
Dynamics of Local Vibrational Modes in Semiconductors

LPC Meeting, Jefferson Lab

March 10th, 2005

Outline

- I. Summary of Previous Work: Vibrational Lifetime Study of Stretch Modes
- II. Vibrational Lifetime of Bend Mode in Si
- III. Future Work
 - 1. O-H complex in ZnO
 - 2. H-dopant complexes in compound semiconductors

What we have done:

- 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
 - Does not decay via lowest-order channel
- 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 ($T_1 \sim 10$ ps).
 - $^{16}O_i$ modes in Ge show much longer lifetime, $T_1 = 125$ ps, than in Si, which is resulted from different infrared activities of decay channels

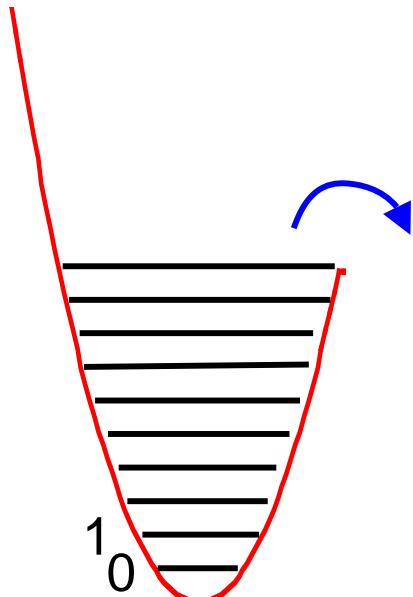
What determines the lifetime of local vibrational mode?

Four factors:

1. Order of decay channel: Energy of Si-H is larger than Si-D($\sim\sqrt{2}$), 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. (Nitzan's gap law)
2. 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))
3. IR vs. Raman activity of the accepting modes
4. Density of states of accepting phonon modes

Motivation to study bend modes

- Dissociation of Si-H bonds is controlled by the Si-H bend mode
- Bend modes can be the accepting channel of stretch modes



Dissociation rate:

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

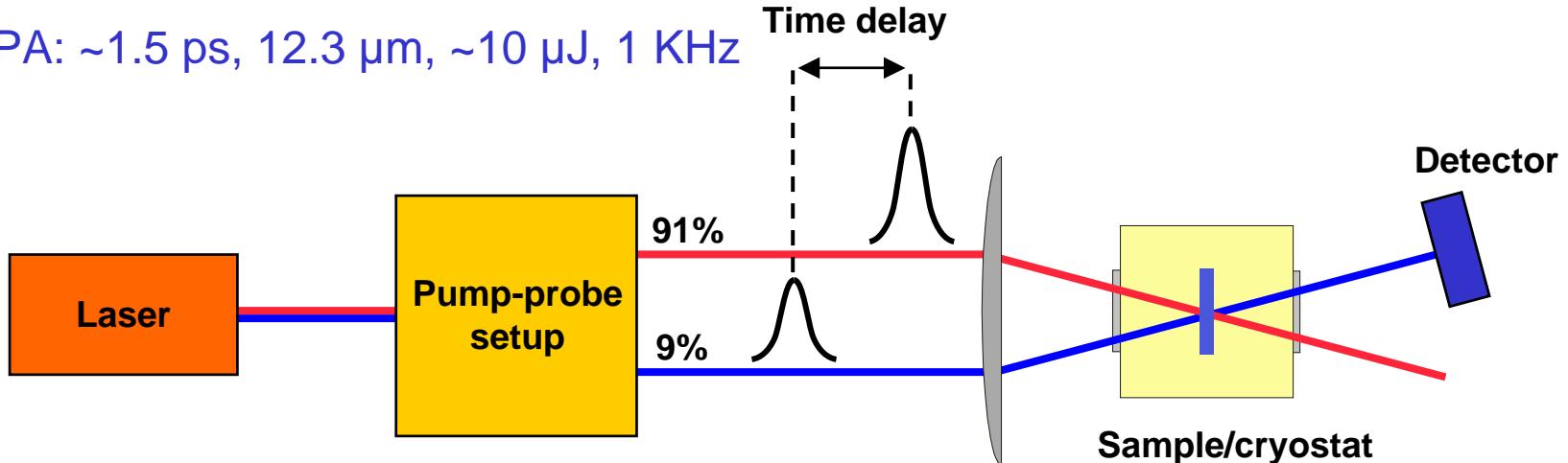
Dissociation rate extremely
dependent on vibrational lifetime

