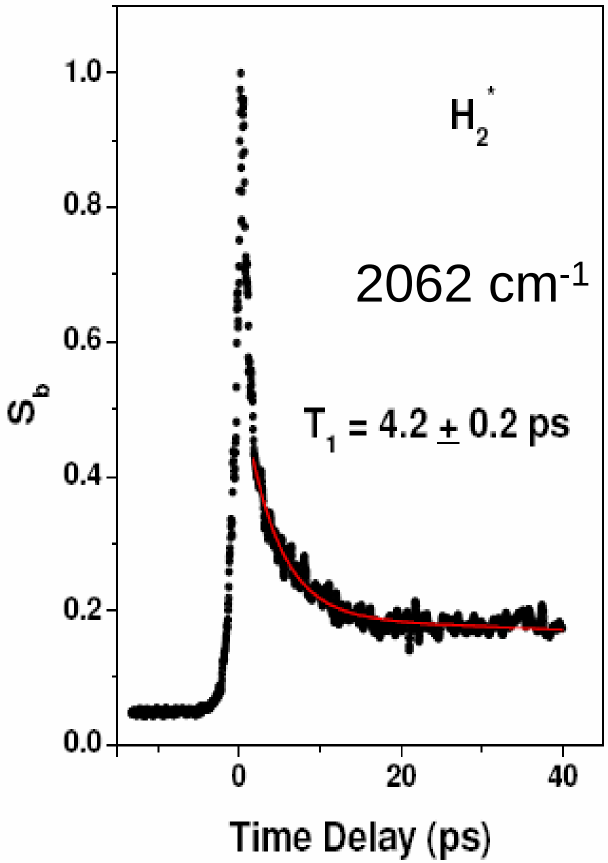
H_2^*

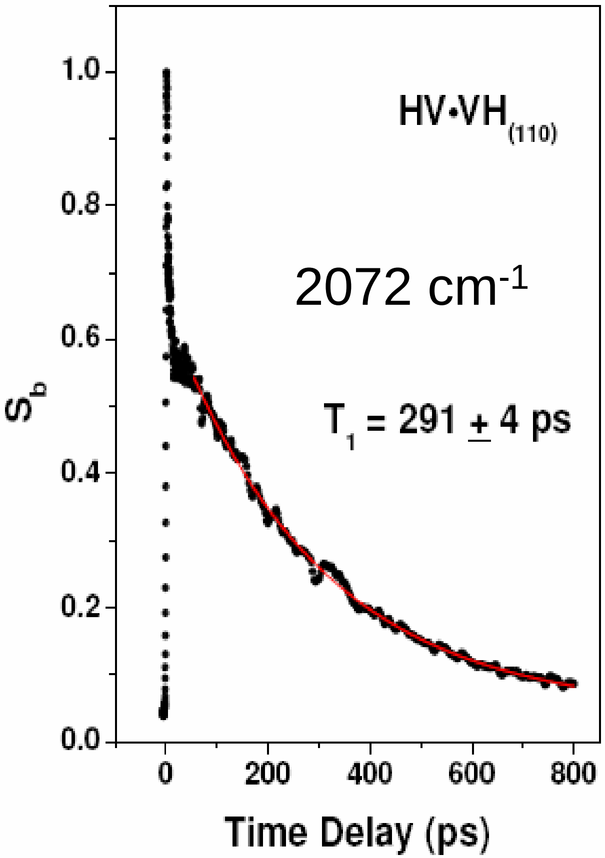


$HV \cdot VH_{(110)}$



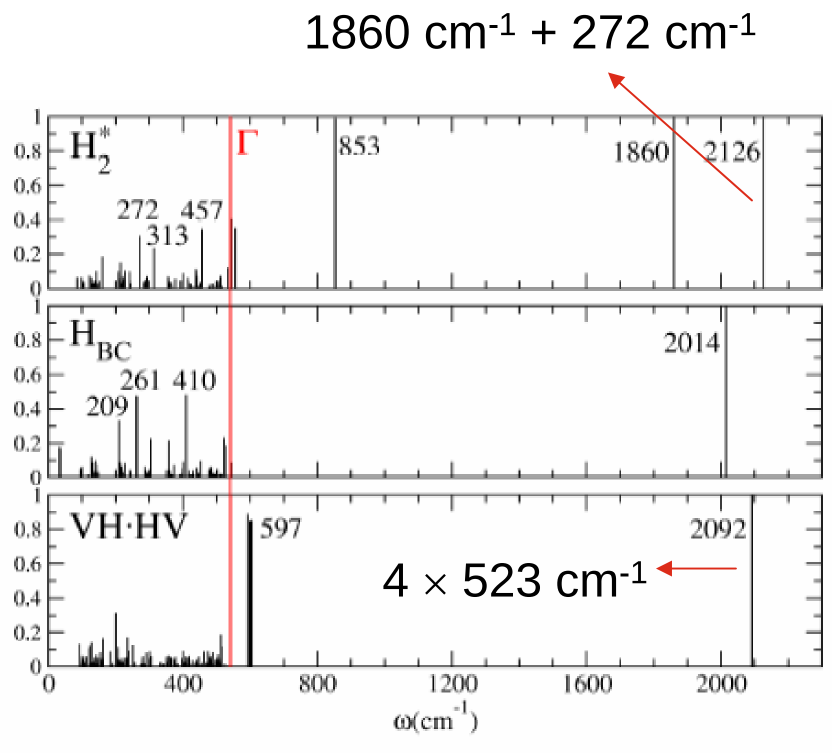
Vibrational Lifetime of H_2^* and HV·VH$_{(110)}$ Stretch

