# Driving Chemical Reactions: Laser Assisted Catalysis and Chemical Vapor Deposition

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Motivation

- Desirability of Low T_S Chemical Vapor Deposition (CVD)

  - Monolithic integration of microsensors and circuitry (e.g., micromirror arrays)

    - Circuitry must be kept at low temperatures ($\cong$ 750 K), but film growth and treatment requires significantly higher temperatures ($\blacklozenge$1000 K)

  - Band gap engineering of strained Si/Ge transistors

    - Miscibility of dopants can be low (e.g., 1 ppm of C in Ge) so kinetic control of growth is advantageous

Integrate Circuits	Microsensor

| Microsensor |
|---|
| Integrate Circuits |
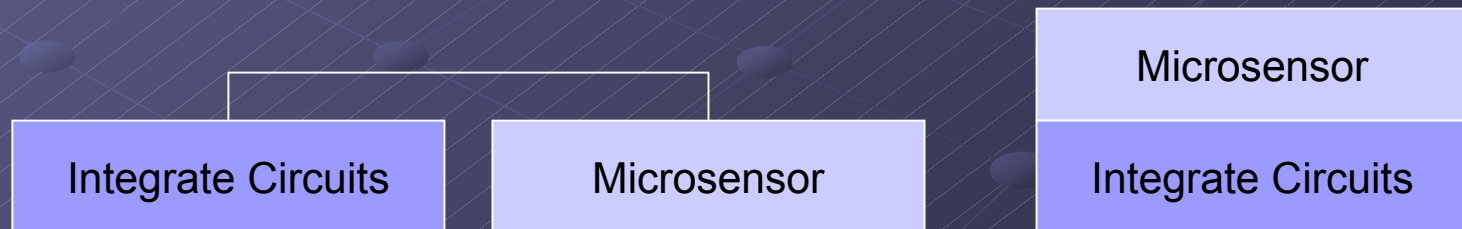
IR Laser Assisted Catalysis (ILAC)

- Photons are used to excite a particular vibrational mode of the reactants, increasing dissociation and deposition rates

- This technique is used in conjunction with CVD/MBE

- ILAC has the potential to

  - Grow nanostructured films under low T_s conditions where thermal diffusion can be minimized

  - Utilize mode specific chemistry to deposit a particular gas from a mixture

  - Increase dissociative sticking probabilities by several orders of magnitude

    - e.g., pumping the ν_3 vibration of CH_4 at 300 K can give enhancements in sticking of 10^8

Microcanonical Unimolecular Rate Theory (MURT)

- Surface chemistry is a local phenomenon.

- The energy of the adsorbate plus "*s*" surface oscillators (i.e., the "physisorbed complex" or PC) suffices to fix RRKM rate constants for reaction and desorption.

- Energy exchange between the PC and bulk may be accounted for using a Master Equation approach.

