
Vibrational Lifetimes and Isotope Effects of Interstitial Oxygen in Silicon and Germanium

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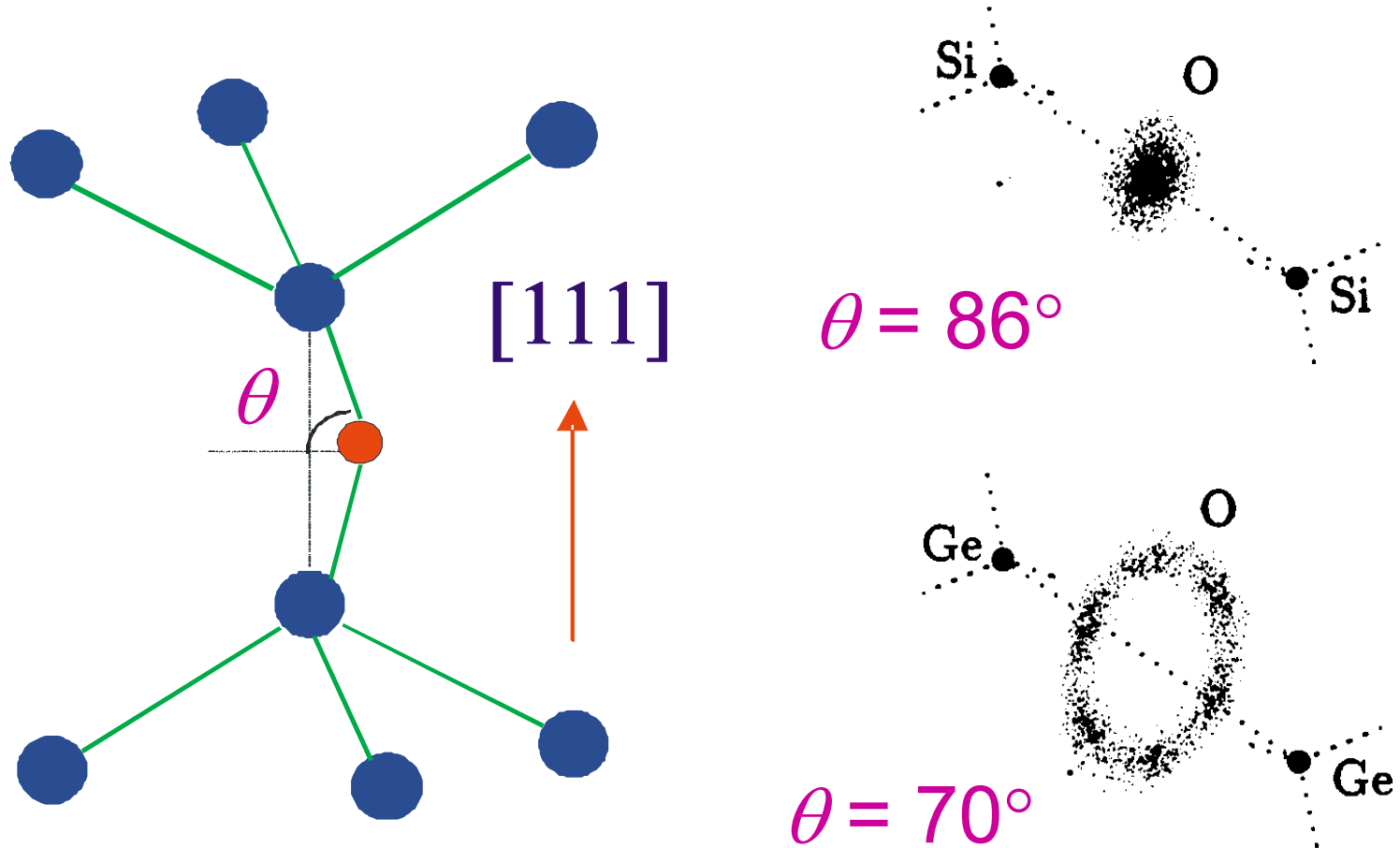
Interstitial Oxygen in Si and Ge

- Oxygen in Si and Ge is one of the very early examples of an impurity studied by vibrational spectroscopy. It has been well characterized experimentally and theoretically.
- However, the dynamics and relaxation channels of oxygen vibration is unknown, which can affect the reactivity of impurity, their diffusion and desorption rates.

Our Goals:

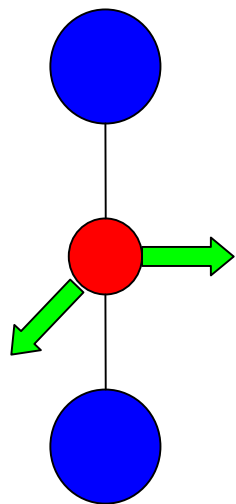
- To determine the Vibrational Lifetime of the Local Mode.
- To identify the Energy Relaxation Channels.

Interstitial Oxygen Defect



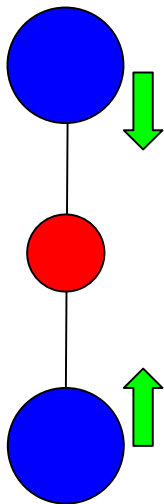
Vibrational Modes of Interstitial Oxygen