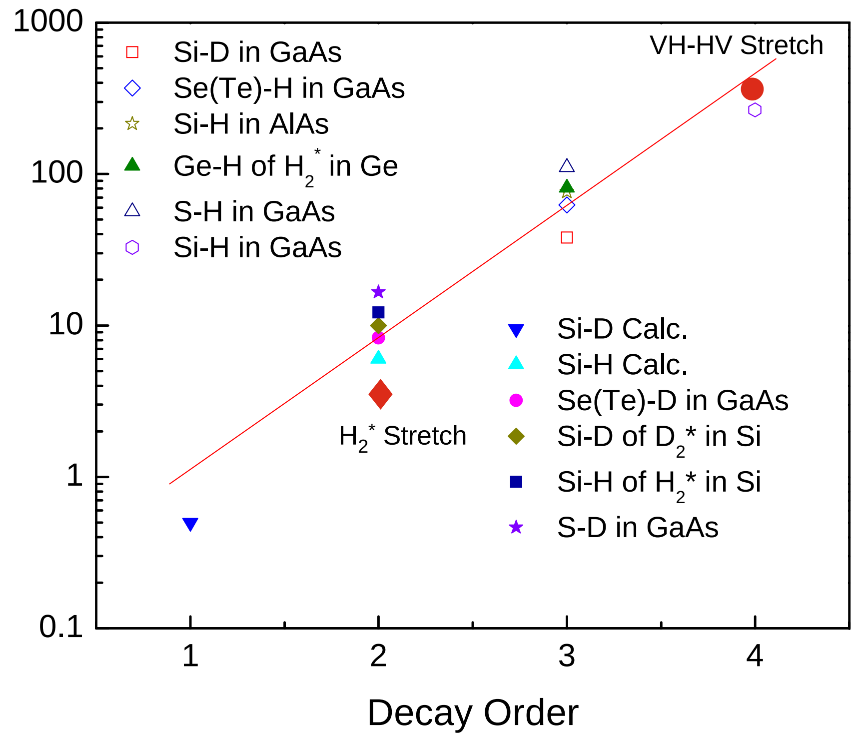




G. Lüpke *et al*, PRL 88, 135501 (2002)

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.