- Directly compares experiment and EST with only 3 adjustable parameters.
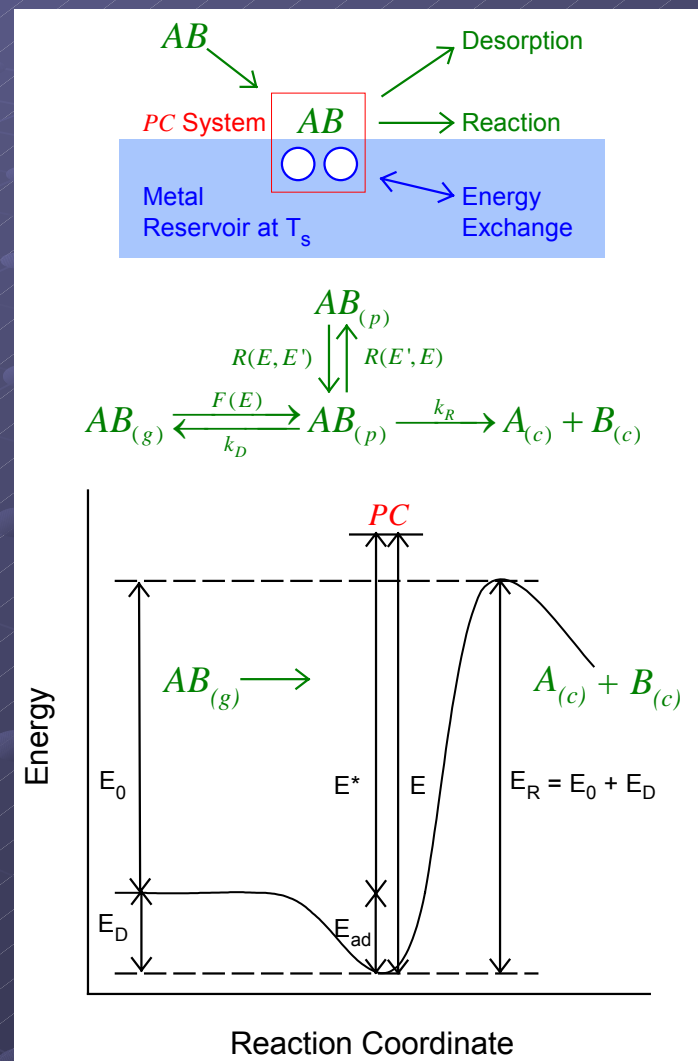
Physisorbed Complex-Microcanonical Unimolecular Rate Theory (PC-MURT)
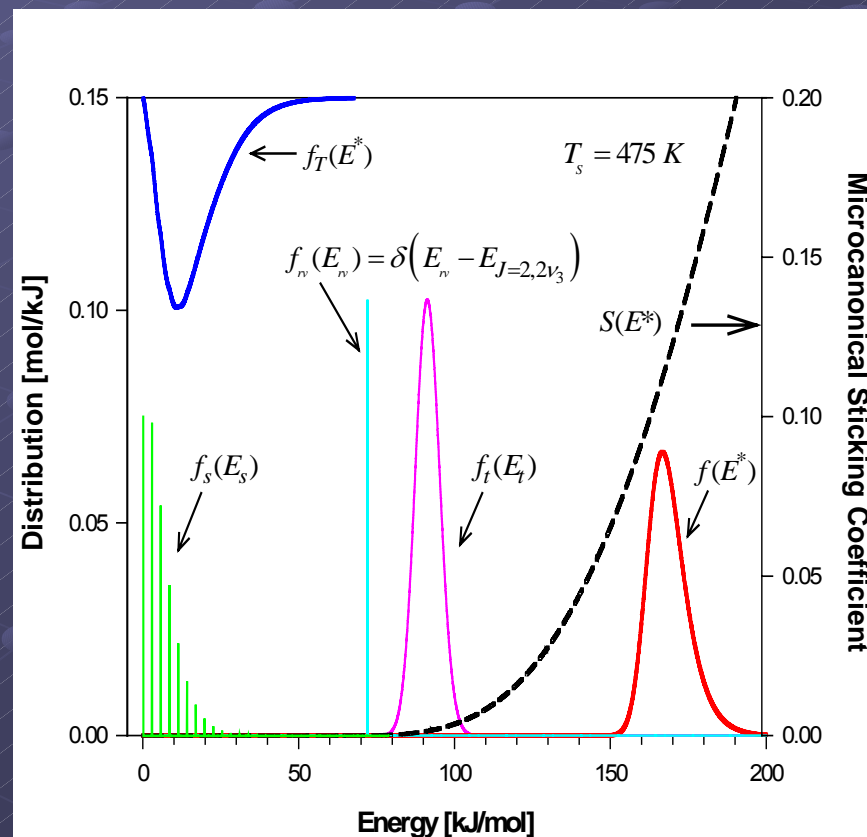
- Microcanonical Sticking Coefficient

$$S(E^*) = \frac{k_R}{k_R + k_D}$$

$$= \frac{W_R^\ddagger(E^* - E_0)}{W_R^\ddagger(E^* - E_0) + W_D^\ddagger(E^*)}$$