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)

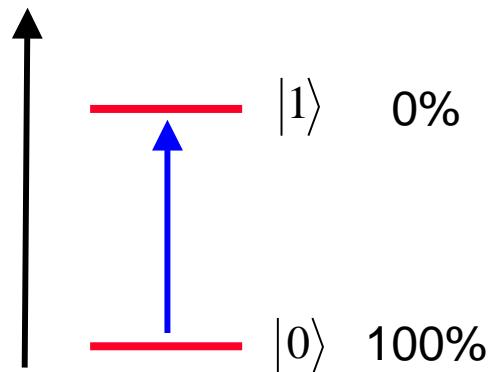
Truncated harmonic oscillator

Transient Bleaching Spectroscopy

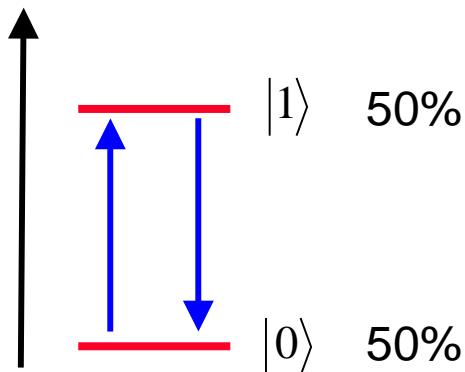
OPA: ~1.5 ps, 12.3 μm , ~10 μJ , 1 kHz



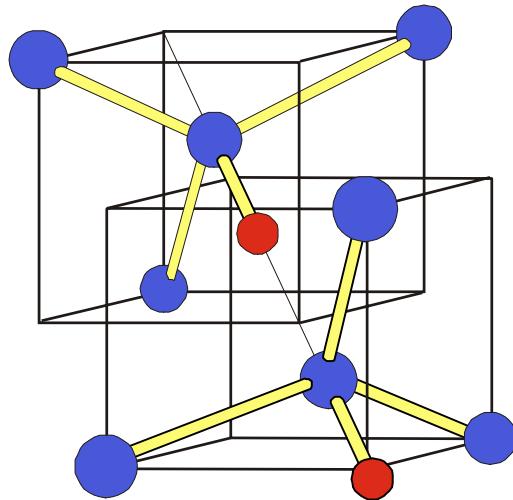
Thermal equilibrium



Bleached



Bend Mode in H_2^*



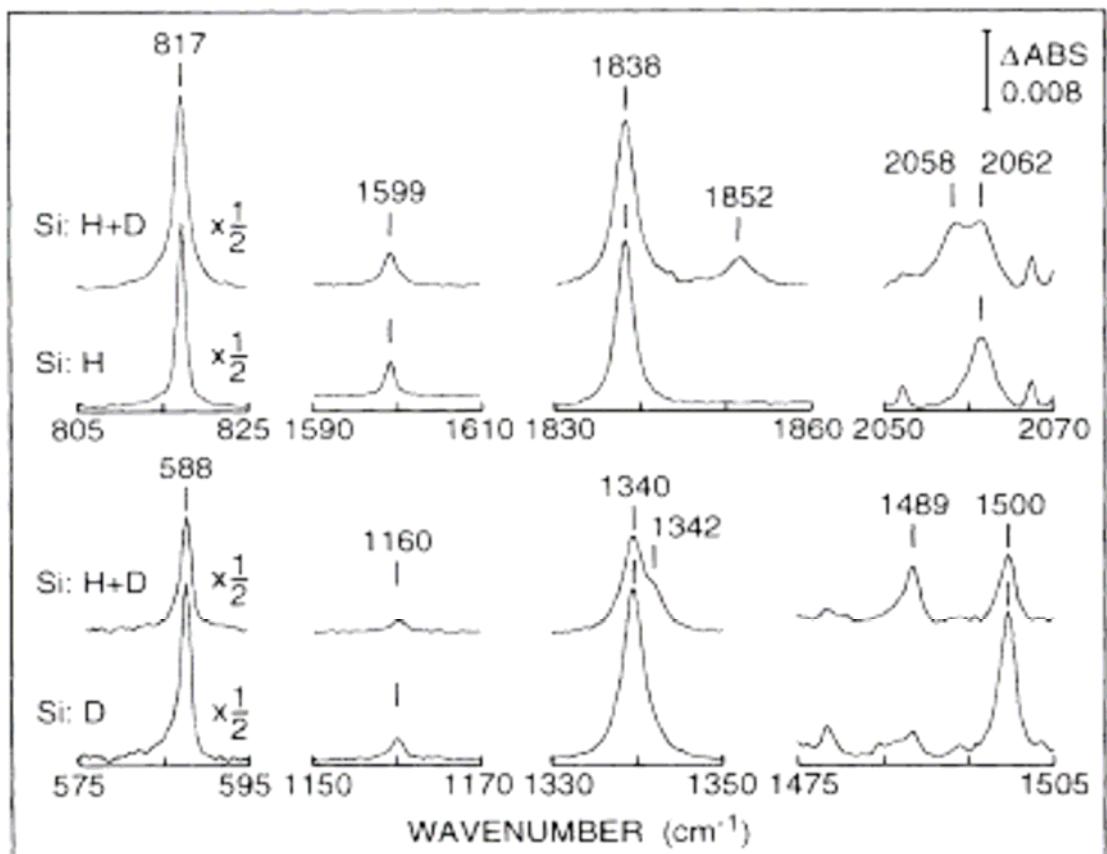
Four absorption modes:

817 cm^{-1} Bend mode

1599 cm^{-1} Overtone

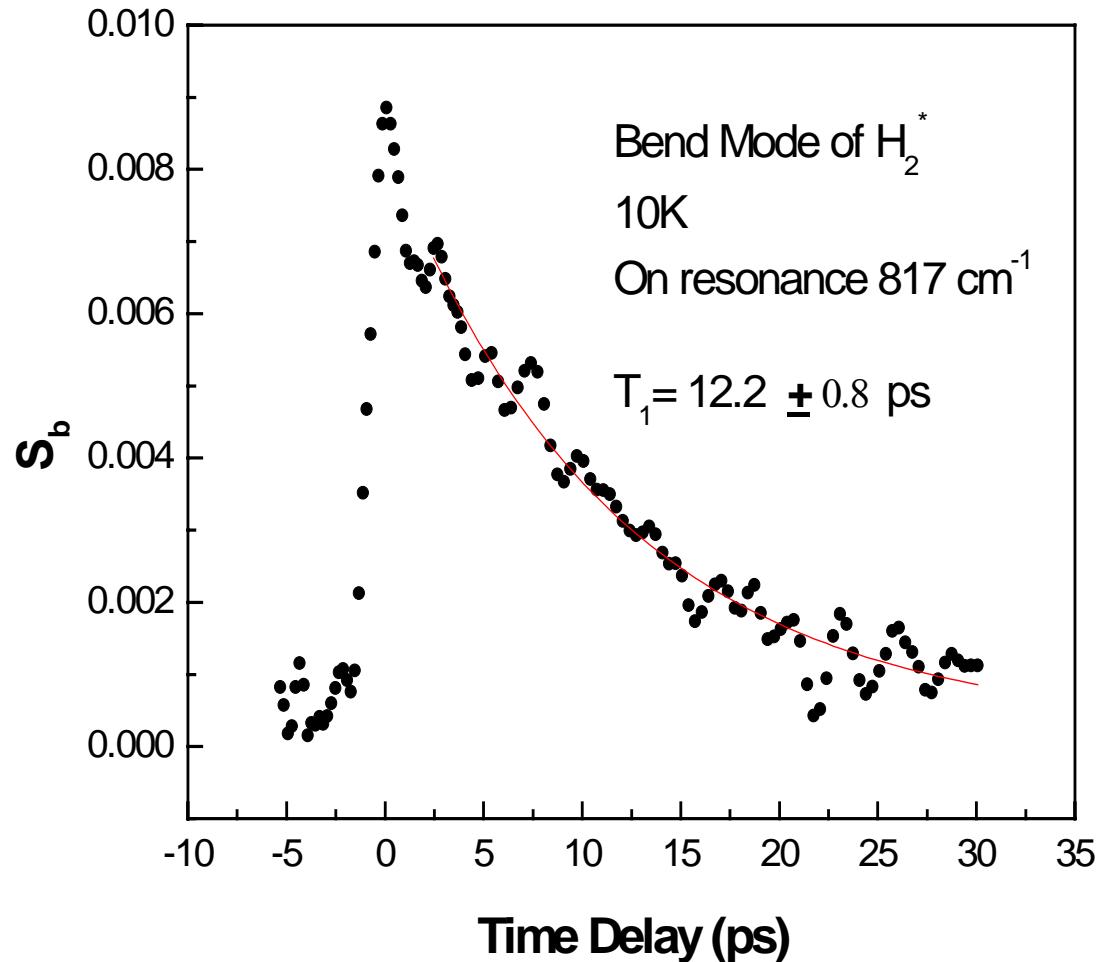
1838 cm^{-1} Stretch (AB)