● Silicon ● Oxygen



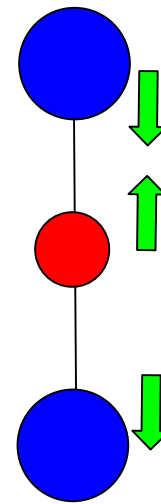
Transverse
Mode

29 cm⁻¹



Symmetric Stretch
Mode

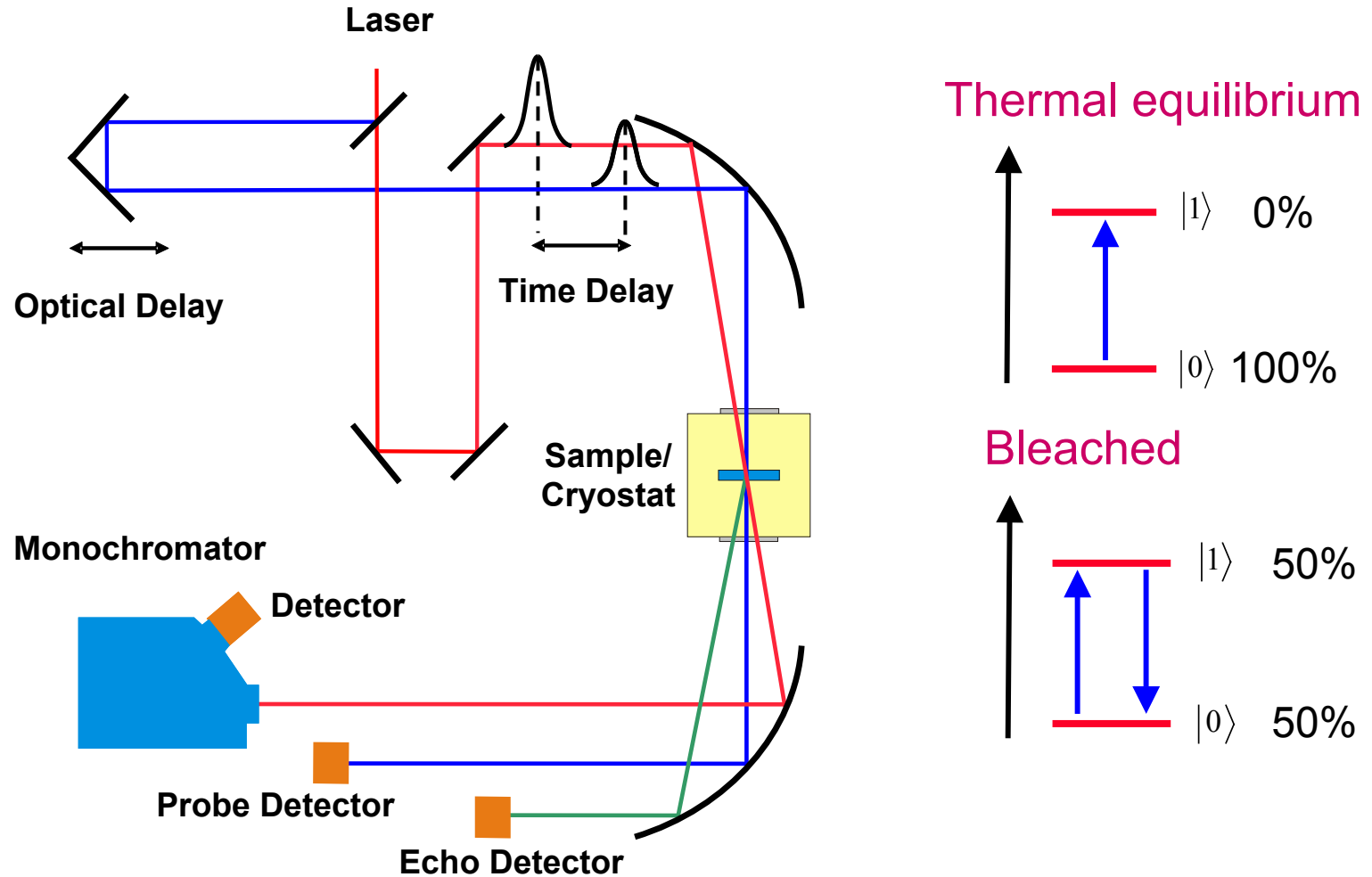
518 cm⁻¹



Asymmetric Stretch
Mode

1136 cm⁻¹

Experimental Setup



Isotope Effect of Interstitial Oxygen in Si

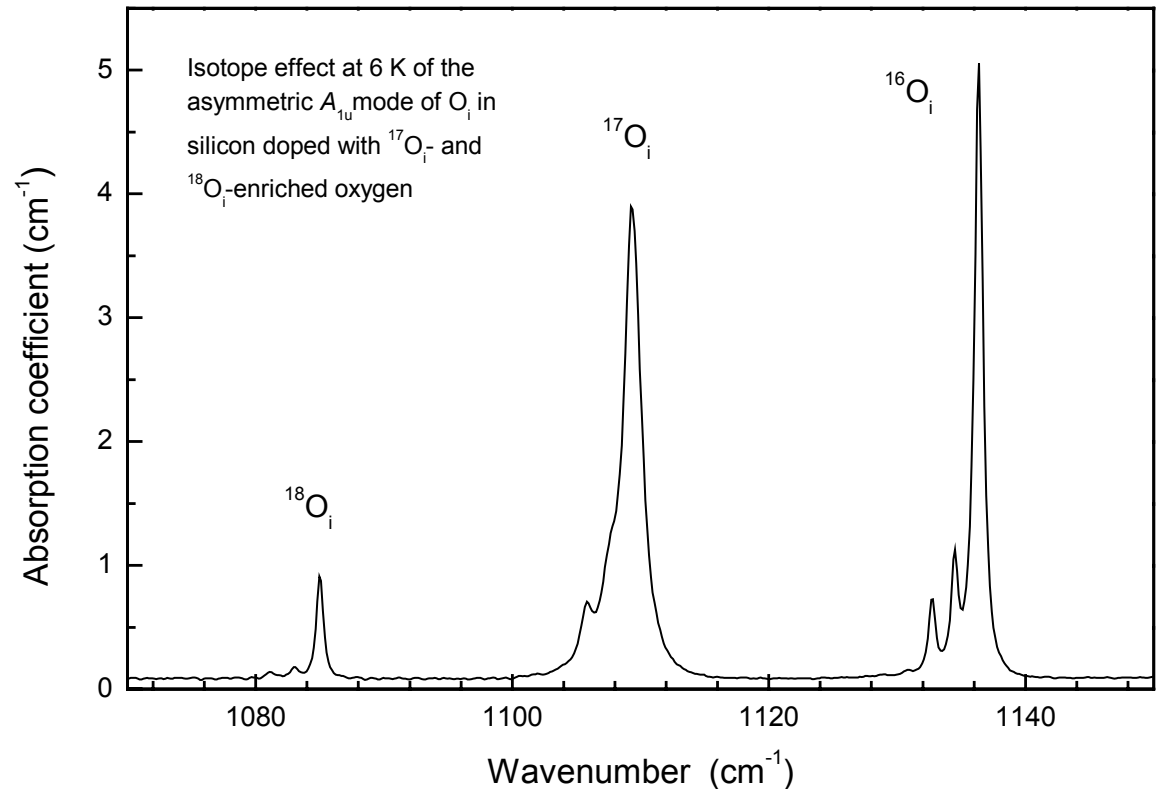
Float-zone grown Si:
enriched with oxygen
isotopes by diffusion
near 1400°C

Concentration:

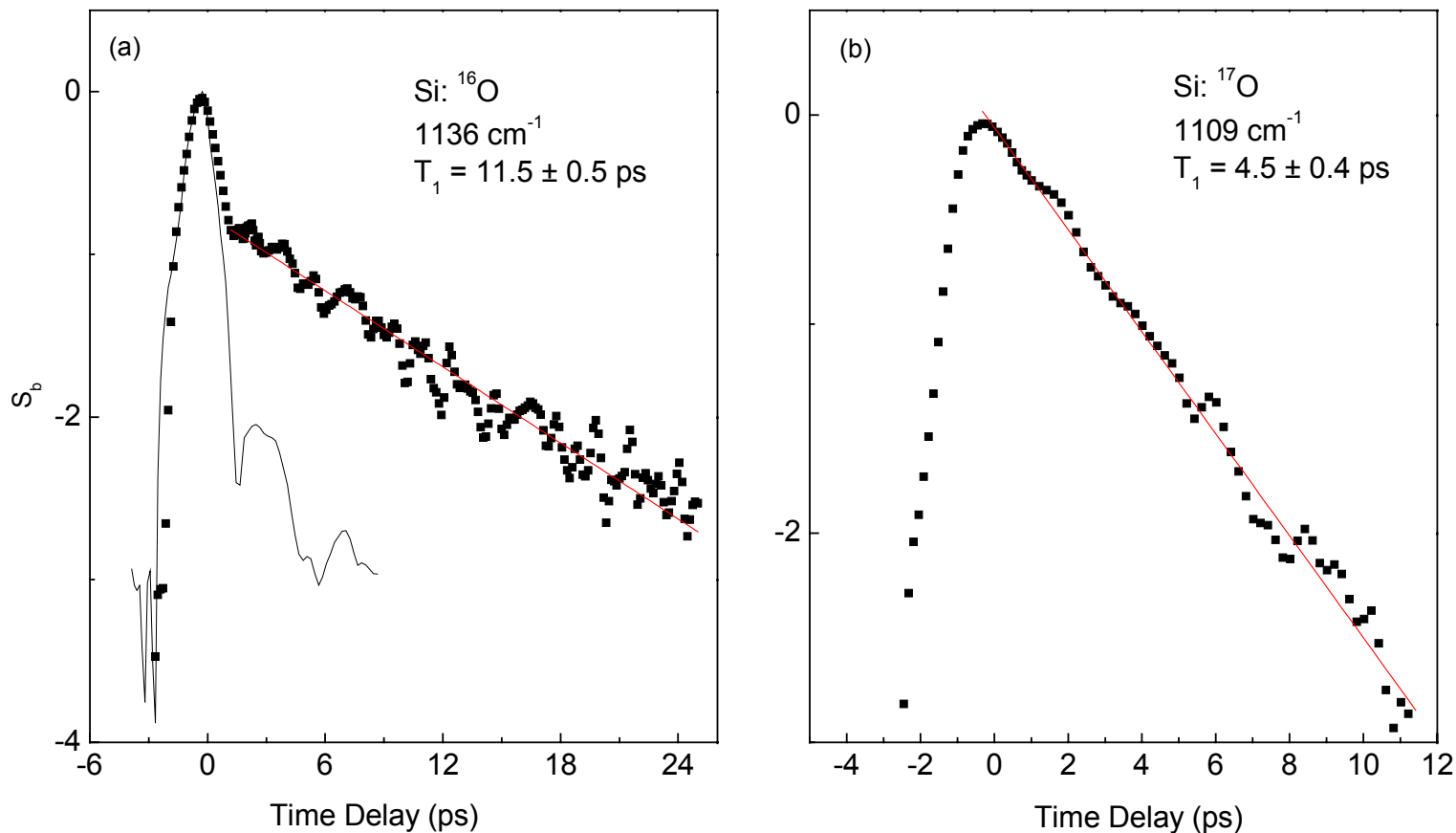
$[^{16}\text{O}_i] = 20 \times 10^{16} \text{ cm}^{-3}$
 $[^{17}\text{O}_i] = 25 \times 10^{16} \text{ cm}^{-3}$
 $[^{18}\text{O}_i] = 2.4 \times 10^{16} \text{ cm}^{-3}$

Linewidth:

0.55 cm^{-1} for $^{16}\text{O}_i$
~1.2 cm^{-1} for $^{17}\text{O}_i$
~0.6 cm^{-1} for $^{18}\text{O}_i$



Vibrational Lifetime of ^{16}O and ^{17}O in Si



B. Sun et al, Phys. Rev. Lett., accepted

Decay Mechanism

Decay of LVM into
“phonon” bath:

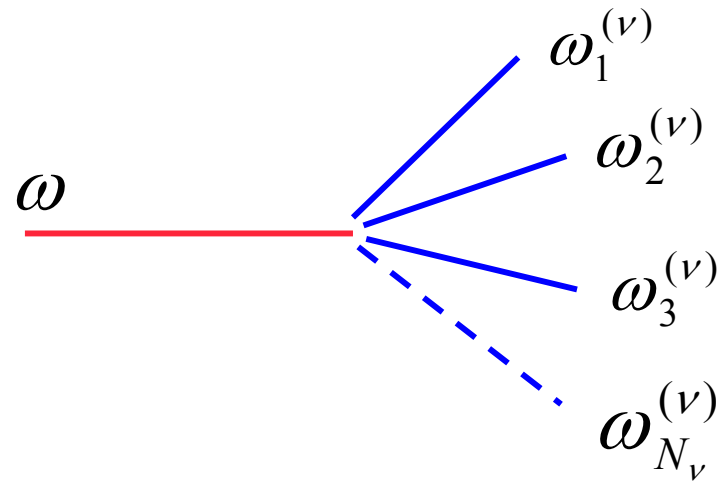
$$\frac{1}{T_1} = 2\pi \sum_{\{v\}} |G_{\{v\}}|^2 n_{\{v\}} \rho_{\{v\}}$$

Each channel v :

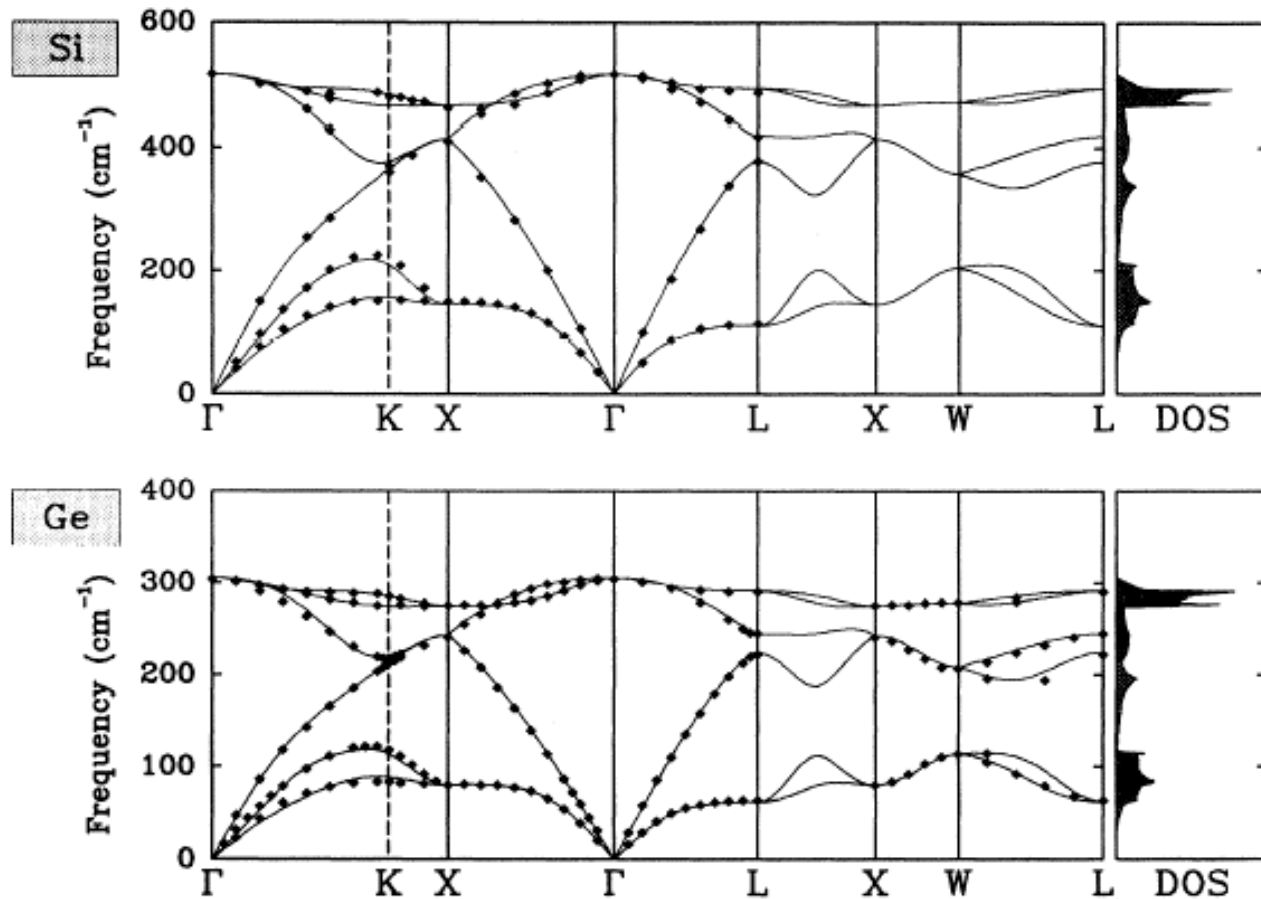
$$\omega = \sum_{j=1}^{N_v} \omega_j^{(v)}$$