- Overall Sticking Coefficient

$$S = \int_0^\infty S(E^*) f(E^*) dE^*$$

Applications of PC-MURT: CH_4/Ni(100)

- Dissociative sticking probabilities for

  - Laser pumped and thermally populated molecular beam experiments

  - Thermal "bulb" equilibrium experiments

- Comparison of theoretically and experimentally predicted activation energies

- Optimized parameter set:

  - E_0 = 65 kJ/mol
  - s = 2
  - ν_D = 180 cm^{-1}

→ References
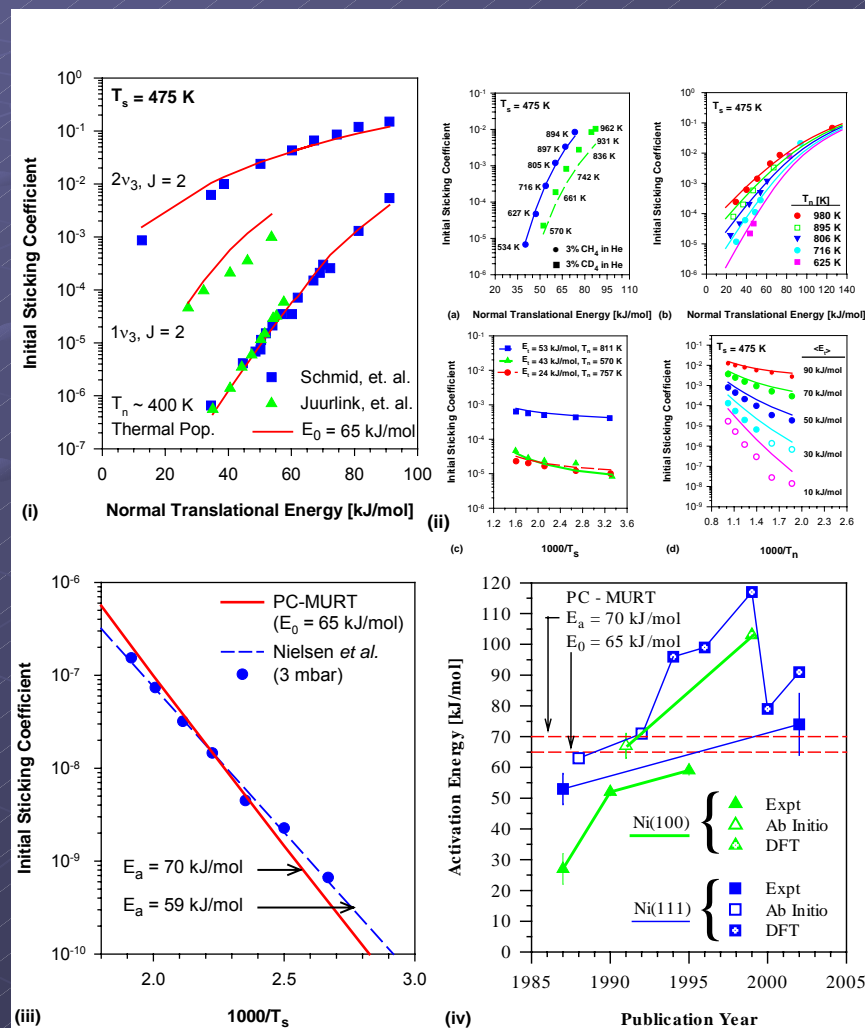
Applications of PC-MURT: SiH_4/Si(100)