2062 cm^{-1} Stretch (BC)

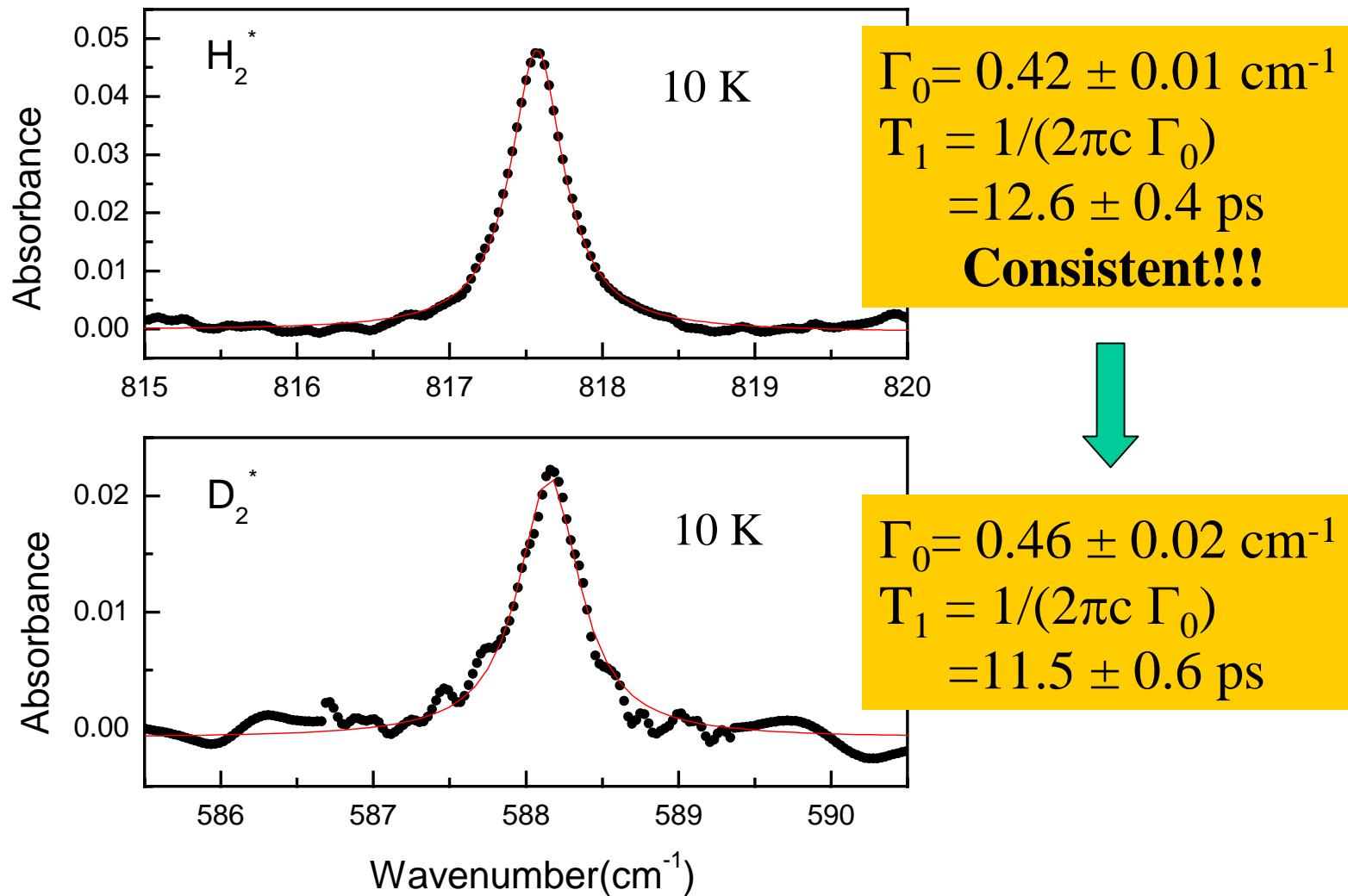


J. D. Holbech *et al*, PRL, 71, 875(1993)

Vibrational Lifetime Measurement at 10 K



Natural Linewidth of Bend Modes



Decay Mechanism

Decay of LVM into
“phonon” bath:

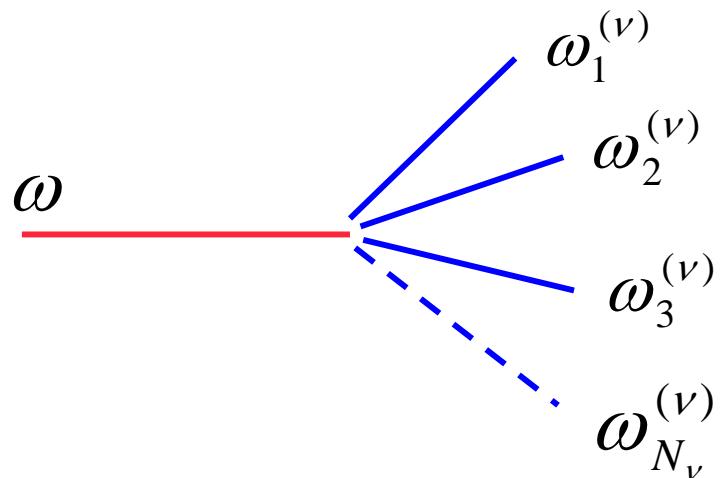
$$\frac{1}{T_1} = 2\pi \sum_{\{\nu\}} |G_{\{\nu\}}|^2 n_{\{\nu\}} \rho_{\{\nu\}}$$

Each channel ν :

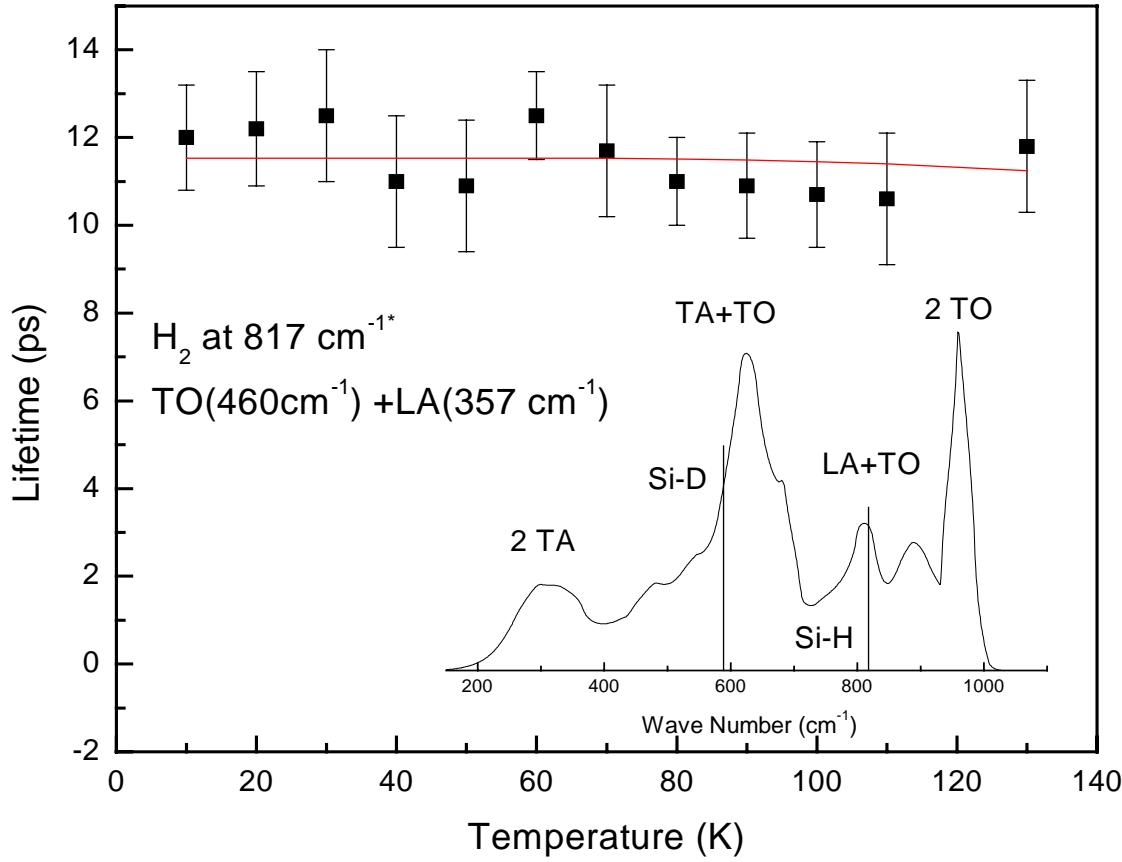
$$\omega = \sum_{j=1}^{N_\nu} \omega_j^{(\nu)}$$