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

$$\rho_{\{v\}} = \int d\omega_1^{(v)} \dots \int d\omega_{(N_v-1)}^{(v)} \rho_1^{(v)}(\omega_1^{(v)}) \dots \rho_{N_v}^{(v)}(\omega_{N_v}^{(v)})$$



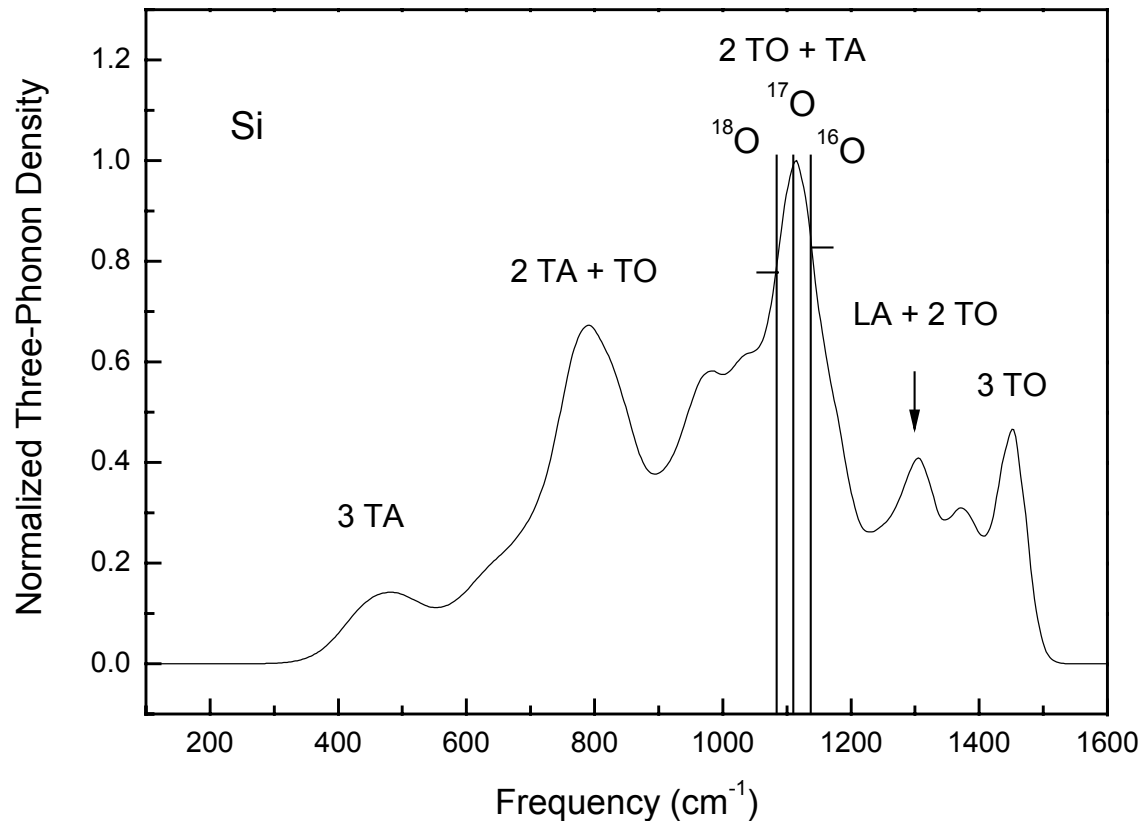
Density of Phonon States in Si and Ge



Paolo Giannozzi, et al, Phys. Rev. B, 43, 7231 (1991)

Three-Phonon Density of States in Si

$$\rho^{(3)}(\omega) = \int d\omega_1 \int d\omega_2 \rho^{(1)}(\omega - \omega_1) \rho^{(1)}(\omega_1 - \omega_2) \rho^{(1)}(\omega_2)$$



Vibrational Spectrum of ^{16}O in Ge

Natural Ge:

^{70}Ge (20.5%)

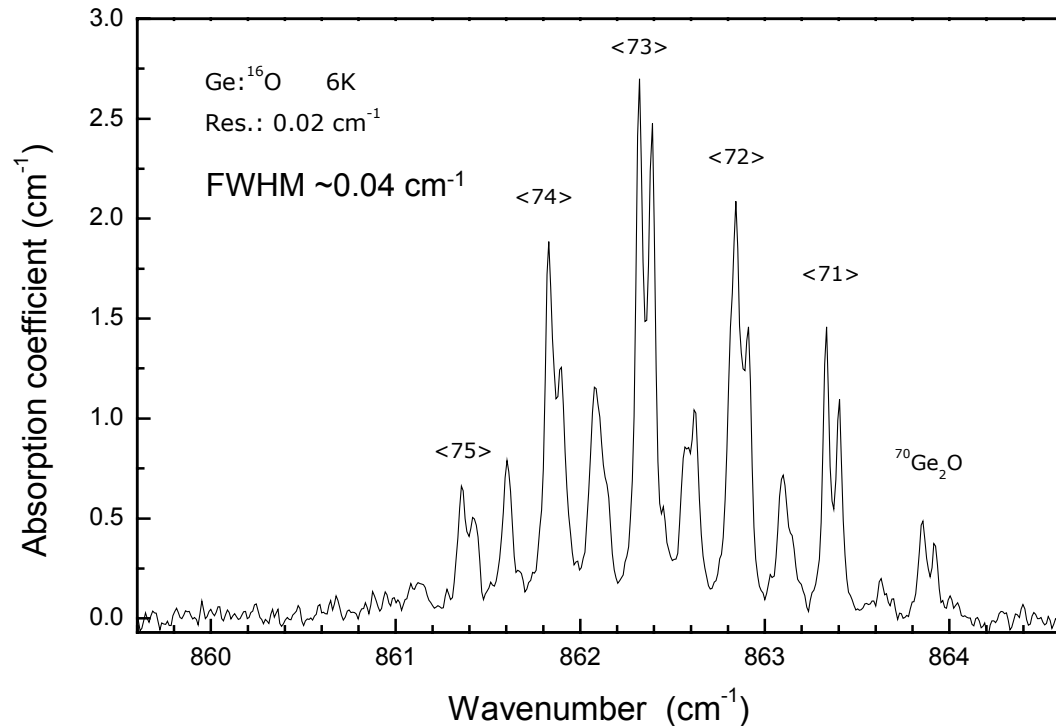
^{72}Ge (27.4%)