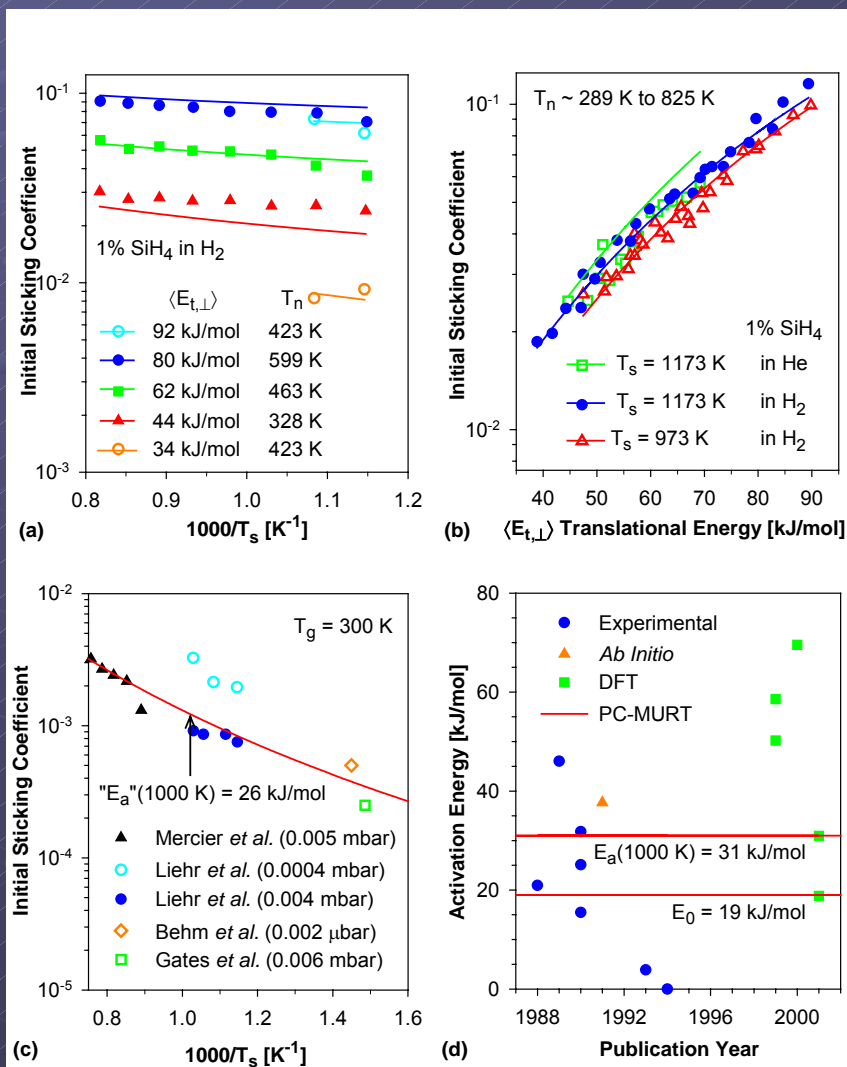- Dissociative sticking probabilities for
  - Thermally populated molecular beam experiments
  - Thermal nonequilibrium experiments