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

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



Temperature Dependence of Lifetime & Two-phonon Density Calculation



Si-H: $\text{TO}(\text{X}) + \text{L}(\text{X})$ (IR active) & $\text{TO}(\text{L}) + \text{L}(\text{L})$ (Raman active)

Si-D: $\text{TO}(\text{X}) + \text{TA}(\text{X})$ & $\text{TO}(\text{L}) + \text{TA}(\text{L})$ (IR active)

Anharmonicity of bend mode potential

Morse Potential $V_M(\xi) = V_{eq} [1 - \exp(-\alpha_M \xi)]^2 - V_{eq}$

The eigenvalues of the Morse potential :

$$\omega_m(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2$$

Where $x_e = \omega_e / 4V_{eq}$, is an anharmonicity parameter, like ω_e and V_{eq}
The fundamental and first overtone are $\omega_1 = \omega_M(1) - \omega_M(0)$,
 $\omega_2 = \omega_M(2) - \omega_M(0)$, So $\omega_e = 3\omega_1 - \omega_2$, $x_e = (2\omega_1 - \omega_2) / 2(3\omega_1 - \omega_2)$

Si:H $x_e = 2\%$

Si:D $x_e = 1.3\%$

Anharmonicity plays a roll in the lifetime of VH_4 in Si

Position	FWHM	PA (I)	PA (II)	Remarks	
4388.54	0.6(1)	0.010(1)	0.008(3)	$2\nu(T(\text{VH}_4))$	$T_1 = 56 \text{ ps}$
2222.97	0.11(1)	1	1	$T(\text{VH}_4), 2210$ at 300 K	

Position	FWHM	PA	r	Remarks	
3208.07	0.15(5)	0.008(3)	1.3680	$2\nu(T(\text{VD}_4))$	$T_1 = 143 \text{ ps}$
1617.53	0.06(1)	1	1.3743	$T(\text{VD}_4)$	

Anharmonicity parameter x_e for $T(\text{VD}_4)$ and $T(\text{VH}_4)$.

$\text{VH}_4 \ x_e = 1.3\%$

$\text{VD}_4 \ x_e = 0.8\%$

Other Si-H Bend Modes

Defect type	Vibrational Frequency (cm ⁻¹)	Line Width & Lifetime	Decay order
H ₂ * in Si	817	0.42 cm ⁻¹ (12.2 ps)	2
Si-H in AlAs	890	0.07 cm ⁻¹ (76 ps)	3
Si-H in GaAs	896	0.02 cm ⁻¹ (265 ps)	4