^{73}Ge (7.8%)

^{74}Ge (36.5%)

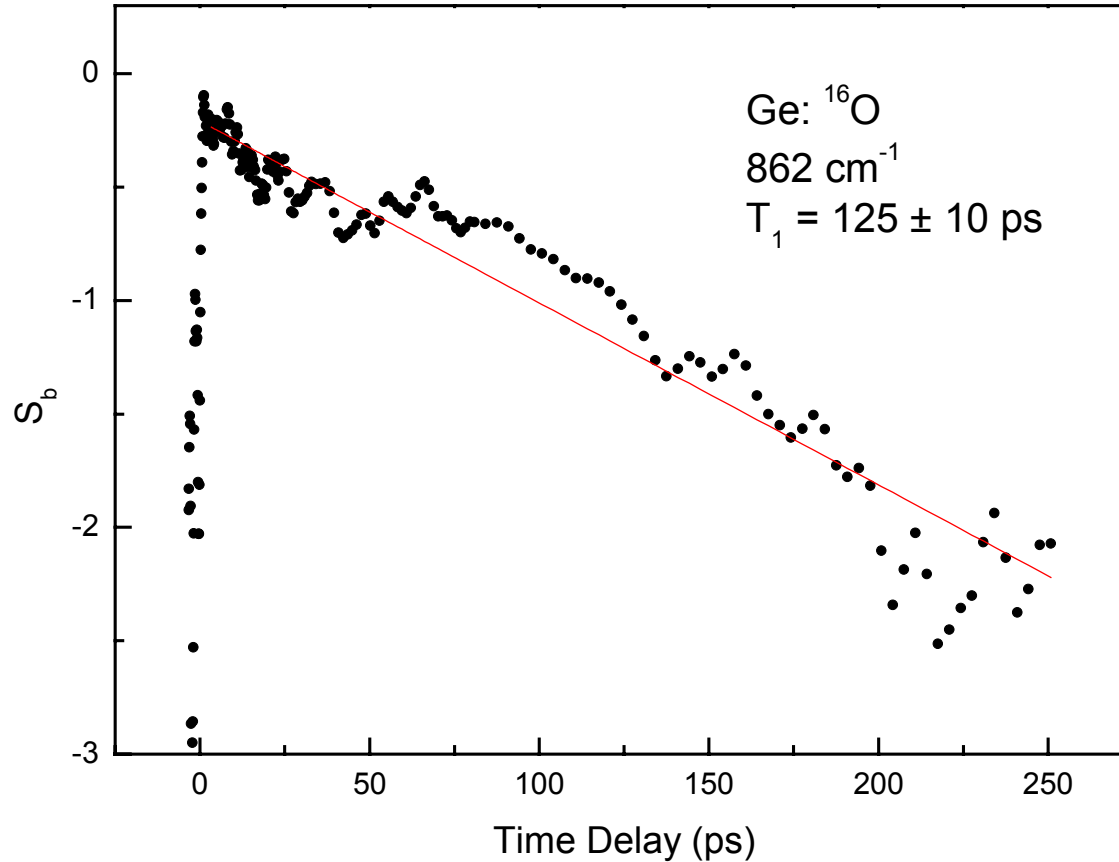
^{76}Ge (7.8%)

$[\text{O}_i] = 4.9 \times 10^{16} \text{ cm}^{-3}$



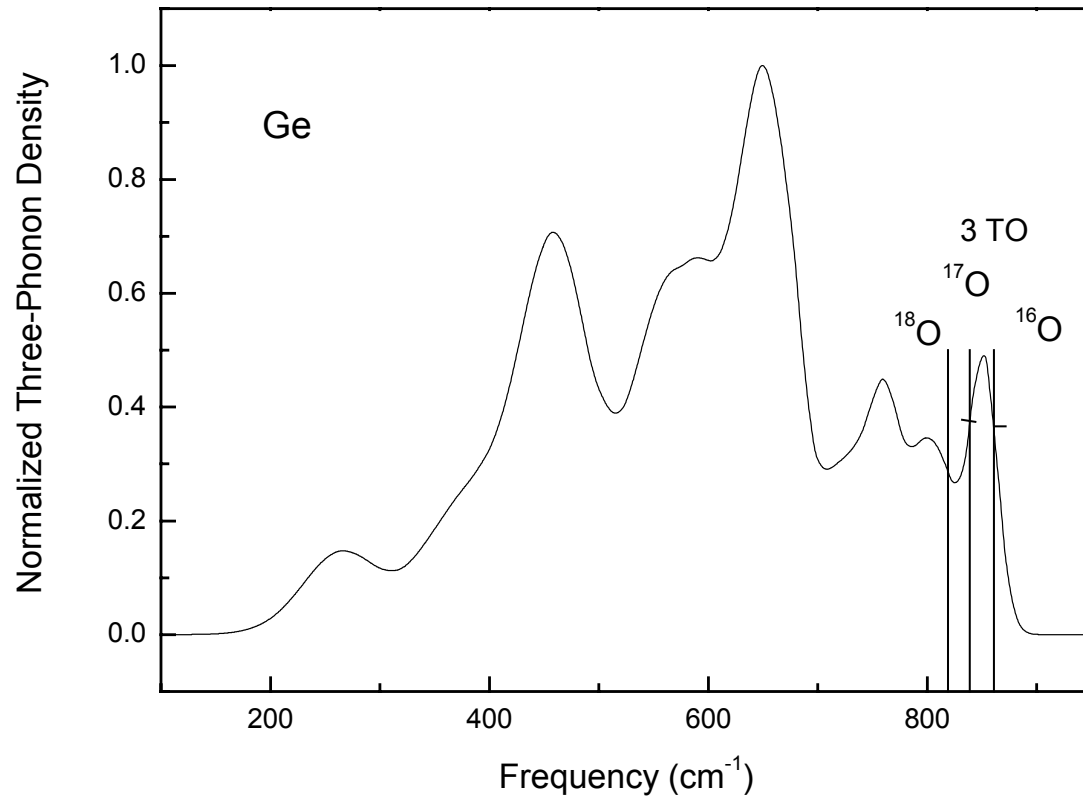
Vibration-rotation scheme: $(\Delta l=0)$, $|0, \parallel \rightarrow |1, \parallel$, $l=0, \pm 1, \pm 2, \pm 3$,
separated by $\sim 0.07 \text{ cm}^{-1}$

Vibrational Lifetime of ^{16}O in Ge



Time and frequency domain consistent

Three-Phonon Density of States in Ge



A factor of 2 between the density of accepting states can not explain an order of magnitude difference in lifetimes!!!