- Comparison of theoretically and experimentally predicted activation energies
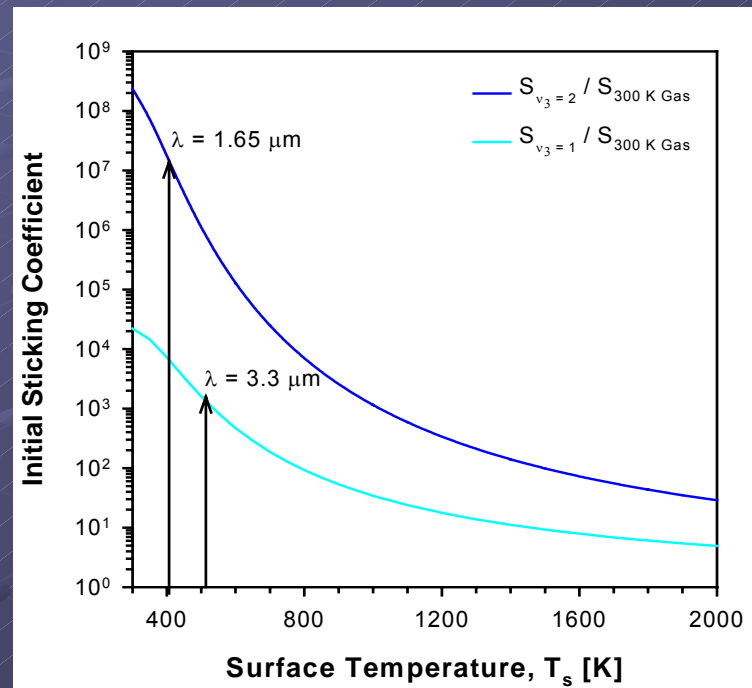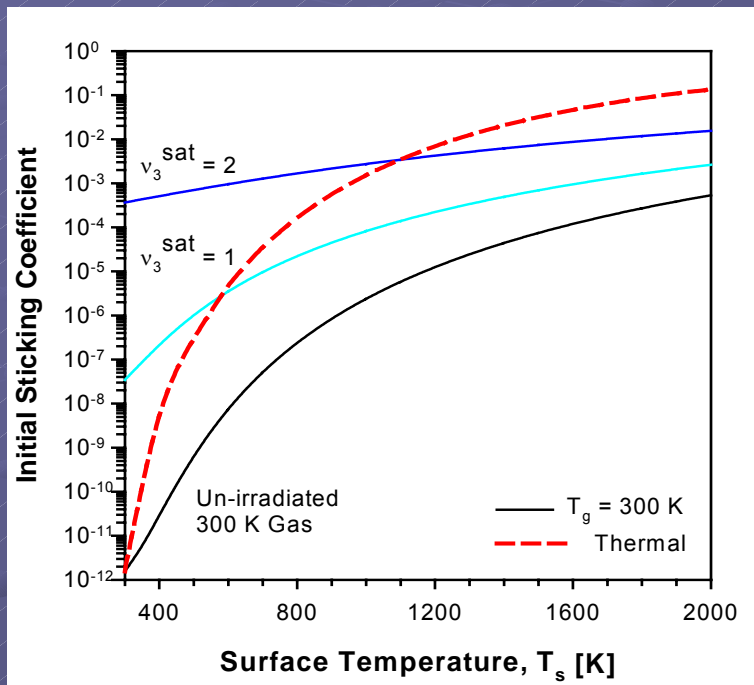
- Optimized parameter set:
  - E_0 = 19 kJ/mol
  - s = 2
  - ν_D = 230 cm^{-1}

➡ References

Laser Pumping vs. Thermal Activation

CH_4 Dissociation on Ni(100)

- Laser pumping a 300 K thermal CH_4/Ni(100) system leads to reactivity levels appropriate to surface temperatures of T_s = 675 K and T_s = 1875 K for $1\nu_3$ and $2\nu_3$ respectively.

- Sticking enhancements for a 300 K ambient CH_4 gas pumped to saturation over a 500 K Ni(100) surface would be ~10^3 and ~10^6 for $1\nu_3$ and $2\nu_3$ respectively.

# Laser Pumping vs. Thermal Activation

- Typically, experiments are performed with $T_s > 1000$ K to avoid H passivation of the surface.

- The threshold energy for dissociation is low ($E_0 = 19$ kJ/mol) on Si(100), but on the H-passivated surface the threshold energy may be significantly higher ($E_0 \sim 100$ kJ/mol).
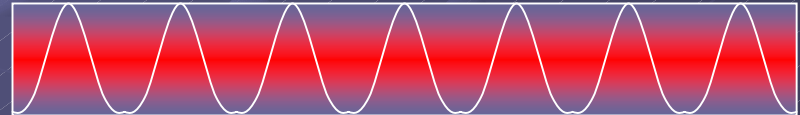
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  Possibly large enhancement of sticking at low T_s (i.e., 10^8 - 10^{12}) on the passivated surfaces.