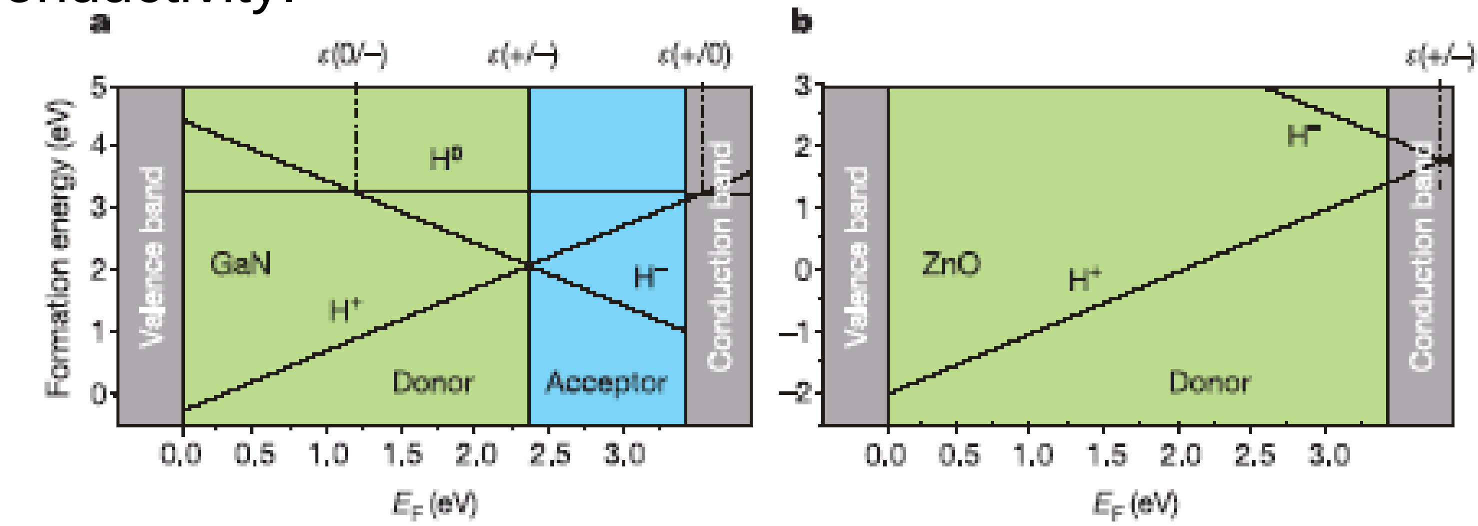
Future Experiments

- H (dopant) in ZnO: O-H complex at 3 μm
- O-H complexes in MgO: V_{OH}, V_{OD}, V_{OH}^{-}, V_{OD}^{-}

Hydrogen in ZnO: A Shallow Donor

Why ZnO: It is a wide band-gap (3.37 eV) compound semiconductor that is suitable for blue optoelectronic applications. ZnO has unique piezoelectric, optical and electrical properties.

A puzzle is that ZnO almost always exhibits strong n-type conductivity.



Theory: Recent calculations found that H is a source of the conductivity.

Van de Walle, *et al*, Nature 43, 626(2003)

IR Spectroscopy of H in ZnO and Defect Structure

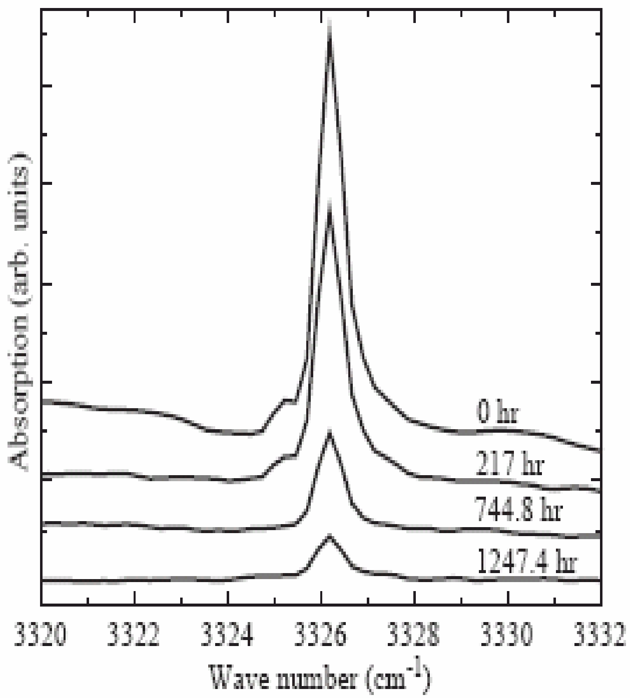
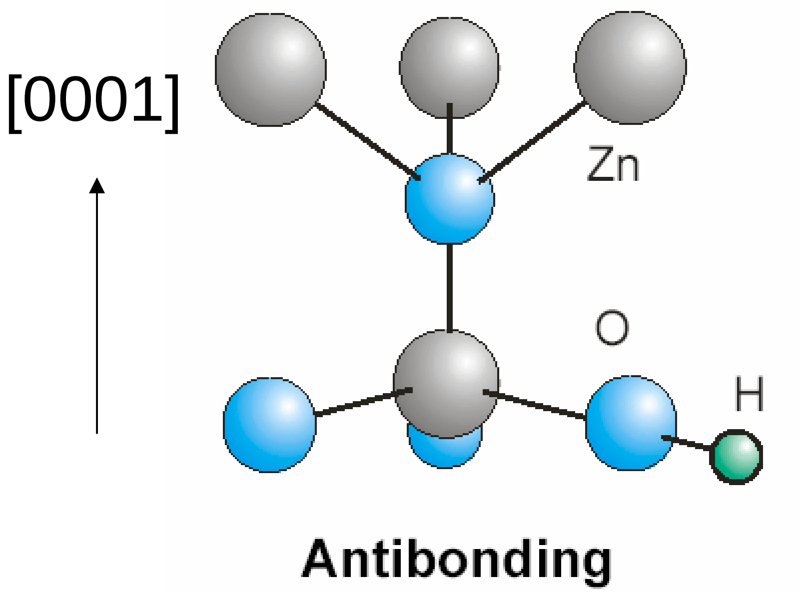