Symmetry Selection Rules

Asymmetric stretch mode of O_i : A_{2u} symmetry

Decay channel must contain A_{2u} or $\Gamma_{15'}$.

$\Gamma_{15'}$ is the representation of the infrared dipole operator in diamond structure, which can be reduced to $A_{2u} \oplus E_u$.

The allowed transition into phonons must satisfy:

$$2TO + TA \supset (M) \Gamma_{15'} (A_{2u} \oplus E_u) \text{ for Si}$$

$$3TO \supset (M) \Gamma_{15'} (A_{2u} \oplus E_u) \text{ for Ge}$$

M (coefficient of $\Gamma_{15'}$) must be nonzero.

Decay Channels of Oxygen in Si and Ge

Activity (M)	Phonon Combinations	Frequency (cm ⁻¹)
	<u>Silicon</u>	
3	TO(X)+O(Γ)+TA(X)	1129
6	TO(L)+O(Γ)+TA(L)	1122
3	2TO(L)+TA(X)	1134
6	TO(L)+TO(X)+TA(L)	1071
2	2TO(X)+TA(X)	1078
	<u>Germanium</u>	
1	2TO(X)+O(Γ)	856
3	2TO(L)+O(Γ)	888

J. L. Birman, Phys. Rev. 131, 1489 (1963)

Summary

- ✓ First measurements of vibrational lifetimes of interstitial oxygen in silicon and germanium.
- ✓ In silicon, the $^{17}\text{O}_i$ mode lies in the highest density of three-phonon states (2TO+TA phonons).
- ✓ This gives rise to a shorter lifetime ($T_1 = 4.5$ ps) than for the $^{16}\text{O}_i$ and $^{18}\text{O}_i$ modes ($T_1 \sim 10$ ps).
- ✓ $^{16}\text{O}_i$ modes in Ge show much longer lifetime, $T_1 = 125$ ps, than in Si.
- ✓ Ge_2O modes decay into 3TO phonons, which have different infrared activities.
- ✓ This results in different coupling strengths and very different lifetimes.

Future Work

- In a variety of group-IV and III-V semiconductors the *interaction of hydrogen with dopants* can have important technological consequences.
- In GaN, H bonded to Mg acceptors prevents p-type activation in as-grown MOCVD material.
- Large isotope effect on hot-electron-induced debonding rate of dopant-hydrogen complexes.
- Two distinct mechanisms have been discussed:
 - ❖ Excitation of the bonding electron to an anti-bonding state leading to a repulsive force on the H.
 - ❖ Multiple, cumulative excitations of H-local mode vibrations leading to instability of the bond.

Mg⁻ H⁺ complex in GaN

Technological consequences of H:

- ☹ H is grown in during MOCVD of Mg-doped, p-type GaN, passivating Mg acceptors.
- ☺ This is believed to reduce the formation of compensating donor defects during growth.
- ☹ Acceptor activation by outgassing occurs >700°C where thermal damage becomes significant.
- ☺ Such stable passivation may provide a basis for patterning of conduction paths.

Some key early developments:

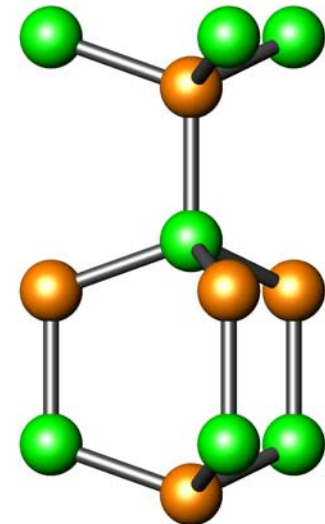
P-type conduction in Mg-doped GaN by LEEBI
[H. Amano et al., 1989](#)

P-type conduction by annealing and recognition of H passivation.
[S. Nakamura et al., 1992](#)

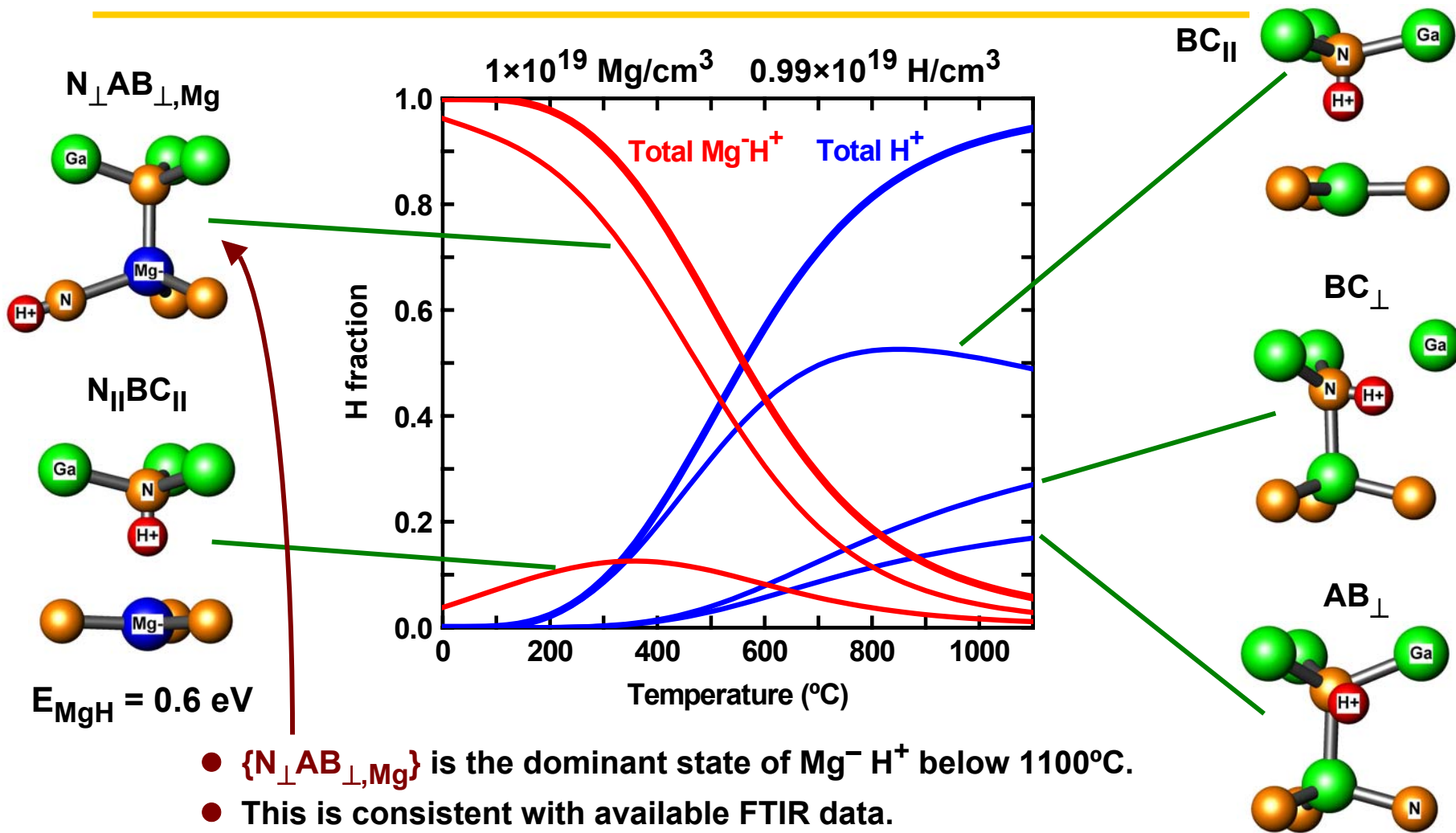
Theoretical identification of the Mg⁻ H⁺ complex.
[J. Neugebauer & C. G. Van de Walle, 1995](#)