SiH_4 Dissociation on Si(100)
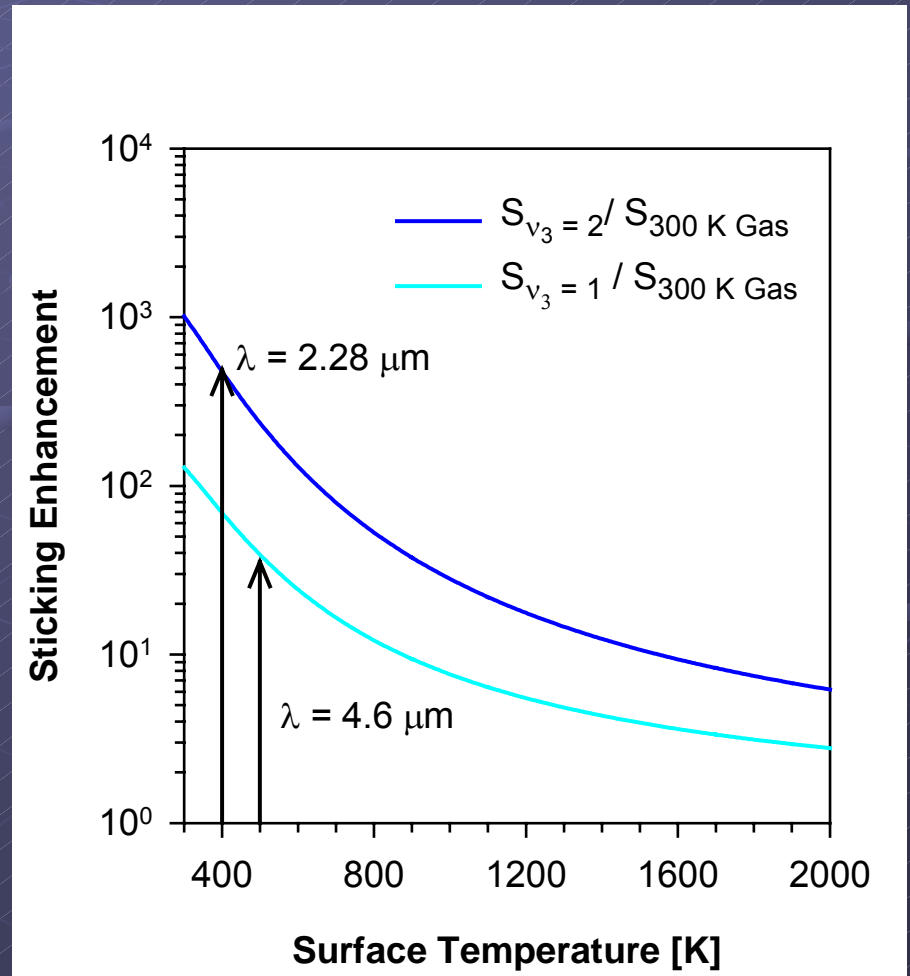
Comparison of Lasers

- Jefferson Lab Free Electron Laser

  - A tunable IR laser with 10 kW (133 μJ/pulse)

  - Individual pulses are 800 fs in duration and 20 cm^{-1} in bandwidth
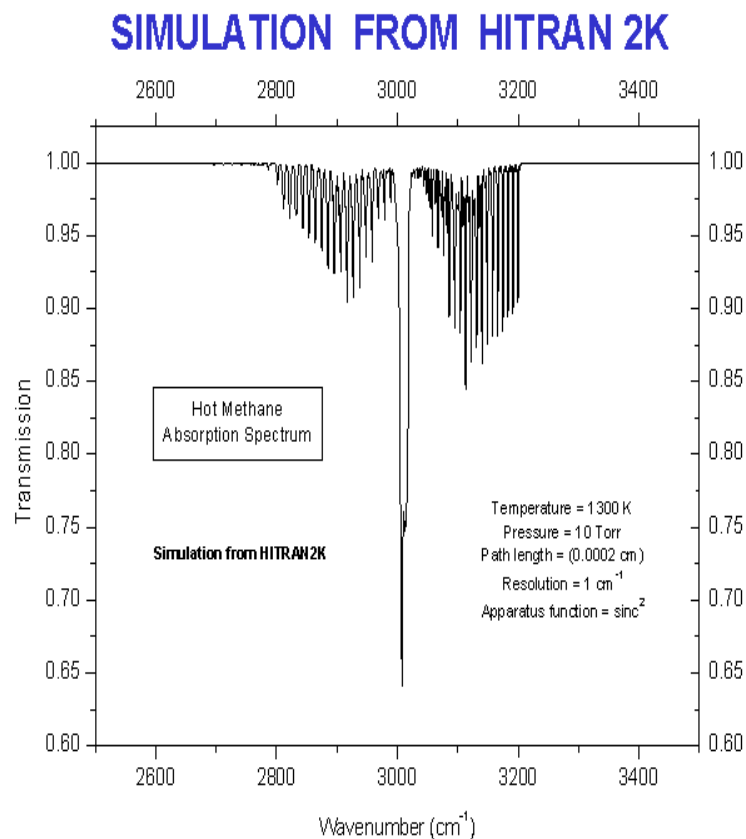
  - Repetition rate of 75 MHz