Decay Order is an important factor to determine the lifetime of bend modes

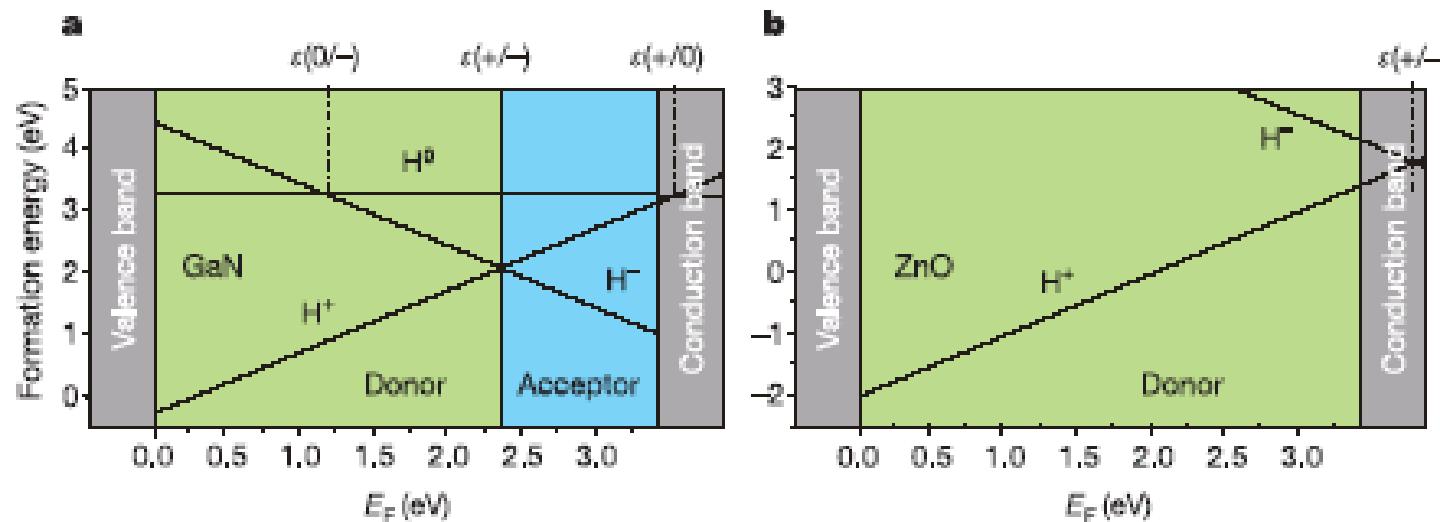
Future Experiments

- H (dopant) in ZnO: O-H complex at 3 μm
- H-dopant complexes in compound semiconductors

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

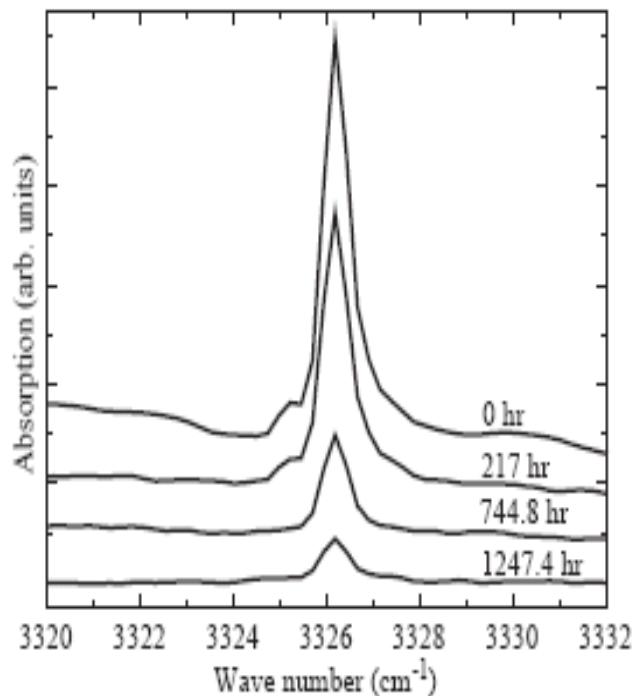
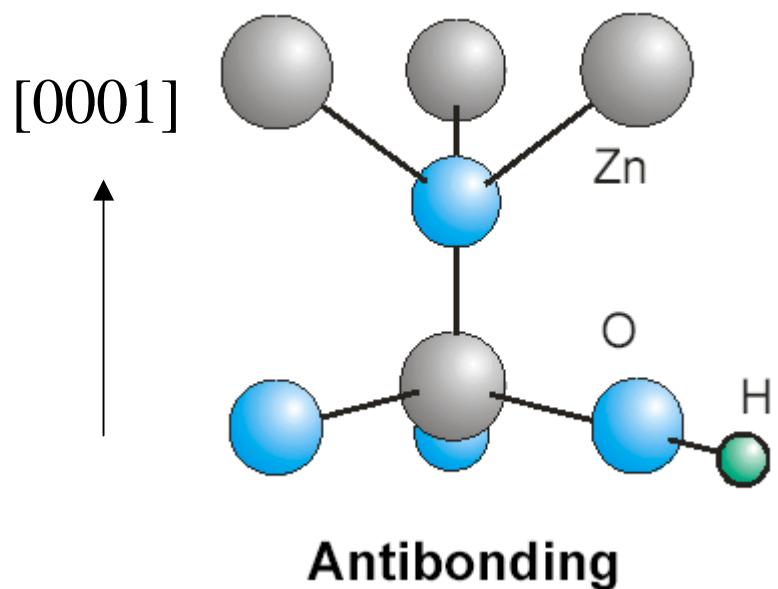