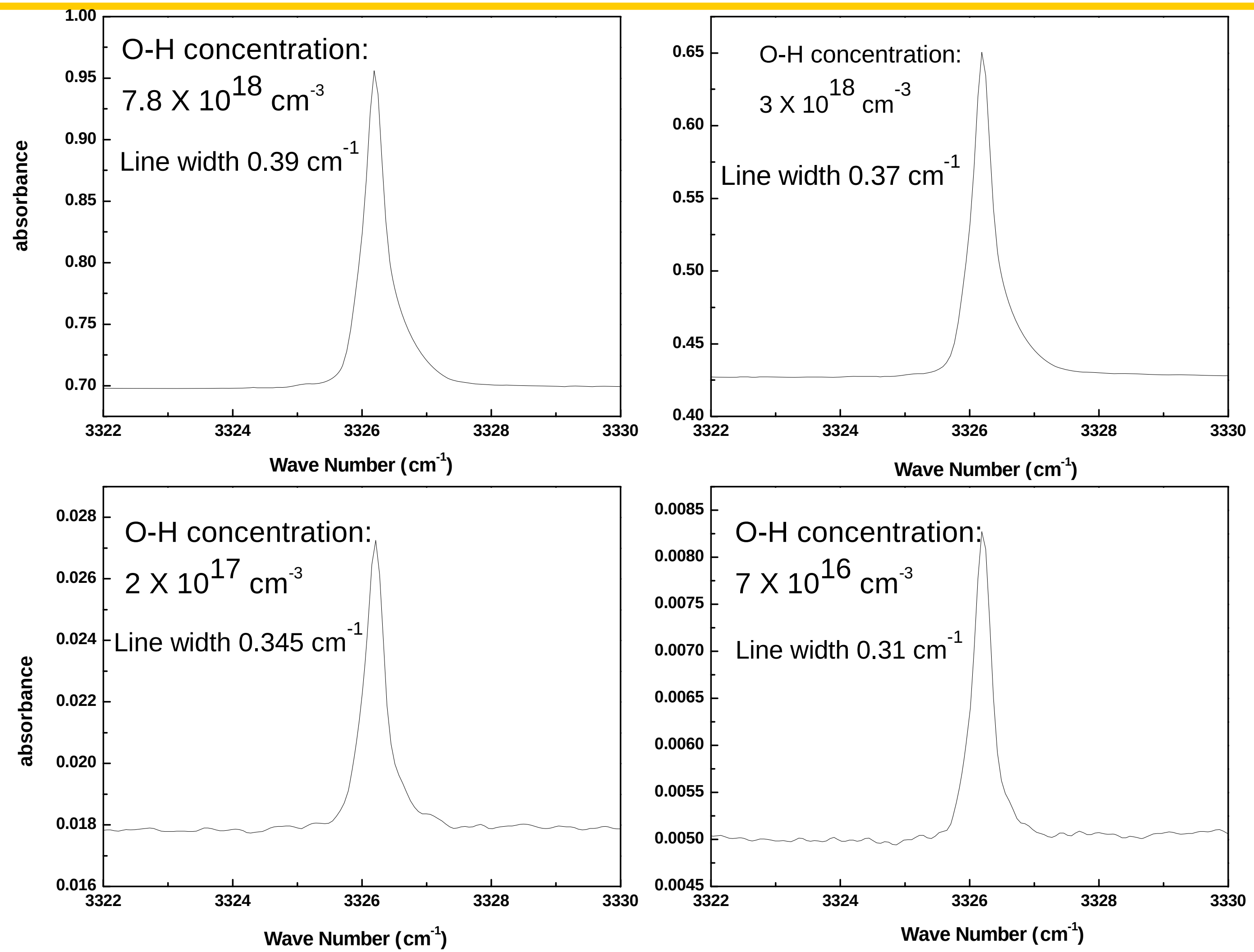
Fig. 3. Decay of the O–H LVM. The annealing temperature was 300 K and the sample temperature was 14 K.



M.D. McCluskey, *et al*, APL, 81, 3807(2002)

S. J. Jokela, *et al*, Physica B 340-342,221(2003)

Free Carrier Dependence of Linewidth



Michael Stavola, unpublished

Summary

- First measurements of the vibrational lifetime of H(D)- and O-related stretch modes in Si and Ge,
- 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.
- Future experiments are concerned with H(dopant) and O-H complexes in ZnO and MgO.