Observation of IR absorption by the Mg⁻ H⁺ complex.
[W. Götz et al., 1996](#)

The wurtzite GaN lattice:

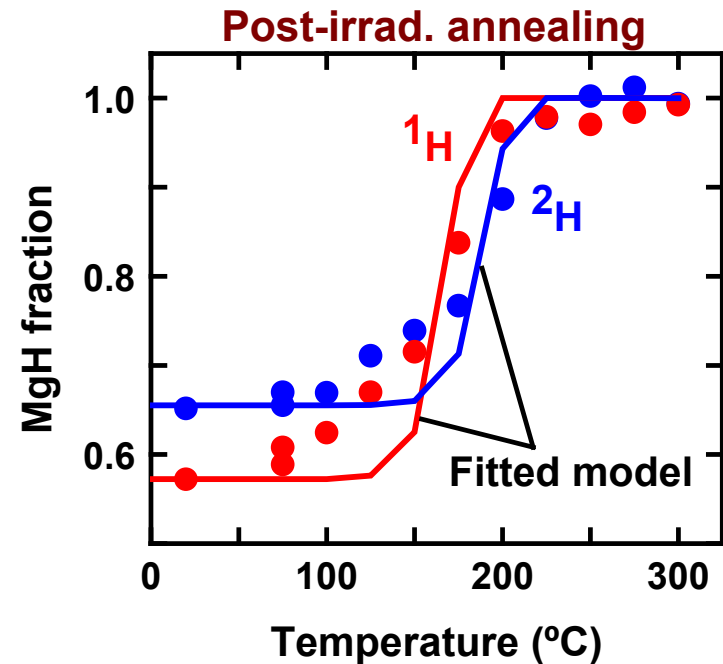
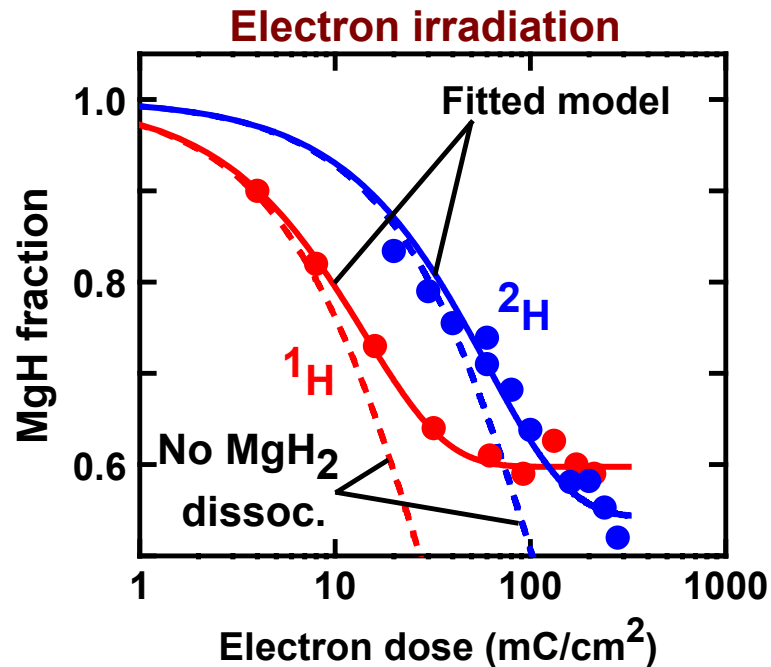


The multiple energy minima of H^+ and their occupancy



- $\{N_{\perp}AB_{\perp},\text{Mg}\}$ is the dominant state of Mg^-H^+ below 1100°C .
- This is consistent with available FTIR data.
- These findings counter recent assertions in the literature.

E-beam dissociation of the Mg⁻ H⁺ complex

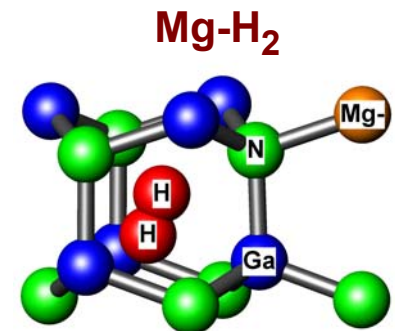


Irradiation:

$$\frac{d[\text{MgH}]}{dt} = -\Phi_e \sigma_{\text{MgH}} [\text{MgH}] + \Phi_e \sigma_{\text{MgH}_2} [\text{MgH}_2] + \alpha^* [\text{H}][\text{Mg}]$$

$$\frac{d[\text{MgH}_2]}{dt} = -\Phi_e \sigma_{\text{MgH}_2} [\text{MgH}_2] + \alpha^* [\text{H}][\text{MgH}]$$

$$\frac{d[\text{H}]}{dt} = \Phi_e \sigma_{\text{MgH}} [\text{MgH}] + \Phi_e \sigma_{\text{MgH}_2} [\text{MgH}_2] - \alpha^* [\text{H}][\text{Mg}] - \alpha^* [\text{H}][\text{MgH}]$$



How do $\text{Mg}^- \text{H}^+$ dissociate and H migrate during electron irradiation at room temperature?