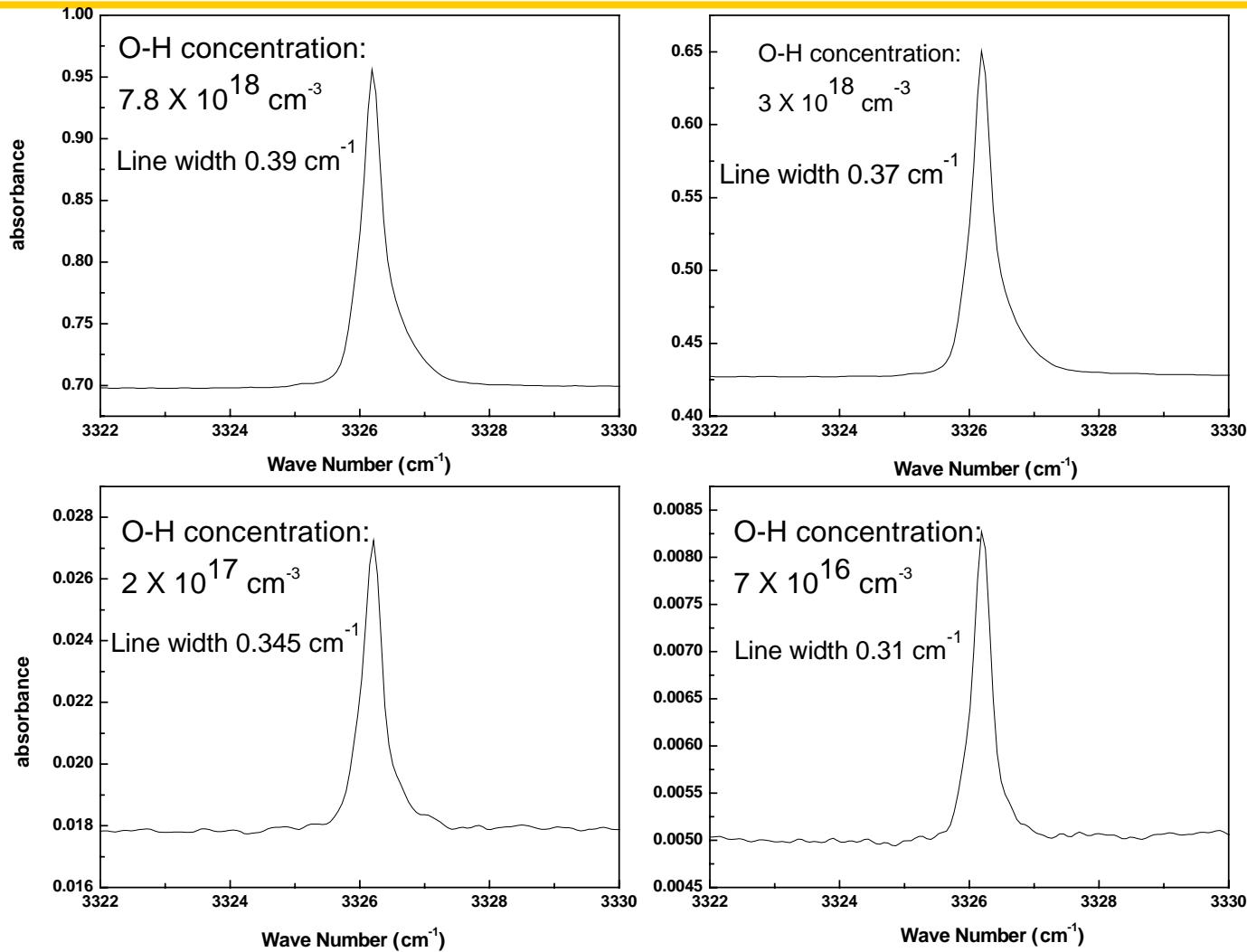
Fig. 3. Decay of the O-H LVM. The annealing temperature was 300 K and the sample temperature was 14 K.



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

Colleagues & Collaborators

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Supported by: NSF, DoE, ONR, Jeffress Foundation