- Amplified Ti:Sapphire/OPA System at UVA

  - A tunable IR laser with 300 mW (300 μJ/pulse)

  - Individual pulses are 100 fs in duration and 150 cm^{-1} in bandwidth
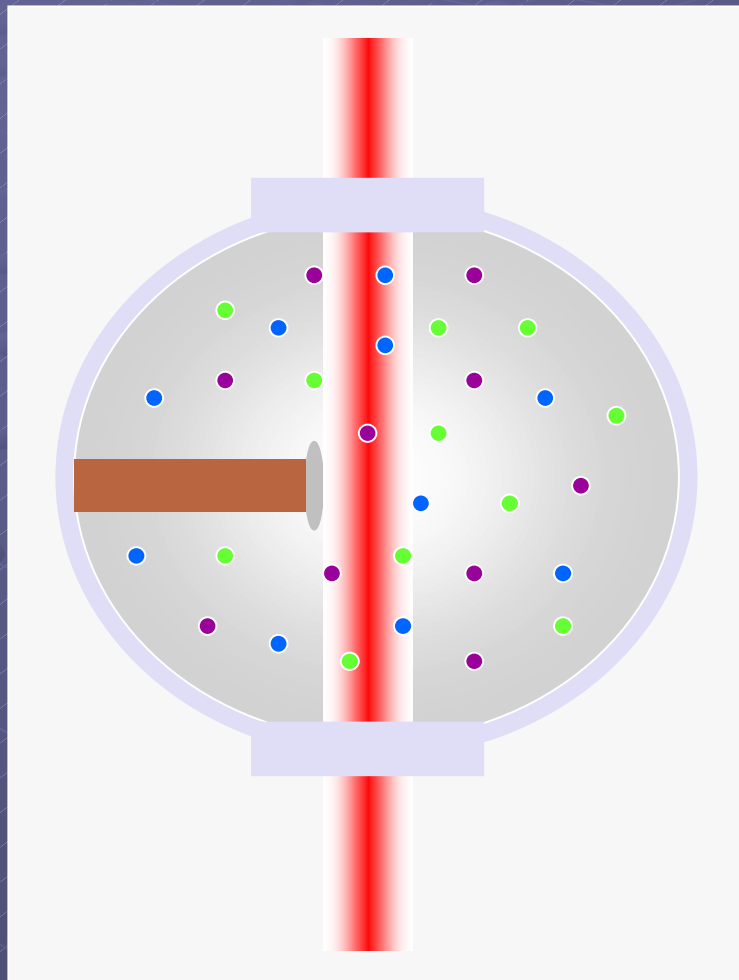
  - Repetition rate of 1 kHz

Advantages of the JLAB FEL

Methane Ro-Vibrational Spectrum

- 20 cm^{-1} bandwidth would allow excitation of all rotational states in the Q-branch ($\triangle$J = 0) to saturation!

- Dynamical effects of rotational energy on reactivity could be examined by pumping selected swaths of rotational states in the P & R branches.

Potential Experiment at JLAB-FEL

- Backfill a chamber with CH_4, SiH_4, and GeH_4 ambient gases above a low T_s growth surface.