Dissociation of $\text{Mg}^- \text{H}^+$

Observations:

$$\sigma_{\text{MgH}} \sim 5 \times 10^{-18} \text{ cm}^2 \text{ for } ^1\text{H} \longleftrightarrow$$

$$\sigma_{\text{MgH}_2} \sim 10 \times 10^{-18} \text{ cm}^2 \text{ for } ^1\text{H}$$

$$\sigma_{\text{MgH}} \sim 1.2 \times 10^{-18} \text{ cm}^2 \text{ for } ^2\text{H}$$

$$\sigma_{\text{MgH}_2} \sim 2 \times 10^{-18} \text{ cm}^2 \text{ for } ^2\text{H}$$

Mechanistic considerations:

$e^- - e^-$ collision imparting $>1\text{eV}$

$\rightarrow \sigma \sim 6 \times 10^{-18} \text{ cm}^2$

- Suggests N-H bond excitation

~~$e^- - p^+$ collision imparting $>1\text{eV}$~~

~~$\rightarrow \sigma \sim 3$ orders of magnitude smaller~~

Relatively small isotope effect \rightarrow

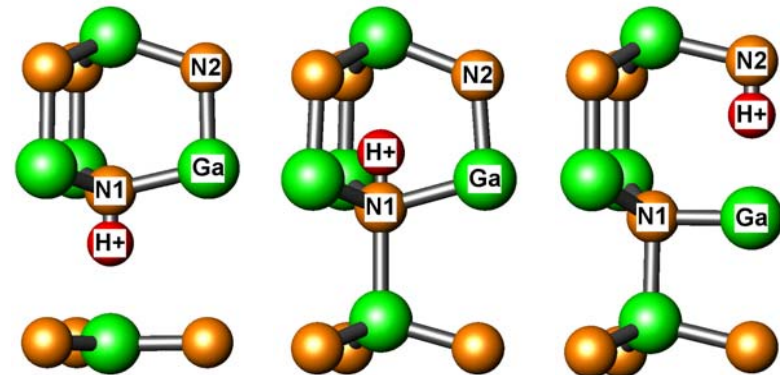
- $\tau\{\text{antibonding state}\} \sim \tau\{\text{H displacement}\}$
- Role of cumulative vibrational excitations?

Migration of H

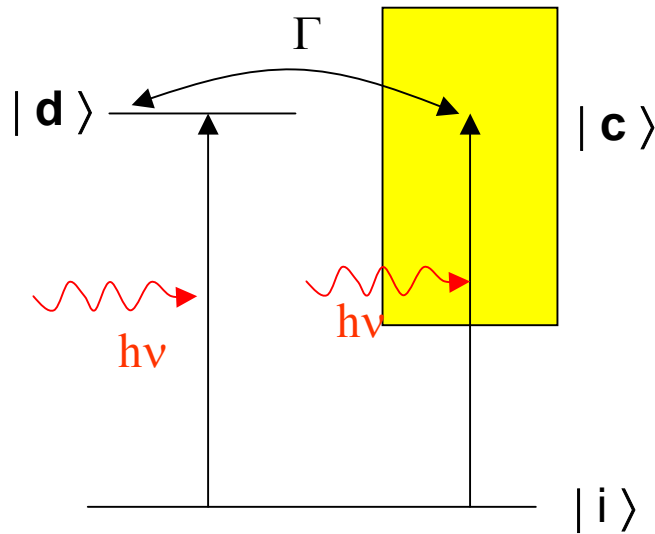
Thermal diffusion too slow per drift experiments.

Hypothesize alternating e^- and h^+ captures by H, bypassing the activation barrier to N-H bond.

[Sam M. Myers: Sandia National Laboratories](#)



Fano System

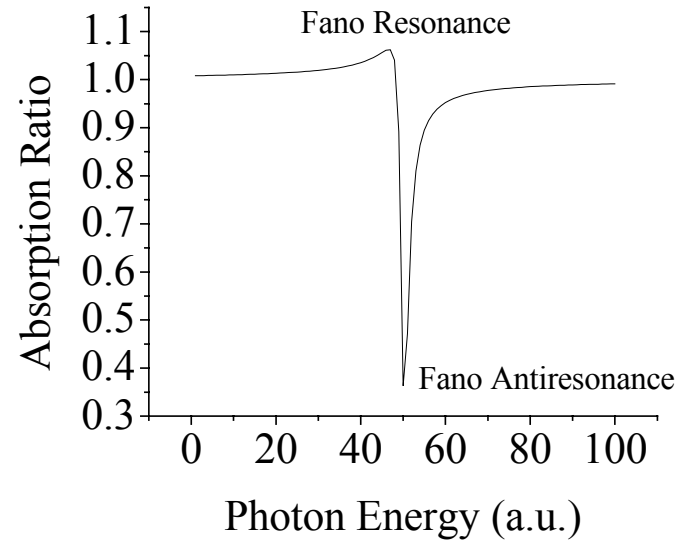
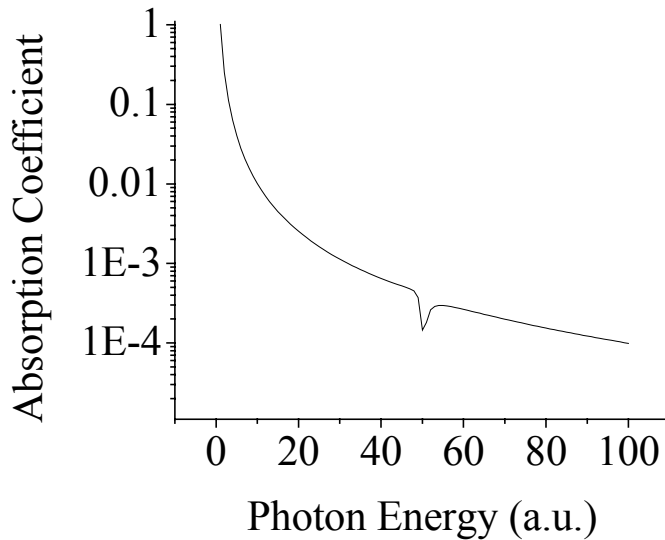


Origin of the interaction
between the discrete level
and the continuum:
electrostatic interaction
PRL 60, 105 (1988)
Coulomb interaction
PRB 51, 4953 (1995)

Γ is called coupling constant or coupling strength.
It is also called the rate of escape from discrete level
to the continuum.

U. Fano, Phys. Rev. 124, 1866 (1961)

Signature of Fano Effect



Fano resonances are characterized by a pronounced *minimum* in the absorption spectrum at an energy where the transition amplitudes of the *discrete state* and the *continuum* interfere *destructively*.

----- PRL 74, 470 (1995)

However, even a *symmetric* line shape is also possible from the Fano effect if the transition to the *phase shifted continuum* is large.

----- PRL 90, 233004 (2003)

Acknowledgement

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Character Table of Point Group D_{3d}

D_{3d}	E	$2C_3$	$3C_2'$	i	$2S_6$	$3\sigma_d$	Linear function, rotation
A_{1g}	1	1	1	1	1	1	
A_{2g}	1	1	-1	1	1	-1	R_z
E_g	2	-1	0	2	-1	0	(R_x, R_y)
A_{1u}	1	1	1	-1	-1	-1	
A_{2u}	1	1	-1	-1	-1	1	z
E_u	2	-1	0	-2	1	0	(x, y)

→ Infrared active