- Change the laser wavelength to excite 2 quanta of the ν_3 asymmetric stretching vibration and selectively enhance the deposition of:

  - C ($\lambda_{2\nu3}$ = 1.656 μm)

  - Si ($\lambda_{2\nu3}$ = 2.282 μm)

  - Ge ($\lambda_{2\nu3}$ = 2.365 μm)

Experimental Calculations: CH_4/Ni(100)

- Beer's Law:

$$I = I_0 e^{-\sigma \Delta N l}$$

where σ is the absorption cross section, ΔN is the gas density (i.e. # molecules/volume) and l is the path length.

- Calculation parameters:
  - Laser beam diameter = 1 cm
  - Growth surface diameter = 1 cm
  - Pressure = 10^{-3} Torr
  - Temperature = 300 K ($T_g = T_s$)
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  - Intensity loss/10 cm path length = 0.041 %

* Possibilities exist for augmenting the growth including multi-passing the beam over a larger area and increasing the pressure.
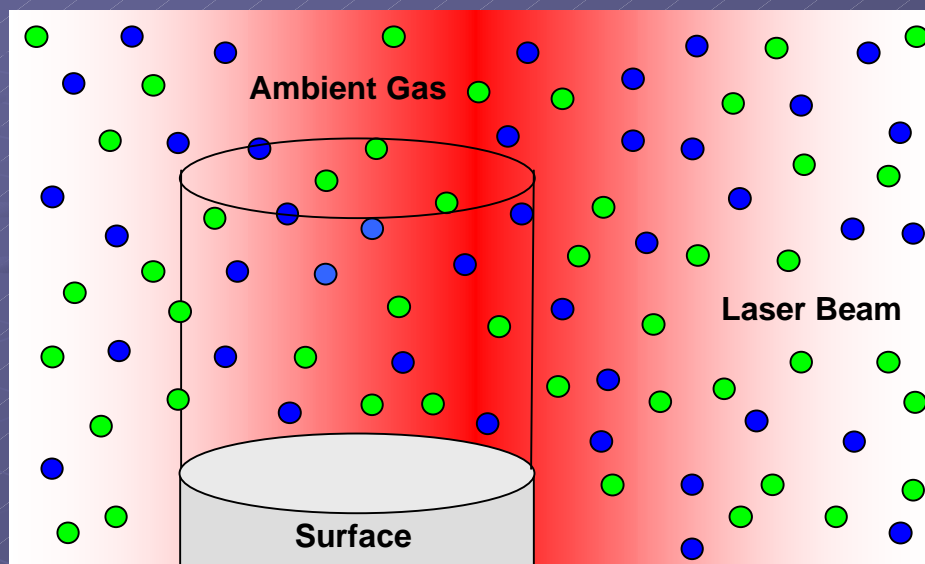
Experimental Calculations: CH_4/Ni(100)

Table 1. Percentage of Molecules Excited and Time to Deposit 1 ML of C for the $0 \rightarrow 2$ Transition of CH_4 on Ni(100)

| Laser	Percent Excited ($\%*s^{-1}$)	Experimental Time
JLAB FEL	saturation	11 minutes
Ti:Sapphire/OPA	0.5 %	1.05 years

Conclusions

- ILAC + CVD can
  - Enhance sticking coefficients by many orders of magnitude
  - Allow the study and use of reactions occurring at low surface temperatures which would otherwise be impossible to detect
- The JLAB FEL offers a significant advantage over other ultrafast laser systems, such as the amplified Ti:Sapphire/OPA at UVA, because of its
  - Appropriate bandwidth to span Q-branch transitions ($\Delta J = 0$)
  - High average power and repetition rate
- The proposed CVD experiments at the JLAB FEL might lead to some technologically useful applications, particularly when the growth surface is constrained to low temperatures
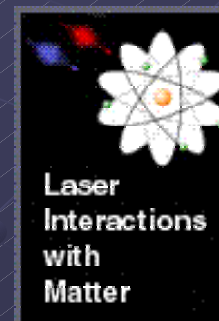
Acknowledgements

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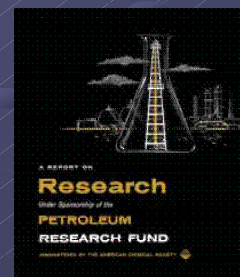
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